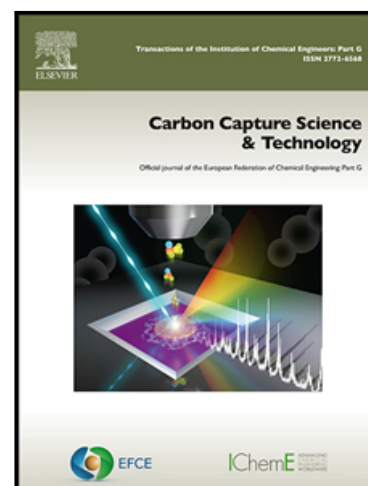


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A comprehensive review of carbon capture science and technologies



Chunfei Wu , Qi Huang , Zhicheng Xu , Ayesha Tariq Sipra , Ningbo Gao , Luciana Porto de Souza Vandenberghe , Sabrina Vieira , Carlos Ricardo Soccol , Ruikai Zhao , Shuai Deng , Sandra K.S. Boetcher , Shijian Lu , Huancong Shi , Dongya Zhao , Yupeng Xing , Yongdong Chen , Jiamei Zhu , Dongdong Feng , Yu Zhang , Lihua Deng , Guoping Hu , Paul A. Webley , Daxin Liang , Zhichen Ba , Agata Mlonka-Mędrala , Aneta Magdziarz , Norbert Miskolczi , Szabina Tomasek , Su Shiung Lam , Shin Ying Foong , Hui Suan Ng , Long Jiang , Xinlong Yan , Yongzhuo Liu , Ying Ji , Hongman Sun , Yu Zhang , Haiping Yang , Xiong Zhang , Mingzhe Sun , Daniel C.W. Tsang , Jin Shang , Christoph Muller , Margarita Rekhtina , Maximilian Krödel , Alexander H. Bork , Felix Donat , Lina Liu , Xin Jin , Wen Liu , Syed Saqline , Xianyue Wu , Yongqing Xu , Asim Laeeq Khan , Zakawat Ali , Haiqing Lin , Leiqing Hu , Jun Huang , Rasmeet Singh , Kaifang Wang , Xuezhong He , Zhongde Dai , Shouliang Yi , Alar Konist , Mais Hanna Suleiman Baqain , Yijun Zhao , Shaozeng Sun , Guoxing Chen , Xin Tu , Anke Weidenkaff , Sibudjing Kawi , Kang Hui Lim , Chunfeng Song , Qing Yang , Zhenyu Zhao , Xin Gao , Xia Jiang , Haiyan Ji , Toluleke E Akinola , Adekola Lawal , Olajide S Otitaju , Meihong Wang , Guojun Zhang , Lin Ma , Baraka C. Sempuga , Xinying Liu , Eni Oko , Michael Daramola , Zewei Yu , Siming Chen , Guojun Kang , Qingfang Li , Li Gao , Ling Liu , Hui Zhou

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## A comprehensive review of carbon capture science and technologies

Chunfei Wu<sup>1\*</sup>, Qi Huang<sup>1</sup>, Zhicheng Xu<sup>2</sup>, Ayesha Tariq Sipra<sup>2</sup>, Ningbo Gao<sup>2†</sup>, Luciana Porto de Souza Vandenberghe<sup>3†</sup>, Sabrina Vieira<sup>3</sup>, Carlos Ricardo Soccol<sup>3</sup>, Ruikai Zhao<sup>4</sup>, Shuai Deng<sup>4†</sup>, Sandra K.S. Boetcher<sup>5†</sup>, Shijian Lu<sup>6\*</sup>, Huancong Shi<sup>7</sup>, Dongya Zhao<sup>8†</sup>, Yupeng Xing<sup>8</sup>, Yongdong Chen<sup>9†</sup>, Jiamei Zhu<sup>10</sup>, Dongdong Feng<sup>11†</sup>, Yu Zhang<sup>11</sup>, Lihua Deng<sup>11</sup>, Guoping Hu<sup>12†</sup>, Paul A. Webley<sup>13</sup>, Daxin Liang<sup>14†</sup>, Zhichen Ba<sup>14</sup>, Agata Mlonka-Mędrala<sup>15</sup>, Aneta Magdziarz<sup>15†</sup>, Norbert Miskolczi<sup>16†</sup>, Szabina Tomasek<sup>16</sup>, Su Shiung Lam<sup>17†</sup>, Shin Ying Foong<sup>17</sup>, Hui Suan Ng<sup>18</sup>, Long Jiang<sup>19†</sup>, Xinlong Yan<sup>20</sup>, Yongzhuo Liu<sup>21</sup>, Ying Ji<sup>19</sup>, Hongman Sun<sup>22†</sup>, Yu Zhang<sup>22</sup>, Haiping Yang<sup>23†</sup>, Xiong Zhang<sup>23</sup>, Mingzhe Sun<sup>24</sup>, Daniel C.W. Tsang<sup>24†</sup>, Jin Shang<sup>25</sup>, Christoph Muller<sup>26\*</sup>, Margarita Rekhtina<sup>26</sup>, Maximilian Krödel<sup>26</sup>, Alexander H. Bork<sup>26</sup>, Felix Donat<sup>26</sup>, Lina Liu<sup>27†</sup>, Xin Jin<sup>8†</sup>, Wen Liu<sup>28†</sup>, Syed Saqline<sup>28</sup>, Xianyue Wu<sup>28</sup>, Yongqing Xu<sup>29</sup>, Asim Laeeq Khan<sup>30†</sup>, Zakawat Ali<sup>30</sup>, Haiqing Lin<sup>31†</sup>, Leiqing Hu<sup>31</sup>, Jun Huang<sup>32†</sup>, Rasmeet Singh<sup>32</sup>, Kaifang Wang<sup>33,34</sup>, Xuezhong He<sup>33,34†</sup>, Zhongde Dai<sup>35†</sup>, Shouliang Yi<sup>36\*</sup>, Alar Konist<sup>37†</sup>, Mais Hanna Suleiman Baqain<sup>37</sup>, Yijun Zhao<sup>11</sup>, Shaozeng Sun<sup>11</sup>, Guoxing Chen<sup>38†</sup>, Xin Tu<sup>39</sup>, Anke Weidenkaff<sup>38,40</sup>, Sibudjing Kawi<sup>41†</sup>, Kang Hui Lim<sup>41</sup>, Chunfeng Song<sup>42†</sup>, Qing Yang<sup>43†</sup>, Zhenyu Zhao<sup>44</sup>, Xin Gao<sup>44†</sup>, Xia Jiang<sup>45†</sup>, Haiyan Ji<sup>45</sup>, Toluleke E Akinola<sup>46</sup>, Adekola Lawal<sup>47</sup>, Olajide S Otitoju<sup>46</sup>, Meihong Wang<sup>46\*</sup>, Guojun Zhang<sup>48</sup>, Lin Ma<sup>48†</sup>, Baraka C. Sempuga<sup>49</sup>, Xinying Liu<sup>49†</sup>, Eni Oko<sup>50†</sup>, Michael Daramola<sup>51</sup>, Zewei Yu<sup>52</sup>, Siming Chen<sup>6</sup>, Guojun Kang<sup>6</sup>, Qingfang Li<sup>53</sup>, Li Gao<sup>54</sup>, Ling Liu<sup>6</sup>, Hui Zhou<sup>29\*</sup>

<sup>1</sup> School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, BT7 1NN, UK

<sup>2</sup> School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, China

<sup>3</sup> Department of Bioprocess Engineering and Biotechnology, Federal University of Paraná, Brazil

<sup>4</sup> Key Laboratory of Efficient Utilization of Low and Medium Grade Energy (Tianjin University), Ministry of Education, Tianjin 300350, China

<sup>5</sup> Embry-Riddle Aeronautical University, Daytona Beach, Florida 32114 USA

<sup>6</sup> China University of Mining and Technology

<sup>7</sup> Huzhou Research Institute of Zhejiang University

<sup>8</sup> College of New Energy, China University of Petroleum (East China), Qingdao 266580, China

<sup>9</sup> College of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500

<sup>10</sup> School of Chemical Engineering and Technology, China University of Mining & Technology, Xuzhou, Jiangsu 221116, China

<sup>11</sup> School of Energy Science and Engineering, Harbin Institute of Technology, 150001, China

<sup>12</sup> Key Laboratory of Rare Earths, Ganjiang Innovation Academy, Chinese Academy of Sciences, Ganzhou, Jiangxi, 341000, China

<sup>13</sup> Department of Chemical Engineering, Monash University, Victoria 3800, Australia

<sup>14</sup> Key Laboratory of Bio-based Material Science and Technology (Ministry of Education), Northeast Forestry University, Harbin 150040, China

<sup>15</sup> AGH University of Krakow, Al. A. Mickiewicza 30, 30-059 Krakow, Poland

<sup>16</sup> MOL Department of Hydrocarbon and Coal Processing, University of Pannonia, H-8200, Veszprém, Egyetem u. 10, Hungary

<sup>17</sup> Institute of Tropical Aquaculture and Fisheries (AKUATROP), Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia

<sup>18</sup> Centre for Research and Graduate Studies, University of Cyberjaya, Persiaran Bestari, 63000 Cyberjaya, Selangor, Malaysia

<sup>19</sup> Institute of Refrigeration and Cryogenics, Zhejiang University, Hangzhou, 310027, China

<sup>20</sup> School of Chemical Engineering & Technology, China University of Mining and Technology, Xuzhou 221116, China

<sup>21</sup> College of Chemical Engineering, Qingdao University of Science & Technology, Qingdao, 266042, China

<sup>22</sup> State Key Laboratory of Heavy Oil Processing, College of Chemistry and Chemical Engineering, China University of Petroleum, Qingdao 266580, China

- <sup>23</sup> *State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan, 430074, China*
- <sup>24</sup> *Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong*
- <sup>25</sup> *School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China*
- <sup>26</sup> *Institute of Energy and Process Engineering, ETH Zürich, Leonhardstrasse 21 Zürich 8092*
- <sup>27</sup> *College of Environmental Science and Engineering, Ministry of Education Key Laboratory of Pollution Processes and Environmental Criteria, Nankai University, Tianjin 300350, PR China*
- <sup>28</sup> *School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459, Singapore*
- <sup>29</sup> *Department of Energy and Power Engineering, Tsinghua University, Beijing, 100084, PR China*
- <sup>30</sup> *Chemical Engineering Department, COMSATS University Islamabad, Lahore, PAKISTAN*
- <sup>31</sup> *Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA*
- <sup>32</sup> *School of Chemical and Biomolecular Engineering, University of Sydney, Sydney, Australia*
- <sup>33</sup> *Department of Chemical Engineering, Guangdong Technion - Israel Institute of Technology, 241 Daxue Road, Shantou, Guangdong, 515063, China*
- <sup>34</sup> *The Wolfson Department of Chemical Engineering, Technion - Israel Institute of Technology, Haifa 3200003, Israel*
- <sup>35</sup> *College of Carbon Neutrality Future Technology, Sichuan University, Chengdu 610065, China*
- <sup>36</sup> *Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA 15236, USA*
- <sup>37</sup> *Department of Energy Technology, Tallinn University of Technology, 19086, Tallinn, Estonia*
- <sup>38</sup> *Fraunhofer Research Institution for Materials Recycling and Resource Strategies IWKS, Brentanostraße 2a, 63755 Alzenau, Germany*
- <sup>39</sup> *Department of Electrical Engineering and Electronics, University of Liverpool, Liverpool L69 3GJ, UK*
- <sup>40</sup> *Department of Materials and Earth Sciences, Technical University Darmstadt, Alarich-Weiss-Str. 2, 64287 Darmstadt, Germany*
- <sup>41</sup> *Department of Chemical and Biomolecular Engineering, National University of Singapore, P.O. Box 117585, Singapore*
- <sup>42</sup> *School of Environmental Science and Engineering, Tianjin University, Tianjin, China*
- <sup>43</sup> *School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan, China*
- <sup>44</sup> *School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*
- <sup>45</sup> *College of Carbon Neutrality Future Technology, Sichuan University, Chengdu, 610065, China*
- <sup>46</sup> *Department of Chemical and Biological Engineering, University of Sheffield, Sheffield S1 3JD*
- <sup>47</sup> *Petrofac, Woking, UK GU21 5BH*
- <sup>48</sup> *Department of Mechanical Engineering, University of Sheffield, Sheffield S1 3JD*
- <sup>49</sup> *Institute for Catalysis and Energy Solutions, University of South Africa, c/o Christiaan de Wet & Pioneer Avenue, Florida, 1709, Johannesburg, South Africa*
- <sup>50</sup> *School of Engineering, Newcastle University, Newcastle upon Tyne, NE1 7RU*
- <sup>51</sup> *Department of Chemical Engineering, Faculty of Engineering, Built Environment and Information Technology, University of Pretoria, Pretoria, South Africa*
- <sup>52</sup> *International CCS Knowledge Centre, 198–10 Research Drive Regina, SK S4S 7J7*
- <sup>53</sup> *Sinopec Engineering Incorporation, Dongying, Shandong, 257088, China*
- <sup>54</sup> *China Energy Jin Jie Power Station, Yulin, Shanxi, 719319, China*

\* Corresponding authors: Dr Chunfei Wu ([c.wu@qub.ac.uk](mailto:c.wu@qub.ac.uk)); Professor Shijian Lu ([lushijian@cumt.edu.cn](mailto:lushijian@cumt.edu.cn)); Professor Christoph Müller ([muelchri@ethz.ch](mailto:muelchri@ethz.ch)); Dr Shouliang Yi ([shouliang.yi@hotmail.com](mailto:shouliang.yi@hotmail.com)), Professor Meihong Wang ([meihong.wang@sheffield.ac.uk](mailto:meihong.wang@sheffield.ac.uk)); Dr Hui Zhou, Tsinghua University ([huizhou@tsinghua.edu.cn](mailto:huizhou@tsinghua.edu.cn))

† Section leaders: 2.1&2.2 - Professor Ningbo Gao ([nbogao@xjtu.edu.cn](mailto:nbogao@xjtu.edu.cn)); 2.3 - Professor Luciana Porto de Souza Vandenberghe ([lucianapsv@gmail.com](mailto:lucianapsv@gmail.com)); 2.4 - Professor Shuai Deng ([sdeng@tju.edu.cn](mailto:sdeng@tju.edu.cn)); 2.4 & 5.3 - Professor Sandra Boetcher ([boetches@erau.edu](mailto:boetches@erau.edu)); 3.1.1.5 – Professor Dongya zhao ([dyzhao@upc.edu.cn](mailto:dyzhao@upc.edu.cn)); 3.1.2 - Professor Yongdong Chen ([yongdongchen@swpu.edu.cn](mailto:yongdongchen@swpu.edu.cn)); 3.1.3 - Dr Dongdong Feng ([08031175@163.com](mailto:08031175@163.com)) ; 3.2.1 - Dr Guoping Hu ([gphu@gia.cas.cn](mailto:gphu@gia.cas.cn)); 3.2.2-Dr Daxin Liang ([daxin.liang@nefu.edu.cn](mailto:daxin.liang@nefu.edu.cn)); 3.2.3.1 - Dr Aneta Magdziarz ([amagdzia@agh.edu.pl](mailto:amagdzia@agh.edu.pl)); 3.2.3.2 - Dr Norbert Miskolczi ([miskolczi.norbert@mk.uni-pannon.hu](mailto:miskolczi.norbert@mk.uni-pannon.hu)); 3.2.3.3 - Professor Su Shiung Lam ([lam@umt.edu.my](mailto:lam@umt.edu.my)); 3.2.4 - Dr Long Jiang ([jianglong@zju.edu.cn](mailto:jianglong@zju.edu.cn)); 3.2.5.1 - Dr Hongman Sun ([hongman.sun@upc.edu.cn](mailto:hongman.sun@upc.edu.cn)); 3.2.5.2 - Professor Haiping Yang ([yanghaiping@hust.edu.cn](mailto:yanghaiping@hust.edu.cn)); 3.2.5.3 - Professor Dan Tsang ([dan.tsang@polyu.edu.hk](mailto:dan.tsang@polyu.edu.hk)); 3.4.1, 3.4.2 & 3.5.1 - Professor Christoph Muller ([muelchri@ethz.ch](mailto:muelchri@ethz.ch)); 3.4.3 - Dr Lina Liu ([liuln@nankai.edu.cn](mailto:liuln@nankai.edu.cn)); 3.5.2 – Dr Xin Jin ([jamesjin@upc.edu.cn](mailto:jamesjin@upc.edu.cn)); 3.5.3, 5.1.2 & 5.3 - Dr Wen Liu ([wenliu@ntu.edu.sg](mailto:wenliu@ntu.edu.sg)); 4.1 & 4.2.1 - Dr Asim Khan ([alaeqkhan@cuilahore.edu.pk](mailto:alaeqkhan@cuilahore.edu.pk)) 4.2 - Professor Haiqing Lin ([haiqingl@buffalo.edu](mailto:haiqingl@buffalo.edu)); 4.3, 3.2.2, 3.2.5.1 - Professor Jun Huang ([jun.huang@sydney.edu.au](mailto:jun.huang@sydney.edu.au)); 4.4 - Dr Xuezhong He ([xuezhong.he@gtiit.edu.cn](mailto:xuezhong.he@gtiit.edu.cn)); 4.5 - Dr Zhongde Dai ([zhongde.dai@scu.edu.cn](mailto:zhongde.dai@scu.edu.cn)); 5.1.1 Professor Alar Konist ([alar.konist@taltech.ee](mailto:alar.konist@taltech.ee)); 5.1.4 - Dr Guoxing Chen ([guoxing.chen@iwks.fraunhofer.de](mailto:guoxing.chen@iwks.fraunhofer.de)); 5.2 - Dr Sibudjing Kawi ([chekawis@nus.edu.sg](mailto:chekawis@nus.edu.sg)); 5.3 Professor Chunfeng Song ([chunfeng.song@tju.edu.cn](mailto:chunfeng.song@tju.edu.cn)); 5.3.8 - Professor Qing Yang ([qyang@mail.hust.edu.cn](mailto:qyang@mail.hust.edu.cn)); 5.4 – Professor Xin Gao ([gaoxin@tju.edu.cn](mailto:gaoxin@tju.edu.cn)); 5.5 – Professor Xia Jiang ([xjiang@scu.edu.cn](mailto:xjiang@scu.edu.cn)); 6.1&6.2 - Professor Meihong Wang ([meihong.wang@sheffield.ac.uk](mailto:meihong.wang@sheffield.ac.uk)); 6.3 & 6.4 - Professor Lin Ma ([lin.ma@sheffield.ac.uk](mailto:lin.ma@sheffield.ac.uk)) 6.5 - Professor Xinying Liu ([liux@unisa.ac.za](mailto:liux@unisa.ac.za)); 6.6 - Dr Eni Oko ([eni.oko@newcastle.ac.uk](mailto:eni.oko@newcastle.ac.uk)); 7.1 – Professor Shijian Lu ([lushijian@cumt.edu.cn](mailto:lushijian@cumt.edu.cn)); 7.2 – Dr Siming Chen ([chsiming@cumt.edu.cn](mailto:chsiming@cumt.edu.cn)); 7.3 – Dr Ling Liu ([liuling@cumt.edu.cn](mailto:liuling@cumt.edu.cn))

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## 1. Introduction

CO<sub>2</sub> is one of the major anthropogenic greenhouse gases in the atmosphere contributing to global warming (Blamey et al., 2010; Mikkelsen et al., 2010). In the last half-century, the concentration of CO<sub>2</sub> has exhibited a dramatic growth from about 310 to over 415 ppm owing to the large-scale utilization of fossil fuels and various chemical refinery processes (Hu et al., 2016; Lackner, 2003; Yu et al., 2008). Thus, worldwide efforts have been devoted to developing new technologies for reducing CO<sub>2</sub> emissions and most of the United Nations members have approved Paris Climate Agreements for greenhouse gas reduction (He et al., 2016; Jacobson, 2009; Obergassel et al., 2016; Wang, S. et al., 2011). The 21<sup>st</sup> conference on global warming (COP21) reached a landmark agreement (the Paris Agreement) to limit the increase of the global average temperature to 2.0 °C in 2100 (Rhodes, 2016). CO<sub>2</sub> emissions from energy- and industry-related sources must decrease dramatically after 2030 and reach net-zero levels between 2050 and 2060 (Rogelj et al., 2016) to enable this target to be reached.

Carbon capture removing CO<sub>2</sub> before releasing it into the atmosphere plays an important role in a zero and/or negative CO<sub>2</sub> emission. It has three categories: pre-combustion, post-combustion, and oxyfuel combustion. For oxyfuel combustion, pure oxygen is used in combustion to produce flue gas with high purity of CO<sub>2</sub>. In the pre-combustion CO<sub>2</sub> capture process, fuels are partially oxidized by steam or oxygen to produce synthetic gas, followed by water gas shift reaction to form hydrogen-enriched gas. The third category of CO<sub>2</sub> capture is post-combustion, which refers to capturing CO<sub>2</sub> after the combustion of hydrocarbon fuels. Among these CO<sub>2</sub> capture technologies, post-combustion with amine solvents is the state-of-the-art mature technology (Rochelle, 2009). In addition, directly capturing CO<sub>2</sub> from the air could meet global climate goals. However, a new study reported that the process needs as much as a quarter of global energy supplies in 2100 (Realmonte et al., 2019).

The direct use of carbonaceous fuels such as fossil fuels and biomass is unavoidable in the future. Therefore, a large amount of CO<sub>2</sub> is still expected to be emitted into the atmosphere. Therefore, post-combustion CO<sub>2</sub> capture, oxyfuel combustion and direct air capture (DAC) represent key technologies to reduce CO<sub>2</sub> emissions and mitigate climate change. Review papers are available regarding the development of carbon capture technologies (Al-Hamed and Dincer, 2021; Buckingham et al., 2022; Mikulčić et al., 2019). However, a more comprehensive review of carbon capture will be beneficial to the research community. Therefore, this paper provides a thorough description and analysis of carbon capture technologies, including solid and liquid-based sorbents for capturing CO<sub>2</sub> from different sources (e.g. flue gas, biogas, syngas and air). Various liquid solvents, including amines, ion liquid and ammonia, were studied. In addition, solid adsorbents were analyzed based on their working temperatures, such as low-temperature adsorbents (carbon, biochar, zeolite, amine-loaded solid, covalent organic frameworks (COFs) and aerogels), medium-temperature adsorbents (MgO and K<sub>2</sub>CO<sub>3</sub>) and high-temperature adsorbents (CaO). In section 4 of

this review paper, membrane-based CO<sub>2</sub> separation is critically analyzed, followed by the investigation of oxyfuel combustion, chemical looping, cryogenic CO<sub>2</sub> capture, and bioenergy-related CO<sub>2</sub> capture. Process modelling using Aspen, CFD and machine learning for CO<sub>2</sub> capture is also included and critically analyzed in this review paper. Furthermore, techno-economic analysis and evaluation of typical large-scale CO<sub>2</sub> capture plants were carried out.

## **2. CO<sub>2</sub> capture from various CO<sub>2</sub> sources**

### **2.1. Flue gas as the CO<sub>2</sub> source**

#### **2.1.1 Current status of flue gas**

Currently, as the world's second-largest energy source, coal contributes to more than 40% of the total global emissions in 2021, reaching a record high of 15.3 billion tons. The power industry accounts for a third of global CO<sub>2</sub> emissions, which will continue to grow on an annual basis (Rahman et al., 2017; Younas et al., 2020). Around 60% and 39% of the total carbon emissions from the electricity industry were derived from coal-fired and natural gas-fired power plants, respectively (Administration, 2020). Therefore, carbon capture from flue gas as the CO<sub>2</sub> source is the key to achieving net-zero global CO<sub>2</sub> emissions. In addition, capturing and utilising CO<sub>2</sub> in flue gas will reduce the pressure of greenhouse gas emissions and generate substantial economic benefits (Khalifa et al., 2022; Maina et al., 2021).

Carbon capture from flue gas refers to the process of separating and collecting CO<sub>2</sub> from industrial production and energy use, such as power plants, cement manufacturing and stainless-steel factory, etc. (Cheng et al., 2022; Wang and Song, 2020a). CO<sub>2</sub> emissions from fossil fuel-fired flue gas in the power industry are characterised by large flue gas volume, low CO<sub>2</sub> partial pressure (0.03-0.2 bar), high total emissions and relatively low CO<sub>2</sub> concentration (3-20%)(Buvik et al., 2021; Figueroa, José D. et al., 2008). Usually, the flue gas from other manufacturing industries contains a higher CO<sub>2</sub> concentration than that from the power plant. As for the components of flue gas from power plants, except for N<sub>2</sub> in air, CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>S are approximately 20%, 5% and < 1%, respectively, produced by complete fuel combustion, together with large amounts of water vapor generation(Cheah et al., 2015; Maina et al., 2021; Wang and Song, 2020a). The properties of a few typical flue gases from different sources are summarised in Table 2.1.

Table 2.1 Typical CO<sub>2</sub> concentration and impurities of flue gas from various sources.

Flue gas source	CO <sub>2</sub> conc. (vol%)	Pressure (atm)	CO <sub>2</sub> partial pressure (atm)	Impurities	Ref.
Aluminum production	1-2	1	0.01-0.02	SO <sub>x</sub> and NO <sub>x</sub> present, fluoride	Husebye et al., 2012
Gas turbine exhaust	3-4	1	0.03-0.04	low SO <sub>x</sub> and NO <sub>x</sub> levels, O <sub>2</sub> : 12%-15%	Samanta et al., 2011
Fired boiler of oil refinery and petrochemical plant	~8	1	0.08	SO <sub>x</sub> and NO <sub>x</sub> present	Wang and Song, 2020a
Natural gas fired boilers	7-10	1	0.07-0.10	SO <sub>x</sub> and NO <sub>x</sub> present	Wang and Song, 2020a
Oil-fired boilers	11-13	1	0.11-0.13	high SO <sub>x</sub> and NO <sub>x</sub> levels, O <sub>2</sub> : 2%-5%	Wang and Song, 2020a
Coal-fired boilers	12-14	1	0.12-0.14	high SO <sub>x</sub> and NO <sub>x</sub> levels, O <sub>2</sub> : 2%-5%	Samanta et al., 2011
IGCC syngas turbine	12-14	1	0.12-0.14	low SO <sub>x</sub> and NO <sub>x</sub> levels	Wang and Song, 2020a; Song et al., 2019b
Hydrogen production	15-20	22-27	3-5	high NO <sub>x</sub> levels	Husebye et al., 2012
Steel production (Blast furnace)	20-27	1-3	0.2-0.6	SO <sub>x</sub> and NO <sub>x</sub> present	Husebye et al., 2012
Cement process	14-33	1	0.14-0.33	SO <sub>2</sub> and NO <sub>x</sub> , trace elements, particulates	Husebye et al., 2012

### 2.1.2 Challenges to CO<sub>2</sub> capture from flue gas

Until now, coal is still the dominant fuel combusted for electricity generation in most power plants worldwide (Zou, Lanfang et al., 2017). Thereby, as an “end-of-pipe” process, post-combustion carbon capture is the most widely used and mature carbon capture technology due to its good viability and feasibility for existing power plants, without the requirement for large-scale renovation and upgrading (Cheng et al., 2022; Han et al., 2020; Zhao, H. et al., 2018). The main post-combustion CO<sub>2</sub> capture technologies include absorption separation (physical and chemical absorption) (Fang, M. et al., 2020; Wang, M. et al., 2015), adsorption separation (physical and chemical adsorption) (Wilcox et al., 2014; Zhao, H. et al., 2018) and membrane separation (Feron et al., 2020; Han et al., 2020). According to the statistics, there are more than 60% of post-combustion technologies employing absorption-based methods. Among those, the chemical absorption method, represented by the MEA absorption, is considered the most promising for industrial applications because of its applicability to large air volumes and simplicity of operation, which mainly consists of two important processes, including chemical absorption of CO<sub>2</sub> in the absorption tower and thermal regeneration of the absorber in the desorption tower (Akeeb et al., 2022).

However, carbon capture from flue gas sources is still confronted with major challenges, restraining its further development and commercialisation (D'Alessandro et al., 2010; Notz et al., 2011). First, after fossil fuel combustion, there is a high volumetric flow rate together with a large amount of CO<sub>2</sub> in flue gas derived from most conventional thermal power plants, which is in the temperature range of 50-150°C because of a series of gas cleaning procedures after fuel combustion. Then, the discharge flue gas is mainly in atmospheric pressure, but the partial pressure of CO<sub>2</sub> is at a relatively low level due to insufficient volumetric concentration of CO<sub>2</sub> in flue gas, as discussed above. Last, the surplus O<sub>2</sub> used during the combustion process results in the presence of SO<sub>x</sub> and NO<sub>x</sub>, and the humidity due to the existing steam poses additional difficulties for the currently preferred CO<sub>2</sub> capture process, such as amine-based absorption technology.

Solid amine-based adsorbents are promising candidates for carbon capture from flue gas, especially at low CO<sub>2</sub> partial pressure (10–15%) (Wang and Song, 2020a). However, the low oxidative stability of amines could significantly influence the performance of flue gas carbon capture using amine-based adsorbents, because the presence of O<sub>2</sub> (3-4%) can result in the rapid oxidative degradation of amines (Sreedhar et al., 2017). Min et al. investigated amine-based solids for CO<sub>2</sub> capture by enhancing the oxidation resistance of polyethyleneimine (PEI)/silica adsorbent, as shown in Figure 2.1, with two strategies adopted. First, 1, 2-epoxybutane was used to functionalise PEI to produce tethered 2-hydroxybutyl groups. Besides, metals that could assist amine oxidation were poisoned through using chelator. After improvement, only a surprisingly low decay of CO<sub>2</sub> capture capacity (8.5%) was observed under aging by flue gas with oxygen at 110°C after 30 d, 50 times higher stability compared

with conventional PEI/silica (Min et al., 2018). This work may provide the further commercialisation prospect of these adsorbents when used for carbon capture from flue gas containing oxygen, which may cause the oxidation of adsorbents (Bali et al., 2013; Heydari-Gorji and Sayari, 2012).

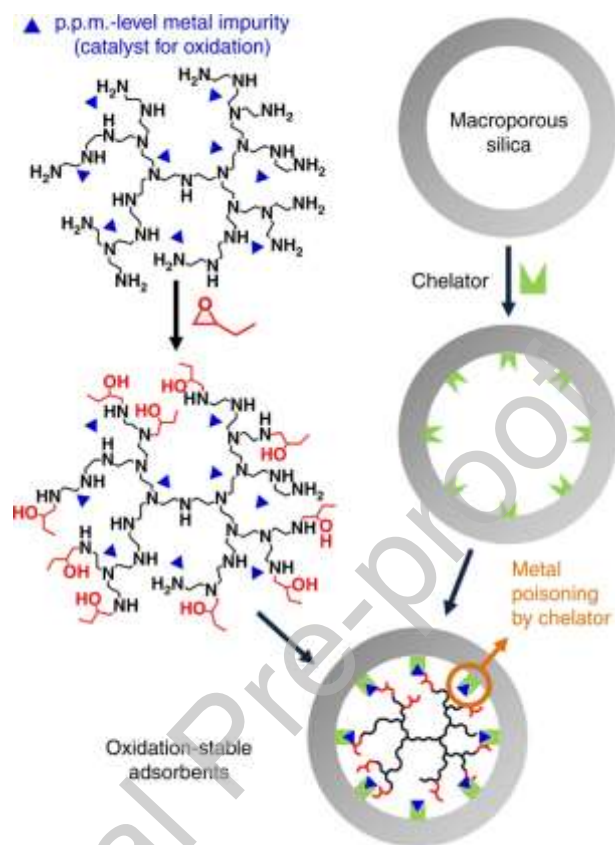


Figure 2.1 Synthesis of oxidation-stable PEI functionalised CO<sub>2</sub> adsorbent (Min et al., 2018).

It is known that traditional amine-containing adsorbents are vulnerable to acidic conditions in flue gas caused by SO<sub>x</sub> and NO<sub>x</sub>, which could lead to irreversible poisoning effects and, eventually, fast deactivation of sorbents. Thus, the basic sites in amine-based adsorbents can be significantly influenced by acidic compounds (Maina et al., 2021; Zhao, H. et al., 2018). Hence, designing and developing SO<sub>x</sub>- and NO<sub>x</sub>-resistant amine-based adsorbents are of great importance for carbon capture from flue gas in terms of solid adsorption technologies. Kim and co-workers (Kim, C. et al., 2019) employed a facile fabrication route to impregnate porous silica with PEI to form a surface layer composed of tertiary amines, which exhibited improved SO<sub>2</sub> resistance during flue gas CO<sub>2</sub> capture. As shown in Figure. 2.2, the tertiary amine layer can capture SO<sub>2</sub> to enhance CO<sub>2</sub> adsorption by the beneath layer. The results showed that, compared with conventional PEI/silica for 65.1% carbon uptake ability, this novel sorbent achieved a significant reduction of capacity loss (only 8.52%) after 1000 cycles for simulated flue gas carbon capture with 50 ppm SO<sub>2</sub> (Kim, C. et al., 2019). In

addition to the improvement of adsorbents for carbon capture from flue gas with existing impurities of  $\text{SO}_x$  and  $\text{NO}_x$  as  $\text{CO}_2$  resources, another method is to establish desulfurisation and denitrification units for enhancing sorbents regenerability during real-world power plant applications.

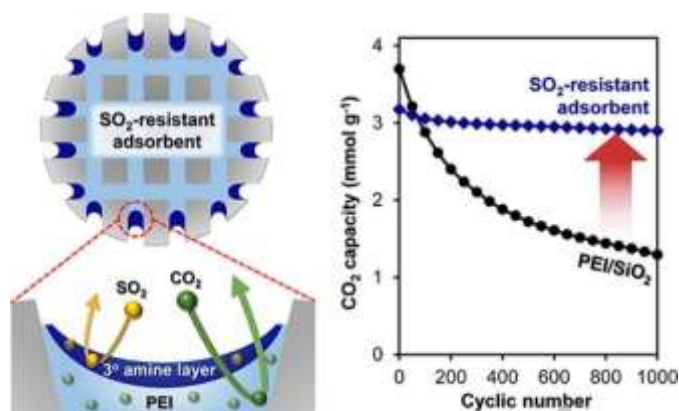


Figure 2.2 Synthesis of  $\text{SO}_2$ -resistant  $\text{CO}_2$  adsorbent. Tertiary-amine-rich layer plays a role of protection for  $\text{CO}_2$  capture by beneath PEI layer (Kim, C. et al., 2019).

In most cases of practical power plants, the flue gas after post-combustion could be in humid conditions between  $40^\circ\text{C}$  to  $80^\circ\text{C}$ . The presence of moisture in wet flue gas may be detrimental to carbon capture, because the resulting steam not only results in competitive adsorption to  $\text{CO}_2$ , but could decompose the adsorbents due to their low hydrothermal stability (Ray et al., 2021). However, modifying the existing power plant for pretreatment of water removal in flue gas may significantly aggregate the economic burden of the overall process. Therefore, novel sorbent materials should be designed and fabricated with high hydrothermal stability and high  $\text{CO}_2$  uptake selectivity.

Lenoir and co-workers (Soubeyrand-Lenoir et al., 2012) studied three different MOFs (HKUST-1, UiO-66(Zr) and MIL-100(Fe)) for  $\text{CO}_2$  uptake with varying relative humidity (RH). As shown in Figure 2.3a, 5 times higher carbon capture ability ( $105 \text{ mg/g}$ ) was achieved by MIL-100(Fe) with escalating RH from 3% to 40%, compared with the other two MOFs. As depicted in Figure. 2.3b, the filled water on MIL-100(Fe) formed microporous pockets to enhance  $\text{CO}_2$  capture (A, B and C). However, the water in microporous MOFs could antagonise the carbon uptake by blocking  $\text{CO}_2$  molecules (D and E) (Soubeyrand-Lenoir et al., 2012). In addition to the route of water-enhanced  $\text{CO}_2$  uptake from flue gas reported in the above research, there are other key strategies for improving the carbon capture from wet flue gas, including hydrophobic modifications, the introduction of functional groups and amine modifications.



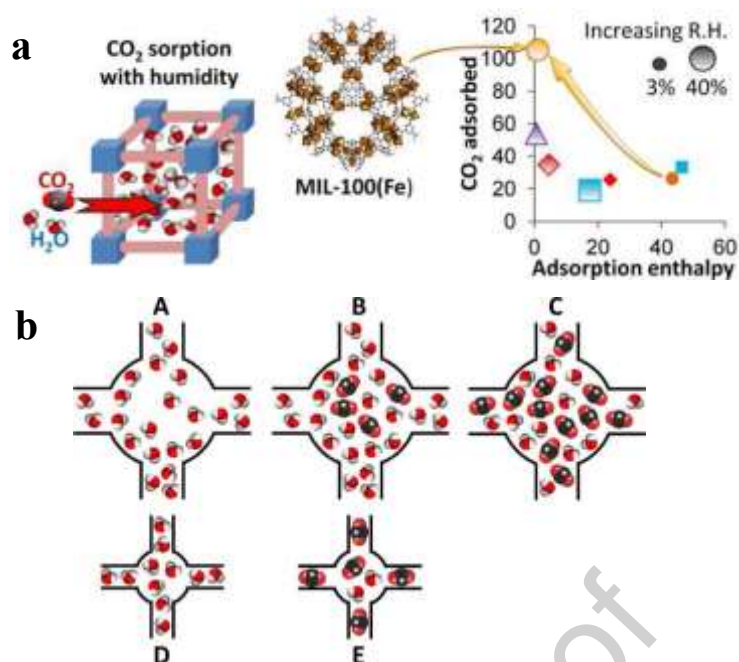


Figure 2.3 Three MOF samples studied under various R.H. levels (a); Schematic representation of possible mechanisms of CO<sub>2</sub> adsorption in the presence of humidity (b) (Soubeyrand-Lenoir et al., 2012).

Therefore, it is essential to optimise the post-combustion CO<sub>2</sub> capture processes to deal with flue gas impurities, for example, O<sub>2</sub>, moisture, SO<sub>x</sub> and NO<sub>x</sub>, in terms of cost reduction, sorbents performance and regeneration, together with power plant units of drying, desulfurisation and denitrification. First, it is recommended to develop advanced materials with favourable stability, high capture capacity and low cost for promotion of the CO<sub>2</sub> capture from flue gas. Second, system and process optimisation is also crucial to make the new approach from bench-scale experiments to practical application. Besides, most of the research work in current literature used simulated gas or pure CO<sub>2</sub> as the carbon sources. In the future, the real-world flue gas with impurities should be applied for carbon capture investigations, in order to obtain more viable and feasible processes for carbon capture from flue gas to facilitate CO<sub>2</sub> reduction, collection and utilisation.

## 2.2. Syngas as the CO<sub>2</sub> source

### 2.2.1. Characteristics of syngas

Syngas is comprised of methane (CH<sub>4</sub>), hydrogen (H<sub>2</sub>), carbon monoxide (CO), water vapors (H<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), condensable compounds, and hydrocarbons (HCs). It is the major product of the gasification of carbonaceous materials, like natural gas, heavy oil and coal. Syngas is a favourable

alternative fuel because it burns cleanly and has low greenhouse gas emissions. Its composition largely depends on the choice of feedstock and the production process. The main source of carbon dioxide emissions is coal. Syngas obtained from coal is non-renewable; however, producing syngas from coal gasification by Integrated Gasification Combined Cycle (IGCC) power plants will help reduce CO<sub>2</sub> emissions compared to burning coal directly (Casleton et al., 2008).

As described in the previous section, there are three key approaches for capturing CO<sub>2</sub> from fossil fuel-based power plants: post-combustion, oxy-fuel combustion and pre-combustion. In an IGCC power plant with pre-combustion carbon capture, syngas generated from the gasification of coal are processed in a water-gas shift (WGS) unit where after desulfurisation most of CO is converted to CO<sub>2</sub> and steam. This allows for the separation of CO<sub>2</sub> before the combustion of the fuel (H<sub>2</sub>) (Subraveti et al., 2019b). The CO<sub>2</sub> in the syngas can be separated by various methods like adsorption, absorption, membranes etc. According to Table 2.2, CO<sub>2</sub> concentration in the syngas is much higher compared to flue gas, pre-combustion CO<sub>2</sub> capture is a potentially cheaper method than post-combustion CO<sub>2</sub> capture. This is because, for an equal quantity of CO<sub>2</sub> captured, a relatively smaller volume of gas needs to be processed, resulting in lower capital costs due to smaller equipment size (Laboratory). Therefore, syngas is a better and more economical source for CO<sub>2</sub> capture as compared to flue gas in IGCC power plants (Trapp et al., 2015). However, further research needs to be carried out in order to integrate pre-combustion CO<sub>2</sub> capture technologies into IGCC power plants successfully.

Table 2.2 Advantages of syngas over flue gas in terms of CO<sub>2</sub> capture(Laboratory; Wang and Song, 2020b)

Factors	Pre-combustion(Syngas)	Post-combustion (Flue gas)
CO <sub>2</sub> Pressure	Partial High	Low
CO <sub>2</sub> concentration	High (~40%)	Low (~3-15%)
Plant modifications	Minimal; requires the addition of only absorber and regenerator	Needs larger and more expensive equipment due to less CO <sub>2</sub> concentration in the exhaust stream

### 2.2.2. Challenges of CO<sub>2</sub> capture from syngas

Since gasification is required to produce syngas in the pre-combustion process, various factors in the gasification process can pose challenges to CO<sub>2</sub> capture from syngas. The gasification can be

classified into oxygen-blown and air-blown processes. The oxygen-blown gasifier contains no nitrogen, having an evidently different composition from the air-blown gasifier syngas, which have a large nitrogen content (Cao et al., 2021). Therefore, both processes can have different configurations for the CO<sub>2</sub> capture process. The type of fuel (coal, oil, natural gas or biomass) can also affect the composition of syngas, which in turn affects the CO<sub>2</sub> capture system. Coal is an abundant fossil fuel used for electricity production. Besides, its up-gradation and developments in better efficiency at present power plants, researchers are concentrating on the growth of innovative technologies, for example, supercritical and ultra-supercritical coal fired power plants and IGCCs. Amongst these technologies, IGCCs exhibit the most promising efficiency and environmental performance, along with the facility to incorporate various kinds of feedstock (James et al., 2019). These power plants are also good for low carbon applications, as syngas has a higher concentration of CO<sub>2</sub> which favours the separation process. At present, absorption is considered to be the most reliable method for CO<sub>2</sub> separation from syngas. The absorption process can utilise chemical solvents like aqueous solutions of amines or hot potassium carbonate and physical solvents (Rectisol, Selexol, Purisol) (Notz et al., 2011). As IGCC power plants yield high partial pressure of CO<sub>2</sub> in the syngas with higher plant operating pressure, physical solvents are deemed more appropriate than chemical ones for CO<sub>2</sub> absorption (Jansen et al., 2015). Therefore, vast research has been performed on pre-combustion CO<sub>2</sub> capture processes using various physical solvents (Park et al., 2015; Siefert et al., 2016; Smith et al., 2022). The cost of carbon capture IGCC facility depends on thermal recovery and pumping, heating and cooling of the liquid and gas stream. Compared to other commercial physical solvent processes, the Selexol process has lower strength, which would result in reduced lower heating value, thereby increasing the overall plant efficiency (Cormos, 2011; Dave et al., 2016). Alternative methods for CO<sub>2</sub> capture are gaining research attention, such as the utilisation of H<sub>2</sub> or CO<sub>2</sub>-selective membranes. The type of membrane selection also depends on the gasification process, which subsequently affects the cost of the pre-combustion capture process (Scholes et al., 2012). Furthermore, the syngas flow rate, hydrogen production, output power, hydrocarbon flow rate, and apparent thermal efficiency also affect the CO<sub>2</sub> capture system. Therefore, all these factors must be considered while selecting appropriate CO<sub>2</sub> capture systems.

From the above discussion, it can be concluded that pre-combustion carbon capture is considered to be the most effective method as compared to other carbon capture methods. This is because of high CO<sub>2</sub> partial pressure. Separating carbon dioxide from syngas is considerably easier than in the post-combustion carbon capture system. Moreover, pre-combustion holds better environmental, economic and social impact as compared to other carbon capture technologies (Olabi et al., 2022). Recently, two commercial pre-combustion carbon capture facilities have been working in the United States, where around 90% of CO<sub>2</sub> is captured by using physical solvent absorption processes (Olabi et al., 2022). Two more power plants are operating in Spain and Netherlands, but only a part of syngas is

being treated for carbon capture (Rubin et al., 2012). Therefore, there is a need to study the commercialisation prospects of the pre-combustion carbon capture process extensively.

## **2.3 Biogas as the CO<sub>2</sub> source**

### **2.3.1 Biogas production and the upgrade necessity**

Anaerobic digestion is a process that involves organic matter digestion to form biogas through hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Fu et al., 2021). The produced biogas is considered to be one of the most important renewable energy sources, whose technology has been used worldwide for organic waste treatment and bioenergy production. In fact, the world is impacted by limited energy alternatives and significant environmental problems, which have stimulated the search for new bioenergy and environmental solutions. That is why the biogas industry has faced accelerated development and increase in the last decades. The world's annual biogas production is expected to reach 300 billion m<sup>3</sup> by 2020 (Fu et al., 2021), representing around 1.43 exajoules (Sönnichsen, 2022).

Traditionally, most of the raw biogas is used to produce electricity and heat directly (Khan et al., 2021). In general, biogas is a mixture of gases consisting of 50–75 % methane (CH<sub>4</sub>), 25–50 % carbon dioxide (CO<sub>2</sub>), 0–10 % nitrogen (N<sub>2</sub>), 0–3 % hydrogen sulfide (H<sub>2</sub>S), 0–1 % hydrogen (H<sub>2</sub>) and a minimal concentration of other gases (Aghel et al., 2022). With this composition, it does not meet natural gas specifications, so the content of CH<sub>4</sub> in biogas should be upgraded, and, in this case, it can be called biomethane or natural gas, enlarging its commercial value and range of applications, such as vehicle fuel (Yanuka-Golub et al., 2019). Natural gas contains 98–75 % of CH<sub>4</sub>, promoting higher burning energy, with higher burning velocity and flammability. Also, when used as vehicle fuel, CO<sub>2</sub> gas occupies more space in the cylinder tanks, which leads to the necessity of additional energy during biogas compression, thus, increasing costs. So, CO<sub>2</sub> content must be reduced through biogas upgrade solutions for the elimination of impurities using different techniques (Aghel et al., 2022a).

### **2.3.2 Developed technologies for CO<sub>2</sub> capture from biogas**

The main applied technologies worldwide for biogas upgrade are: absorption (water scrubbing, chemical absorption, physical absorption), swing adsorption (temperature, electrical, pressure), and membrane-based gas permeation are employed worldwide for biogas up-gradation (Shah et al., 2021) (Figure 2.4). High-pressure water scrubbing is the most simple and reliable biogas absorption technology. This technology promotes large-volume biogas processing. However, it presents higher electricity consumption (0.30–33.0 kWh/Nm<sup>3</sup>) (Aghel et al., 2022a). So, the development and optimisation of biogas upgrade must pass through less energy consumption and the generation of

methane-rich gas high-energy biogas. In situ technologies for methane enrichment have been explored, which include cryogenic separation, and hybrid membrane-cryogenic technologies to limit energy costs and improve CO<sub>2</sub> capture efficiency (Shah et al., 2021). Apparently, hybrid technologies seem to be more economic, but they must still be tested on a large scale (Scholz et al., 2013). Table 2.3 presents the characteristics, parameters, and advantages of the most employed biogas purification techniques, which will be described as follows (Fu et al., 2021; Shah et al., 2021).

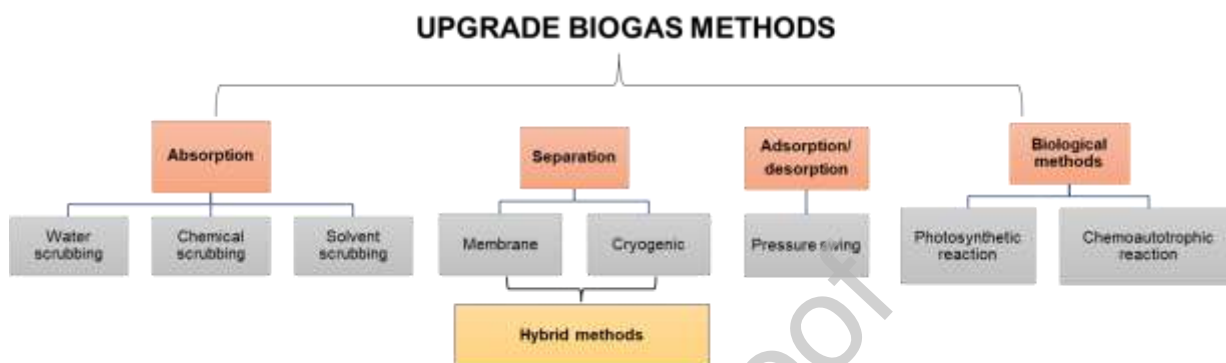


Figure 2.4 Methods for CO<sub>2</sub> capture from biogas

Water purification is the most common and well-developed method for removing CO<sub>2</sub> from biogas, and is based on the principle of physical absorption of gas in water, because of the property of gas solubility. Temperature is a factor that directly influences the process, because the solubility of gases increases with the decrease in temperature. Pressurised biogas is injected through the bottom of the absorption column, and water is channelled inward through the top of a column. The absorption of CO<sub>2</sub> in the water washing process is usually performed at 8-10 bar, although pressures are also used in the range of 10-20 bar. Biogas flows up in the column, and water flows from the top to the bottom of the column. Biomethane with more than 90% CH<sub>4</sub> is obtained from the top of the purifier, while water containing CO<sub>2</sub> and absorbed H<sub>2</sub>S is channelled from the bottom of the column to a flash vessel. Pressure reduction (2.5-3.5 bar) is applied, which results in the release of a gaseous mixture rich in CO<sub>2</sub> (80-90%) (Kapoor et al., 2019). The main advantages of this technology are simplicity of design, low overall cost, and low loss of methane during the process (less than 2%). The accumulation of elemental sulfur, corrosion, and unpleasant odour, results of simultaneous absorption of H<sub>2</sub>S in water, are problems that occur in this process.

Aqueous organic or inorganic compounds are used to bind the CO<sub>2</sub> or H<sub>2</sub>S molecules contained in biogas. The commonly used chemical solvents are amines and aqueous solutions of alkaline salts (sodium hydroxide, potassium, ammonium, and calcium) (Abdeen et al., 2016). The solubility of CO<sub>2</sub> in sodium hydroxide is higher than amines. For example, to absorb 1 ton of CO<sub>2</sub>, 1.39 tons of monoethanolamine will be required, and 0.9 tons of sodium hydroxide are needed (Angelidaki et al.,

2018). Aqueous alkaline salts are more economical and readily available compared to amines; however, the regeneration of alkaline solutions is expensive due to the high energy requirement. However, if carbonation products from the inorganic absorption process are used in other applications, such as chemical manufacturing, the process may be advantageous. The chemical purification system consists of a packaged bed column integrated into a desorption unit equipped with a reboiler. In chemical purification, biogas is injected into the packaged bed absorber operating at 1-2 bar from the bottom, and the chemical solvent is supplied from the top counter. The CO<sub>2</sub>-rich solution obtained from the bottom of the absorber is pumped into a stripping column through a heat exchanger. Solvent regeneration is performed in the stripping column at a pressure of 1.5 bar and heating it to 120-160°C (Ullah Khan et al., 2017). Foaming, the cost of chemicals, solvent loss due to evaporation and contaminant accumulation, amine degradation, solvent losses, composition problems, corrosion, and operational problems make this system complex compared to other techniques (Kapoor et al., 2019).

Organic solvents, such as methanol mixtures and polyethylene glycol dimethyl ethers, can be used for the physical absorption of CO<sub>2</sub> from biogas. The use of organic solvents has advantages: reduction of recycling rates of absorbents, investment, and operating costs. In addition, another advantage of organic solvent is the low vapour pressure of polyethylene glycol dimethyl ethers, which leads to a low solvent loss during the washing process. During the process, the raw biogas is compressed to 7-8 bar, and the column is cooled to 20 °C before injection into the absorption. The organic solvent is also cooled before being injected from the top. After washing, the organic solvent is regenerated by heating and depressurisation at 80°C and 1 bar, respectively, in a desorption column. The first step of the process is the compression and cooling of the crude biogas (7-8 bar, 20°C), followed by its injection into the bottom of the absorption column. The regeneration of the organic solvent is done in the desorption column by heating it to 80°C while the pressure is decreased to 1 bar. The final methane content in the biogas updated using this technology can reach 96-98.5% and less than 2% of CH<sub>4</sub> losses, which can be achieved in an optimised plant on a full scale.

Adsorption involves the selective adhesion or bonding of one or more components to the surface of a microporous solid. The adsorption is classified according to the adsorbent regeneration method. The procedure can occur: a) in a cyclic operation by closing the inlet valve or by using a vacuum (vacuum swing adsorption -VSA), by reducing the pressure to atmospheric level (pressure swing adsorption - PSA), or by varying temperature (30-120 °C) that is carried out at the same pressure level (temperature swing adsorption - TSA) (Nie et al., 2013). Pressure swing adsorption - PSA presents interesting advantages to remove CO<sub>2</sub> from biogas because it employs compact equipment, has low energy requirements, and requires low investment. It is safe, simple, and stable compared to other methods. Another point is that it is suitable for small-scale plants (Aghel et al., 2020). It uses structural adsorbents in the form of granules, pellets, and laminates to separate CO<sub>2</sub> from biogas,

which is based on size-selective adsorption strategies (Kadam and Panwar, 2017). Porous carbon is widely used in gas phase separation, and it can be produced by the thermal decomposition of natural and synthetic polymers. However, natural polymers are advantageous due to their high availability and lower costs. Activated carbon is commonly used as an adsorbent due to its high surface area, developed microporosity, thermal stability, ease of reduction, and low production costs (Aghel et al., 2022a).

Vacuum pressure oscillation adsorption (VPSA) technology for CO<sub>2</sub> removal from biogas has low capital investment and low energy consumption and greater applicability in areas with water deficiency (Shen et al., 2018). In adsorption, atoms, molecules or ions adhere to the surface of materials creating an adsorbent layer on the adsorbent surface. Gas adsorption can be based on temperature and pressure, as high pressures and low temperatures promote adsorption efficiency (Zhou, K. et al., 2017). VPSA methods drew more attention to the removal of CO<sub>2</sub> from biogas due to its low capital investment and low energy consumption, which can be applied in areas with water deficiency (Shen et al., 2018).

Cryogenic processes are based on temperature differences for the liquefaction of biogas compounds (Ma et al., 2018). The separation depends on different sublimation points where CH<sub>4</sub> (-161.5 °C) has a lower sublimation point than CO<sub>2</sub> (-78.5 °C). Another strategy is the gradual temperature reduction, which allows the selective separation of CH<sub>4</sub> from other components (Aghel et al., 2022a). In this case, biogas is cooled and compressed until CO<sub>2</sub> is liquefied. With the lower sublimation point of CH<sub>4</sub>, the two gases can be separated through distillation (Budzianowski et al., 2017). In cryogenic separation, the difference in the boiling point of the various gas components is explored to separate the components, and obtain high content of CH<sub>4</sub> and CO<sub>2</sub> recovery, generating biomethane of high purity and with minimal methane losses (<1%). In addition, liquid CO<sub>2</sub> can be generated (usually up to 98% purity), and this high-purity liquid CO<sub>2</sub> can be produced at a high-pressure level, which makes it interesting, especially about storage, saving dense compression of energy to store CO<sub>2</sub> as gas (Hashemi et al., 2019). However, some obstacles are encountered by separating CO<sub>2</sub> under the required very low-temperature conditions, hindering its development and applicability: the dense consumption of energy via refrigeration cycles used for separation and the formation of dry ice due to cryogenic separation of CO<sub>2</sub>, which generates serious operating problems such as clogging of pipes or other equipment (Yousef et al., 2018b). Although the separation by this method is interesting because it results in very high-purity gas, this method has high electricity consumption and requires a cryogenic production technology of up to -125 °C temperature at pressures of 20-50 bar (Mehrpooya et al., 2020). In a study on cryogenic technologies for biogas update and CO<sub>2</sub> separation, three main systems were identified. In the first system, the biogas is first cooled, and the water is removed, then it is cooled, compressed, and gets CO<sub>2</sub> liquid. In the distillation

system, a distillation column is used to remove and liquefy CO<sub>2</sub>. In the desublimation process, CO<sub>2</sub> is removed during its phase change from steam to solid inside a heat exchanger(Tan et al., 2017).

Biological biogas update involves the application of microorganisms for the conversion of CO<sub>2</sub> and H<sub>2</sub> into methane. The two metabolic pathways involved in the updating of biological biogas are that with hydrogenotrophic methanogens involved in the direct conversion of CO<sub>2</sub> into CH<sub>4</sub>, and another with homoacetogenic bacteria that first convert CO<sub>2</sub> into acetate, and then for conversion into methane by acetoclastic methane(Kapoor et al., 2019).

In biological upgrading methods, microorganisms are employed as catalysts to convert CO<sub>2</sub> and H<sub>2</sub> into CH<sub>4</sub>. Different advantages of biological processes can be pointed out over chemical processes, such as the use of moderate temperatures and atmospheric pressure, compared to chemical processes. In addition, higher resistance to gas contaminations, including H<sub>2</sub>S, organic acids, and NH<sub>4</sub> is observed(Aghel et al., 2022a). The most important advantage of biological processes is that CO<sub>2</sub> is captured and recycled to be used in the production of new bioproducts. Biological upgrading methods can involve methanogens binding CO<sub>2</sub> into CH<sub>4</sub>, dicarboxylic-acid-producing bacteria binding CO<sub>2</sub> into dicarboxylic acids such as biosuccinic acid, or algae binding CO<sub>2</sub> into algal biomass(Fu et al., 2021).

In the last years, microalgae, bacteria, or archaea have been used in upgrading biogas processes(Zhu, Xianpu et al., 2020). According to processes' configurations, these technologies are classified into *in situ* biogas upgrading, *ex situ* biogas upgrading, and hybrid biogas upgrading. In situ configuration, H<sub>2</sub> is injected directly into the biogas reactor to capture the endogenously produced CO<sub>2</sub>. In the *ex-situ* strategy, H<sub>2</sub> and biogas are injected into a separate reactor. Hybrid upgrading is a combination of in situ and *ex situ* strategies, where the initial *in situ* process occurs in a favourable pH for biological processes, while the last upgrading step is carried out in an ex-situ process. An advantage of *in situ* biogas upgrading is the integration of biomethanation and biogas upgrading in the same bioreactor in an economically and feasible way(Fu et al., 2021).



Table 2.3 Biogas purification technologies and their characteristics (Modified from (Fu et al., 2021; Shah et al., 2021))

Technology	Operation	Pressure (bar)	Electrical Consumption (kWh/Nm <sup>3</sup> )	Methane losses (%)	Methane purity (%)	Investment (€/Nm <sup>3</sup> biogas)	Maintenance per year (€/year)	Advantages	Disadvantages
<i>Water scrubbing</i>	Absorption	6 – 10	0.30 – 33.0	< 1%	>97%	0.13 – 15	15,000	Easy to handle and simple in operation; The large volume of processed gas; Useful in cold regions where CO <sub>2</sub> solubility increases; High methane purity with less methane loss.	High investment; High pressure and energy needed; A huge amount of water needed; High risk of biological contamination
<i>Chemical scrubbing</i>	Absorption	1 – 1.5	< 0.15	< 0.1%	>99%	0.28	59,000	High efficiency; High CH <sub>4</sub> purity up to 99%; Easy operation; Low CH <sub>4</sub> loss (<0.1%); Simultaneous removal of CO <sub>2</sub> and H <sub>2</sub> S.	High investment in amine solvents; Toxic solvents are needed; Solutions are needed for reasonable disposal.
<i>Solvent scrubbing</i>	Absorption	4-7	< 0.25 – 0.33	2 – 4%	>96%	0.25	39,000	Fewer liquid inputs, smaller dimensions of the upgrading unit; High CH <sub>4</sub> purity up to 98%; Simultaneous removal of CO <sub>2</sub> and H <sub>2</sub> S;	Use of toxic organic solvents; Difficult regeneration of organic solvents (presence of CO <sub>2</sub> ); High temperatures are required

								Simple process and easy operation; Low CH <sub>4</sub> loss.	for H <sub>2</sub> S separation .
<i>Membrane separation</i>	Permeation	20-36	< 0.18 – 0.35	< 5%	90 – 99%	0.22	25,000	Dry process; High selectivity to impurities; Removes water vapor; Less mechanical deterioration; No usage of chemicals.	High cost of membranes; Multiple steps are required for high purity; Low membrane selectivity ; Pretreatment is needed
<i>Cryogenic separation</i>	Compression and condensation	40	< 0.18 – 0.66	< 0.1%	>99%	0.40-0.44	-	Methane purity is high No use of chemicals and water Possible reuse of CO <sub>2</sub>	High investment and operation costs; High energy is needed; Under development.
<i>Pressure swing adsorption</i>	Adsorption/desorption	4 -8	0.25	< 3%	>96%	0.26	56,000	Dry process No solvent to dispose No water requirement No microbial impurity Adsorbent usable for up to 3 years	Higher CH <sub>4</sub> loss; Prepurification equipment is needed to remove H <sub>2</sub> S from biogas; Pre-drying is needed for water remove from biogas; Contamination by impurities in the biogas.
<i>Biological methods</i>	Photosynthetic reaction	Atmospheric	-	-	>99%	-	-	High methane recovery	High investment cost and energy;

								up to ~97% Transformation of CO <sub>2</sub> into other products Production of active biomass Low requirements in terms of land and water	Low photosynthetic CO <sub>2</sub> uptake; Natural sources are required; High risk of biological contamination.
	Chemoautotrophic reaction	Atmospheric	-	-	>99%	-	-	High selectivity, process efficiency, and CH <sub>4</sub> purity Conversion of CO <sub>2</sub> into CH <sub>4</sub> ; Reduction of CO <sub>2</sub> emission; Moderate temperatures and atmospheric pressure; Can be integrated with the AD process; Environmentally friendly.	A high amount of reductant is needed; This technology is still under development.

## 2.4. Direct air capture (DAC)

### 2.4.1 Technological Family of DAC

Large-scale direct air capture (DAC) has been considered since the late 1990s as an additional way to mitigate the growing atmospheric CO<sub>2</sub> concentrations. Lackner et al. (Lackner et al., 1999; Zeman and Lackner, 2004) presented an optimistic look regarding DAC. Although ambient CO<sub>2</sub> concentrations are very low, DAC may not totally be unfeasible and detailed a carbon-capture approach utilising Ca(OH)<sub>2</sub>. A number of DAC approaches have been proposed using adsorption and absorption technologies, although the topic is still developing (Goeppert et al., 2012; Jones, 2011). DAC is a technique for permanently capturing and storing CO<sub>2</sub> in geological storage sites by separating it from ambient air using chemical, physical, or mechanical methods. Since the CO<sub>2</sub> in the atmosphere is quite diluted (~415 ppm), substantial energy is required while utilising specialised materials. Therefore, the process design and ensuing techno-economic and environmental performances will have a significant impact on their future deployment and participation in climate change mitigation (Qiu, Y. et al., 2022).

Pressure swing adsorption (PSA) is utilised in many industrial processes to separate specified gas species from a mixture of gases (usually air). An adsorbent bed (e.g., activated carbon, zeolites, etc.) is used to trap target gas species while the mixture is pressurised. When the pressure is released, the trapped gas species are released. Membranes, such as zeolites, have the potential to become useful for DAC (Gao et al., 2022a; Hong, 2022). Another promising technology is utilising nitrogen-enriched biochar as a CO<sub>2</sub> adsorbent (Sanz-Pérez et al., 2016).

Another technology for carbon capture is temperature swing adsorption (TSA), which alternates the temperature of the sorbent to adsorb and desorb CO<sub>2</sub>. TSA is attractive because it is generally less costly than PSA (Zhao, R. et al., 2017c). Veselovskaya et al. (Veselovskaya et al., 2013) presented an extensive study of utilising K<sub>2</sub>CO<sub>3</sub> in g-AL<sub>2</sub>O<sub>3</sub> as a composite inorganic sorbent for a TSA cycle for direct air capture.

Removing CO<sub>2</sub> from the atmosphere using alkaline solutions has been investigated since the 1940s (A and Dodge, 1946; Tepe and Dodge, 1943). In various wet-scrubbing techniques, CO<sub>2</sub> is absorbed into a NaOH solution, which leaves behind an aqueous solution of NaOH and Na<sub>2</sub>CO<sub>3</sub>. Packed scrubbing towers (Baciacchi et al., 2006; Zeman, 2007) and large convective towers (Lackner et al., 1999) are the most frequently used designs for putting NaOH in contact with CO<sub>2</sub>. Other investigators (Stolaroff et al., 2008) have generated a fine spray of the absorbing solution to the air through an open tower. It has since been proposed that DAC using CO<sub>2</sub> absorption exclusively by an aqueous solution of NaOH is unfeasible economically (Socolow, R. et al., 2011).

Another alternative to chemisorption- and physisorption-based approaches is to take advantage of the temperature advantage that naturally cold climates, such as the arctic and Antarctica, can provide to

desublimates CO<sub>2</sub> directly from the air. Since the outside air temperature is very cold, the idea is not as much energy is needed to cool the air to desublimates CO<sub>2</sub>. DAC via cryogenic heat exchangers is still very nascent. Serious consideration to such devices started in the early 2010s with lab-scale benchtop demonstrations (Agee, Ernest et al., 2013; Agee, Ernest M. and Orton, Andrea, 2016). Follow-on work by several other studies quantified the theoretical energy associated with DAC cryogenic carbon capture plants placed in arctic climates (Boetcher, Sandra K. S. et al., 2020; Perskin et al., 2022; von Hippel, 2018).

## 2.4.2 DAC performance from real world

### 2.4.2.1 Performance map of DAC: adsorption as a case study

The chronological results of the amount and proportion of publications on direct air capture (DAC) since 2004 are presented in **Figure 2.5**. The keywords of (TS=(direct air capture or DAC) AND TS=(CO<sub>2</sub> or carbon dioxide)) NOT (DT=("PATENT")) is applied for the literature research. Until July 2022, a total of 1673 articles were collected, with a significant increase in the past four years. Furthermore, the keywords of (TS=(direct air capture or DAC) AND TS=(CO<sub>2</sub> or carbon dioxide) AND TS=(sorbent or \*sorbent)) NOT (DT=("PATENT")) were applied to final obtain 306 articles among these published articles on DAC sorbents, accounting for 18.2% of the total number of articles. Such results are applied to establish a data pool of DAC performance to explore specific development trends.

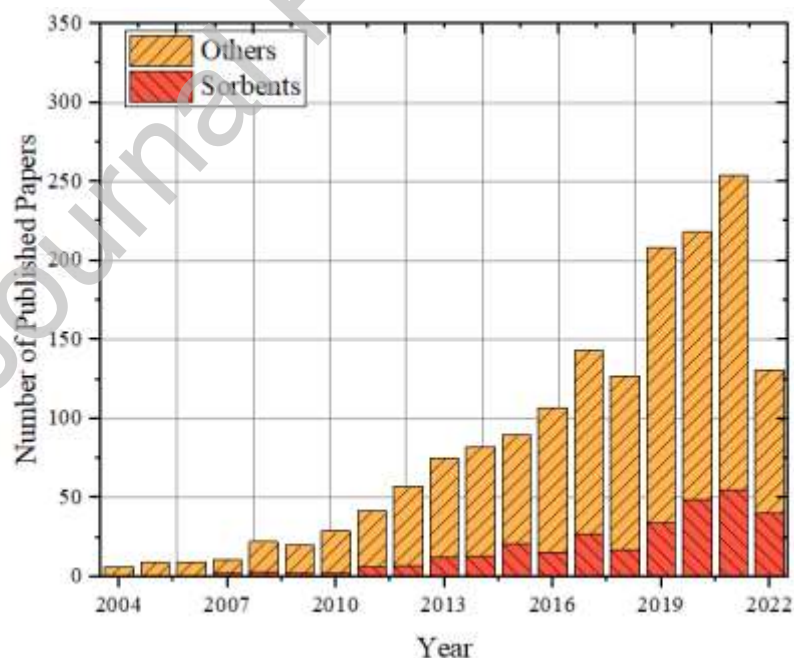


Figure. 2.5 The database pool of DAC performance from 2004 to 2022 (Data collected in July 2022 based on search results of papers from Web of Science).

However, after a detailed screening of summarised data, it could be found that the real-world performance of DAC has not yet demonstrable a clear development trend among various technologies. Due to the relatively active status of research and demonstration, adsorption DAC is taken as the example of the technological family to demonstrate the real-world performance analysis of DAC (Baus and Nehr, 2022; Belmabkhout et al., 2010; Chaikittisilp, Watcharop et al., 2011; Chan et al., 2013; Custelcean et al., 2021; Elfving and Sainio, 2021; Fujikawa et al., 2021; Hemmatifar et al., 2022; Keith et al., 2018; Keller et al., 2018; Mazzotti et al., 2013; Mukherjee et al., 2019; Ruuskanen et al., 2021; Sadiq et al., 2020; Sinha et al., 2017; Sinha and Realff, 2019; Wang, T. et al., 2014; Wang, T. et al., 2020; Wurzbacher et al., 2016; Xu, X. et al., 2020; Zhu et al., 2021). Two main performance indicators of adsorption capacity and energy consumption are employed in **Figure 2.6** with three physical scales: adsorbent-scale, contactor-scale, and system-scale. Due to a lack of standard methods of test and data-report on DAC with different TRLs (Technology Readiness Levels), it is challenging to conduct a fair performance comparison without a classification on various physical scales.

In addition to direct screening of **Figure 2.6**, several points are summarised as follows based on the current data pool:

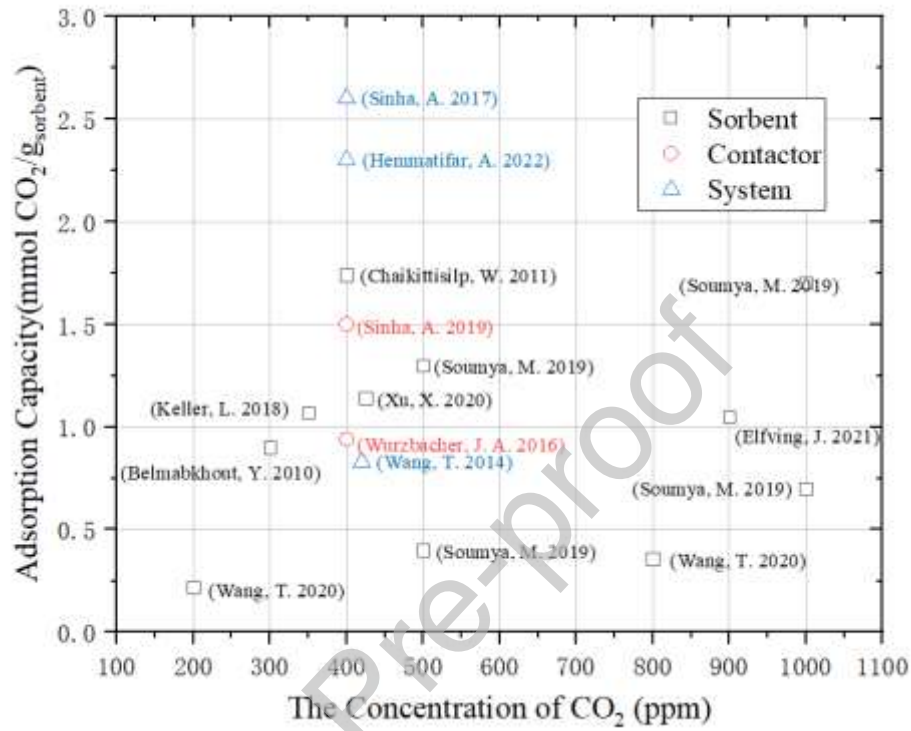
(1) The adsorbents with large sorption capacities, fast reaction kinetics, strong selectivity, as well as low energy consumption, are so-called ‘intrinsic’ pursuit of researches not only on adsorbent scale, but also on contactor and system scale.

(2) The adsorption heat of adsorbent is expected to on a reasonable level of 45-92 kJ/mol CO<sub>2</sub> for potential scale-application of DAC. Thus, amine-modified porous materials have become a primary option due to their excellent comprehensive properties.

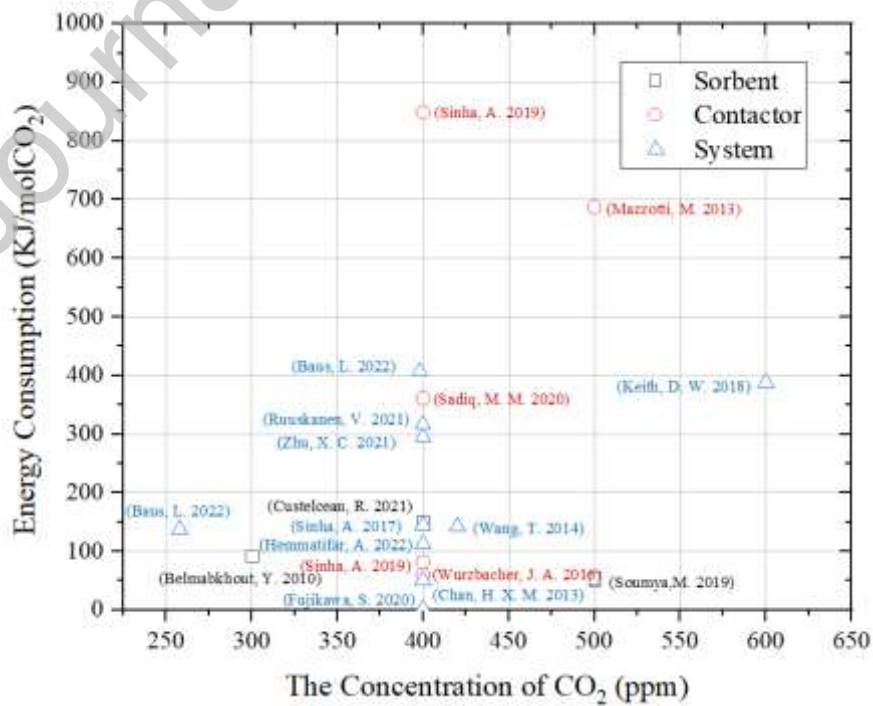
(3) Moisture cannot be ignored in the DAC performance analysis, especially some active candidates of adsorbent, such as amine-modified porous materials. Though the presence of water could increase the capture performance on some specific moisture level, the adsorption of water would increase the heat of adsorption during the desorption process (Jung and Lee, 2020). Drechsler proposed that a well-designed desorption step of DAC could significantly reduce the co-desorption effect of moisture, and the heat of water vapor can be recovered to further compensate for the desorption heat loss (Drechsler and Agar, 2020).

(4) Currently, the condition window for DAC research is commonly in a range of 400–420 ppm and 20–25°C. Considering scenarios of carbon sources are still emerging for potential exploration in industrial, building, etc. sectors, some relatively concentrated range, e.g. 5% vol, of distributed carbon source, could lead DAC application to a wonderland, with improved capture performance and lower energy-consumption (Zhao, R. et al., 2019b), though it may increase the complexity of the capture system to a certain extent.

(5) Integrating DAC technology with other technologies could result in an intensive process with a reasonable energy-consumption and improved energy-efficiency of the entire system (Wang, T. et al., 2014).



(a)



(b)

Figure. 2.6 Performance map of adsorption DAC (a) Adsorption Capacity (b) Energy Consumption.

### 2.4.2.2 Re-thinking the methodology of performance evaluation of DAC

The efficient operation with reasonable energy consumption is a key prerequisite to the practical application of DAC. Hence, a clear and complete performance evaluation method, especially on energy-consumption or energy-efficient aspects, is critical to scale-up. Chen et al. (Chen, L.J. et al., 2021) employed the benchmarking analysis method to compare the energy-consumption results of temperature swing adsorption (TSA) carbon capture systems with various physical boundaries. It was found that the selection of benchmarking boundary has an important influence on the performance evaluation results, as shown in Table 2.4.

Table 2.4 The boundary with various elements of energy-consumption: TSA DAC system as a case study

Reference	Organisation	Heat consumption (MJ/kg)	Electricity consumption (MJ/kg)										
				$e_1$	$e_2$	$e_3$	$e_4$	$e_5$	$e_6$	$e_7$	$e_8$	$e_9$	
Deutz et al. (Deutz and Bardow, 2021)	RWTH University; ETH Zurich	Aachen	11.9	2.52	√	√	√	√	√			√	√
Young et al. (Young et al., 2021)	Heriot-Watt University		9.93	0.8	√	√	√	√	√			√	√
Zhu et al. (Zhu et al., 2021)	Shanghai Jiao Tong University		16.23	1.3	√	√	√	√	√			√	√
Sinha et al. (Sinha et al., 2017, 2020)	Georgia Institute of Technology		0.77	2.5	√		√	√				√	√
Wurzbacher et al. (Wurzbacher et al., 2012)	ETH Zurich; Climeworks Ltd.		11.2	0.28	√	√	√						√

In Table 2.4,  $e_1$ – $e_7$  are elements of energy consumption during the heating process, depending on which scale is applied in performance evaluation, which commonly includes the sensible heat of adsorbent, the sensible heat of adsorbed gas, the heat of desorption, the sensible heat of adsorption chamber, the heat dissipation of adsorption chamber, the sensible heat of pipelines and auxiliary equipment, and the heat dissipation of pipelines and auxiliary equipment. The  $e_8$  and  $e_9$  are the energy consumption of the blower and the vacuum pump, respectively. By analysing the elements of the energy consumption of DAC technology in Table 2.4, it can be found that there are a few consensuses on which evaluation



framework should be applied for the performance analysis of DAC, as a standard framework. Such a knowledge gap would lead to a direct performance comparison among various studies difficult. A simplified guideline would be helpful: according to the specific research aim, the energy consumption of DAC, taking adsorption-kind technology as an example, could be divided into three physical scales: the adsorbent, the adsorption chamber, and the adsorption system. Such rough classification, at least, could be considered as a small step in the scholar community to re-think whether the current confused methodology of performance evaluation is beneficial to the development of DAC.

### 2.4.2.3 Discussion on DAC performance in real world

In addition to capturing rate and purity, energy consumption is taken into consideration in the performance evaluation framework with the emerging attention on initial investment and operation management of DAC. Although it is a widely-applied indicator for the performance evaluation of DAC, the specific amount of energy consumption during operation is deeply affected by operating conditions such as the composition of the air source and the temperature of the heat source (e.g. heat regeneration). Hence, it is challenging to compare the performance of various DAC systems directly without specific descriptions of design or operation conditions. In addition, this indicator should clearly reflect the energy-saving potential of various DAC technology, as well as the maturity degree of technology, in a direct way.

The efficiency of the second law of thermodynamics (ESLT), which has been successfully applied in the performance evaluation of heat pump, organic rankie cycle, etc., can also be applied in the performance evaluation of DAC to solve the above-mentioned problems (Landelle et al., 2017). Generally, the ESLT is applied to evaluate the irreversibility of the energy system with a viewpoint of thermodynamics, which could be considered as an indicator to demonstrate the ratio of performance of actual DAC to that of real DAC. In reference (Zhao, R. et al., 2017a), it is expressed as follows:

$$\eta_{2nd} = \frac{W_{min}}{W_{ac}} = \frac{W_{min}}{W_{min} + LW}, \quad (\text{eq. 4.1})$$

where  $W_{ac}$  is the equivalent work input of the actual system;  $W_{min}$  is the minimum separation work, that is, the work required for the reversible separation of the ideal mixture under constant temperature and pressure;  $LW=T_0\Delta S$  and indicates the irreversibility of the actual system.

Based on the common calculation method, the ESLT of DAC cases from the pool of existing publications is obtained. Due to the lack of real performance data of DAC, more cases of carbon capture are included. The final-chosen cases include absorption, sorption, membrane separation, cryogenics, and integrated technologies (Berstad et al., 2022; Bounaceur et al., 2006; Cau et al., 2014; Clause et al., 2011; Cormos, 2015; Giordano et al., 2017; Grande and Rodrigues, 2008; Hussain and Hägg, 2010; Jiang et al., 2020; Kim and Lee, 2016; Knapik et al., 2018; Krekel et al., 2018; Landelle et al., 2017; Li,

H. et al., 2020; Li, R. et al., 2022; Li, S. et al., 2016; Lin, Q. et al., 2021; Lindqvist et al., 2014; Liu, B. et al., 2020; Matthews and Lipiński, 2012; Mletzko et al., 2016; Oexmann et al., 2008; Oreggioni et al., 2015; Pirngruber et al., 2013; Rezaei et al., 2022; Ruan et al., 2014; Sanpasertparnich et al., 2010; Seo et al., 2022; Shen et al., 2012; Shen et al., 2017; Song, C. et al., 2017; Tajima et al., 2004; Tian, J. et al., 2021; Tuinier et al., 2011a; Tuinier et al., 2011b; Veneman et al., 2015; Versteeg and Rubin, 2011; Wang and Gan, 2014; Wurzbacher et al., 2012; Xie et al., 2014; Zhang, Y. et al., 2016; Zhao, R. et al., 2017a), as well as some DAC cases.

As can be seen in Figure 2.7, the ESLT of adsorption-based carbon capture and DAC ranges from 3–26%, while the absorption-based technologies range from 4–21%. The area enclosed by the grey and red dotted lines represents the ESLT ranges of the state-of-art of adsorption and absorption technologies, respectively. It is worth noting that the purple area shows ELST of DAC-related technologies is in a range of 0.15–13%. The fact of ESLT of DAC is relatively lower compared to that of high-concentration CO<sub>2</sub> capture. It is implied that the current knowledge system has weaker support for DAC than that of carbon capture; more efforts should be input into the DAC field to explore its potential for system optimisation.

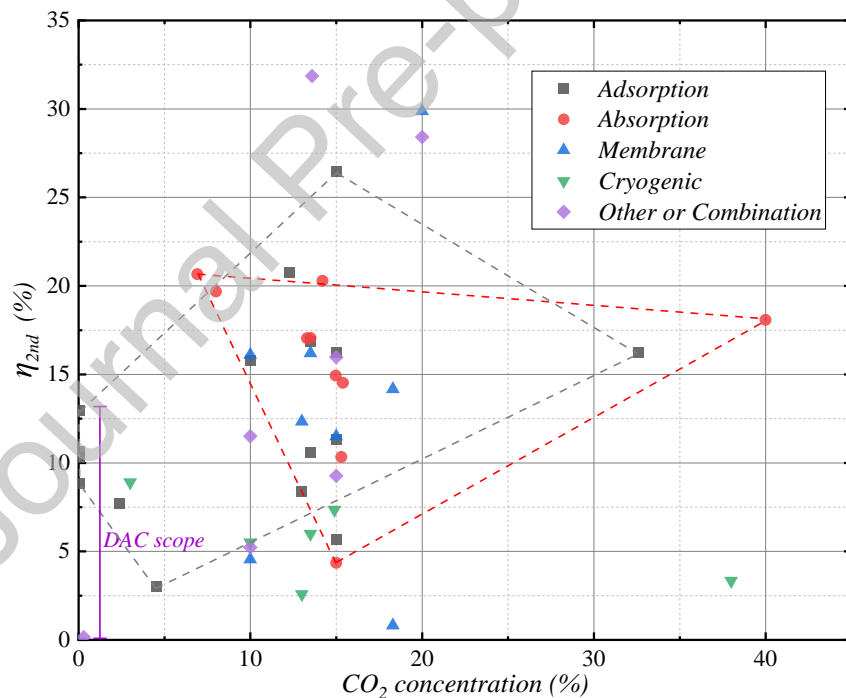


Figure 2.7 The efficiency of the second law of thermodynamic of different technologies (Zhao, R. et al., 2017a).

### 2.4.3 DAC cost from the real world

#### 2.4.3.1 Cost controversy of DAC

The cost of DAC is uncertain and hotly disputed. Due to the limited research that has been done, the available data are not unified and sometimes even inconsistent. The reason is that the research methods are different, and the method of data report is not systematic and comprehensive. The results of different research projects are inconsistent, and the results of the same project are constantly updated to overturn the existing knowledge. Currently, the cost of DAC typically includes the investment cost, operating cost, material loss, and system maintenance cost of the DAC equipment. Other studies also consider the cost of CO<sub>2</sub> transportation, storage, and utilisation. Early studies on CO<sub>2</sub> capture from the atmosphere primarily focused on producing synthetic fuels (Steinberg and Dang, 1977). Subsequently, the concept of DAC was proposed in the field of carbon capture and storage (CCS) (Lackner et al., 1999). Figure 2.8 shows the context of the DAC cost battle in recent years.

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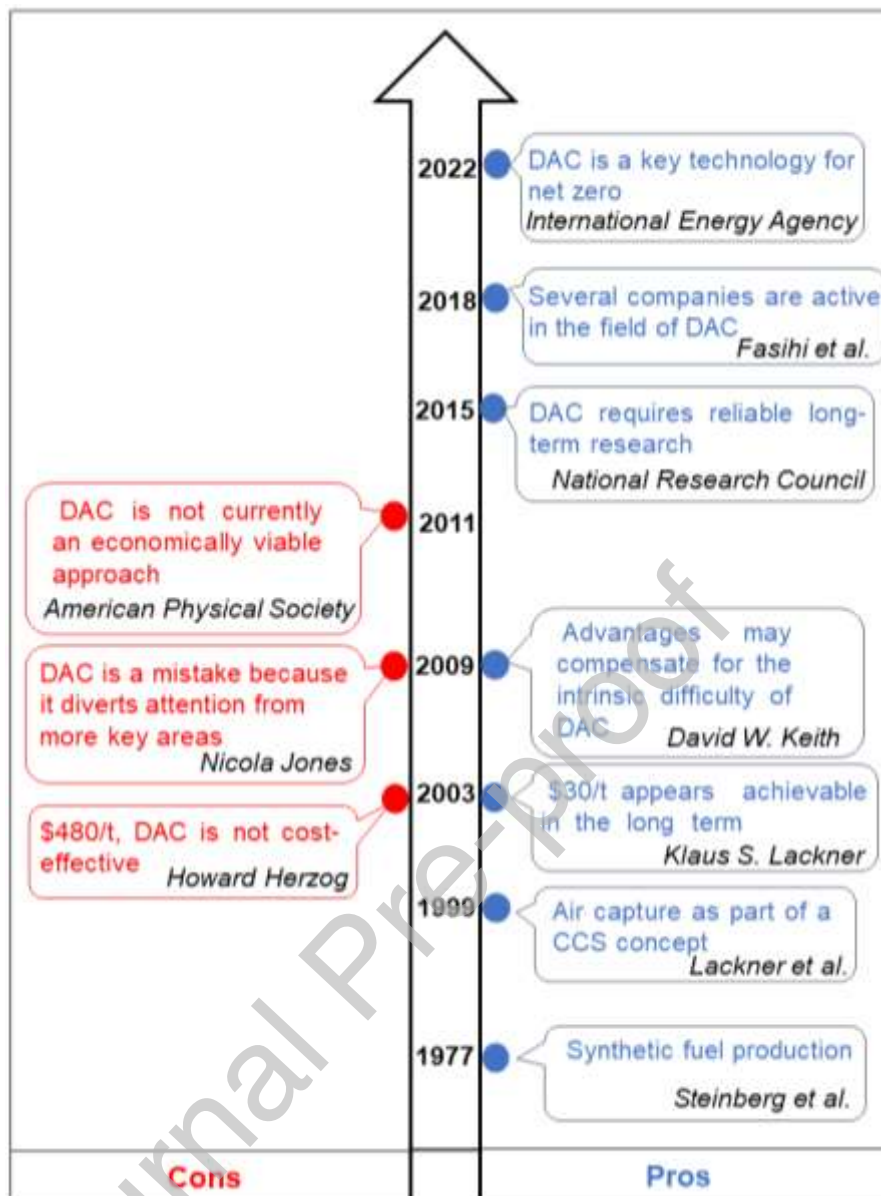


Figure 2.8 Controversy of DAC development.

Some researchers believe that the cost of DAC will be so high that investment in DAC is a mistake because it undermines the incentives for a major clean-modification of the original energy structure. In 2003, Howard Herzog of the Massachusetts Institute of Technology calculated that the cost of DAC technology was as high as \$480–540/t (H, 2003). In 2009, Jones N. of Columbia University argued that the study on DAC may be a complete mistake because it diverted attention and resources from other important fields (Jones, 2009). In 2011, the American Physical Society released a report on *Direct Air Capture of CO<sub>2</sub> with Chemicals*, and stated that DAC was not an economically feasible solution to mitigate climate change (Socolow, Robert et al., 2011). The report used a simplified method to calculate the CO<sub>2</sub> avoidance cost of DAC using a sodium hydroxide solution that was \$600/t. In comparison, the CO<sub>2</sub> avoidance cost of post combustion carbon capture from flue gas using the same solution was only

\$80/t. Hence, the cost of DAC is approximately eight times that of the post combustion carbon capture. In addition, the report also states that DAC cost is likely to decline as technology advances and new concepts are introduced. However, industry experience suggests that considering the necessary compromises in material selection, process conditions, component efficiency, and component lifetime, the cost of all systems will increase after the pilot operation. Therefore, the report concluded that the adoption of DAC technology should be postponed.

In stark contrast, supporters argue that DAC is relatively inexpensive and plays a key role in managing carbon dioxide emissions. In 2003, Klaus S. Lackner of Columbia University showed that the cost of CO<sub>2</sub> emission reduction would be reduced in the long run (Lackner, 2003). In 2009, David W. Keith reported that although the DAC cost would be higher than the cost of power plants with post combustion carbon capture under the same economic conditions. However, DAC enables the partial decoupling of carbon capture from the energy infrastructure, easing the constraints that arise when new energy technologies must be integrated into the existing infrastructures and making it easier to build a capture plant near the best sequestration sites (Keith, 2009). These advantages can compensate for the inherent difficulties of DAC.

After the report of 2014 International Panel on Climate Change (IPCC) (Pachauri and Meyer, 2014), the international academic community generally changed their views on DAC. In 2015, the National Research Council of the United States released a report stating that long-term research support for DAC is required (Board and Council, 2015). Subsequently, Keith et al. designed a plant for DAC using a potassium hydroxide (KOH) sorbent and calcium-alkali coupling cycle. A detailed calculation showed that the cost of CO<sub>2</sub> was \$94–232/t (Keith et al., 2018). DAC has gradually become a major research focus in the United States, Europe, China, and Japan. For example, the Negative Carbon Plan launched by the U.S. Department of Energy in November 2021 enlisted DAC technology as a key development goal. This strategy aims to reduce the DAC cost to less than \$100/t.

#### **2.4.3.2 How high is the DAC cost in the real-world right now?**

As shown in Figure 2.9, many scholars have conducted an economic evaluation of DAC (Baylin-Stern et al., 2022; Chichilnisky, 2021; Clifford, 2022; Fasihi et al., 2019; House et al., 2011; Keith et al., 2018; Mori et al., 2019; Peters, 2022; Socolow, Robert et al., 2011). In 2019, Mori et al. (Mori et al., 2019) conducted a cost assessment of the pilot DAC plant of Climeworks in Iceland. Since the technology and commercial scale was still in the development stage, the cost was approximately \$600–800/t. In 2022, according to Fast company, a start-up company called Heimdal launched the first ocean-assisted carbon removal plant in Hawaii that is currently capable of capturing CO<sub>2</sub> at the cost of \$475/t (Peters, 2022). Some researchers believe that the DAC cost will show a clear downward trend in the long term. In a techno-economic assessment of DAC plants by Fasihi et al. (Fasihi et al., 2019) in 2019, it was reported that the cost of DAC systems would be significantly reduced with large-scale applications in

the 2040s and 2050s. By using a low-temperature sorption DAC system that utilises a hybrid photovoltaic power cell system in Morocco as an example, the CO<sub>2</sub> capture costs in 2020, 2030, 2040, and 2050 were estimated to be \$295, \$200, \$92, and \$72/t, respectively. Jan Wurzbacher, co-founder and co-CEO of Climeworks, told CNBC in an interview that the company is focusing on cost reduction in addition to increasing capacity (Clifford, 2022). It is expected that the cost in 2025, 2030, and 2035, can be reduced to \$500, \$300, and \$200/t, respectively. In December 2021, NOAH Zurich report, Graciela Chichilnisky described the DAC technology of Global Thermostat that captures carbon dioxide from the air using waste heat at 85°C and a proprietary solvent. According to the use of the captured carbon (e.g., beverage filling, carbon dioxide concrete, synthetic fuels, and sequestration), Global Thermostat has divided the 2020 to 2050 period into nine phases and assessed the cost of each phase. It is estimated that the cost will be as low as \$54/t by 2050 (Chichilnisky, 2021). According to the IEA's report on DAC in 2022 (Baylin-Stern et al., 2022), assuming different capture technologies, energy prices, and financial assumptions, the cost of DAC capture under a large-scale application of 1 Mt CO<sub>2</sub>/year is estimated to be in the range of \$125–335/t. In addition, the IEA also predicts that by 2030, the cost of DAC is likely to be less than \$100/t with the large-scale application of the technology.

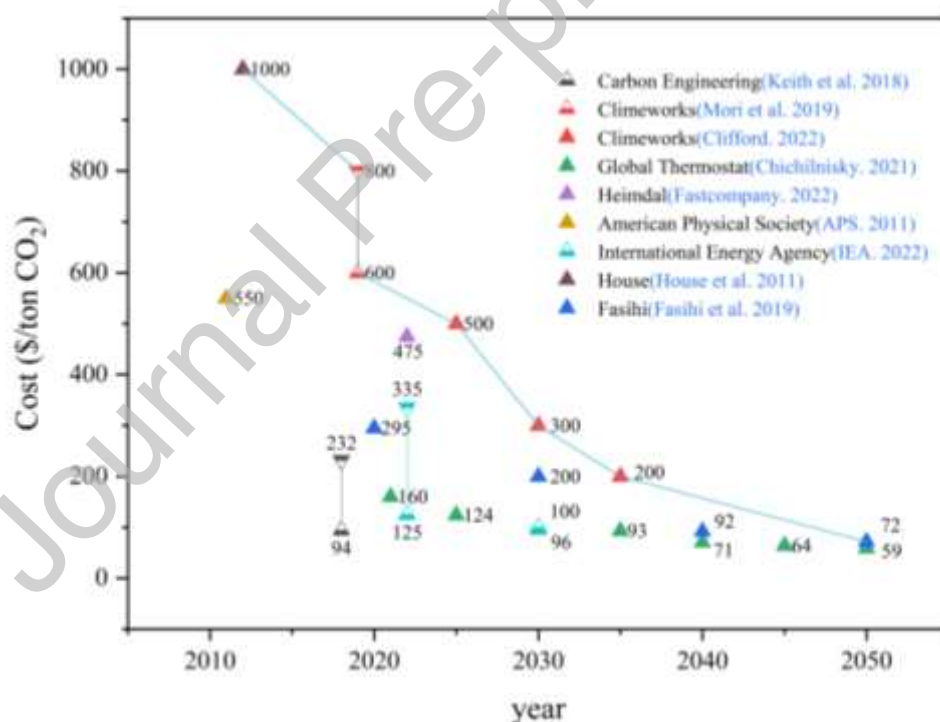


Figure 2.9 The cost summary of DAC.

### 2.4.3.3 High or relatively high cost?

Currently, the high cost has become the primary factor that limits the commercialisation of DAC technology. However, a good question that needs to be addressed is whether the DAC cost is high or

relatively high compared to the environmental cost. The hidden cost can be quantified to a certain extent using external tools such as a carbon tax. As shown in Figure 2.10, as the amount of captured carbon increases, the cost of DAC increases as well. According to IEA, the cost of DAC under large-scale application conditions (1 Mt CO<sub>2</sub>/year) is between \$125–335/t. Low heat and electricity prices could reduce the projected cost to just above the industry target of \$100/t (Baylin-Stern et al., 2022). If the captured carbon could be monetised using some form of carbon pricing scheme, the levelized cost of DAC would be well below \$100/t. Furthermore, a carbon price above \$160/t could make DAC-based capture profitable.

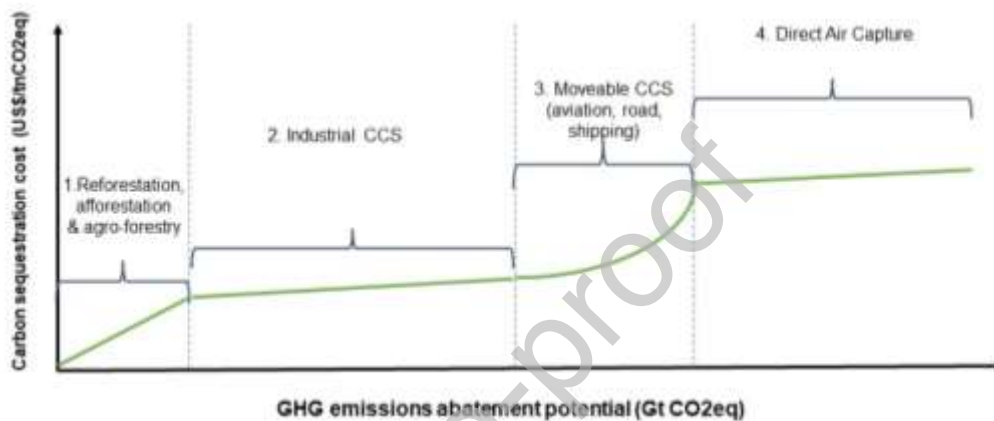


Figure 2.10 Carbon abatement cost curve (Research, 2019).

Due to the high flexibility of DAC technology in terms of plant site selection, the best power generation and heating technology could be used in areas with high renewable energy potentials. By 2030, the cost of DAC could be reduced to less than \$100/t. In addition to strong policy and financial support, technological research and development may also cause industrial upgrades. Therefore, cost reduction could be achieved through technological research and development, learning-by-doing, and large-scale implementation (Fasihi et al., 2019).

Other factors, such as social acceptability, policies, and regulations, can also play a critical role in the cost of DAC (Chauvy and Dubois, 2022). For instance, DAC systems would be difficult to be adopted without a policy-driven carbon tax price. It is worth mentioning that most of the key levers in existing studies are also necessary to facilitate the implementation of other low-carbon technologies, such as photovoltaics and wind power (Chauvy and Dubois, 2022). Therefore, a cost assessment of DAC should not merely focus on a step-by-step reduction of the cost of the DAC technology itself, but a moderately accurate quantitative method should be developed for the environmental cost related to global warming.

#### 2.4.4 Perspectives on DAC

In order to meet specific climate targets, such as those outlined in the Paris agreement, it is imperative that all CO<sub>2</sub> removal technologies be explored (Allen, 2019; Shayegh et al., 2021). Capturing CO<sub>2</sub> at the source, such as at power plants, may not be enough. Other avenues, such as DAC, although more costly than capturing at the source, will be required. Although several groups are conducting research on various DAC approaches such as adsorption, absorption, and cryogenic capture, considerable research will need to go into scaling up these technologies so that they can be feasibly implemented in real-world systems. The risks of implementing such systems are enormous, including environmental, ethical, and technical risks (Lenzi, 2018). Furthermore, massive spending, estimated to reach a third of government general expenditures in developed countries, will be required (Bednar et al., 2019).

The five pillars of DAC, as shown in Figure 2.11, are (1) capture technology, (b) energy demand, (c) cost, (d) environmental impact, and (e) political support (Ozkan et al., 2022). Currently, DAC technologies need to be improved to reduce costs. Costs of less than \$100/tonne of CO<sub>2</sub> are needed to make DAC viable economically. The costs include capital equipment, maintenance, and operation due to the very low concentrations of CO<sub>2</sub> found in the atmosphere.

According to a recent report (Budinis., 2022), there are currently 18 DAC plants in Europe, Canada, and the United States that are in operation that captures nearly 0.01 MtCO<sub>2</sub>/year. As stated by the “net-zero emissions by 2050 scenario,” (2021) DAC should be scaled-up to capture at least 60 Mt/CO<sub>2</sub> by 2030. The first 1 Mt/CO<sub>2</sub> DAC plant is expected to be fully operating in the United States by 2025, with even more DAC facilities planned.

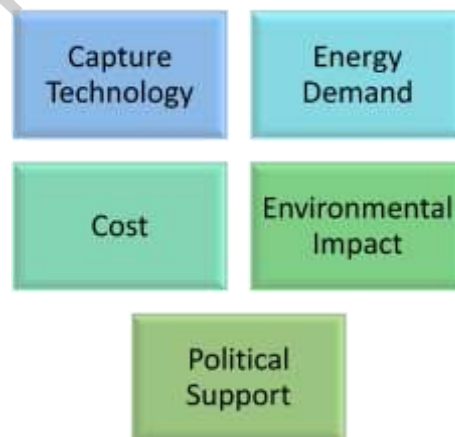


Figure 2.11 The five of DAC as outlined by Ozkan et al. (Ozkan et al., 2022).



### 3. CO<sub>2</sub> capture with sorbents

#### 3.1 Liquid-based sorbents amine solutions

##### 3.1.1 Amine solution

Chemical absorption using amine solvent is a relatively mature post-combustion CO<sub>2</sub> capture method at present, which has realized industrial application from large fixed emission sources such as coal/gas power plant flue gas (Wang, Junyao et al., 2021; Zhang and Liu, 2013). It is an important technical route to achieve large-scale CO<sub>2</sub> reduction at this stage, and it is also the only low-concentration CO<sub>2</sub> capture technology in the world that can achieve large-scale commercial applications (Weidong et al., 2009). Taking monoethanolamine (MEA) as an example, CO<sub>2</sub> can react with it to form corresponding water-soluble salt and release CO<sub>2</sub> when heating it at 100~140 °C, thus realizing the capture and enrichment of CO<sub>2</sub>. The CO<sub>2</sub>-rich MEA solvent enters the digestion unit after being heated by the heat exchanger and releases CO<sub>2</sub>. However, the shortcomings of the chemical absorption method using amine solvents are also very obvious (Xuepeng, 2014). Due to the large flue gas flow and low CO<sub>2</sub> partial pressure, the investment cost and operation energy consumption of the chemical absorption method are high. Secondly, amine solvents such as MEA have poor stability and are easy to degrade in contact with oxygen in the air. (Lin Haizhou et al., 2019). In addition, it is necessary to control the concentration of sulfur oxide and nitrogen oxide in the combustion tail gas of the separation unit below 10ppm to prevent the amine liquid from reacting with the above impurities and deteriorating rapidly. In addition, this kind of solution is highly corrosive and requires relatively expensive pipeline and equipment investment in the early stage.

The average energy consumption of amine chemical absorption carbon capture technology in China is about 2.4~3.2 GJ/t CO<sub>2</sub>, reaching the same level in the world, but it is still in the industrial demonstration stage due to lack of large-scale industrial or commercial application. China has designed large-scale and major CCUS demonstration projects, such as the Huaneng Shanghai Shidongkou Carbon Capture Demonstration Project (100000 tons/year) put into operation in 2009, the Shengli Oil Field Flue Gas Carbon Capture Project (40000 tons/year) put into operation in 2010, the CCUS Test Platform Project of China Resources Power Haifeng Company (20000 tons/year) put into operation in 2019, and the National Energy Group Jinjie Carbon Capture Demonstration Project (150000 tons/year) put into operation in 2021, The relatively mature chemical absorption technology of mixed amine solution is adopted.

Internationally, the amine liquid chemical absorption method has a high maturity and is widely used in the existing coal-fired power plants and other flue gas CO<sub>2</sub> capture, and has completed the industrial demonstration and large-scale commercial operation stage internationally. In 2014, Canada put into operation the SaskPower boundary dam project with a capacity of 1 million tons/year, the United States put into operation the world's largest PetraNova project with a capacity of 1.4 million tons/year in 2017,

and Japan put into operation the Mikawa biomass combustion power plant with a capacity of 150000 tons/year carbon capture project in 2020, all of which use amine chemical absorption capture technology. The average energy consumption of amine regeneration is 2.6~3.0 GJ/tCO<sub>2</sub>.

### 3.1.1.1 Mixed amine solution

The mixed amine technology combines the advantages of different organic amines.(Han Shuyi et al., 2014) It reduces the energy consumption of regeneration by optimizing the proportion of amine liquid in different proportions and is widely used in the post-combustion chemical absorption method at this stage. A mini review studied several commercial amine blend solvents licensed by companies such as BASF, DOW, Fluor Daniel Co. MHI Shell Co, etc., with high “energy efficiency”.(Aghel et al., 2022b) Most primary amines exhibit enthalpy of CO<sub>2</sub> solubility that represents CO<sub>2</sub> absorption heat about 80-90 kJ/mol CO<sub>2</sub>, and secondary amines contain lower enthalpy of 70-75 kJ/mol, and tertiary amines contain the reduced enthalpy within the range of 40-55 kJ/mol.(Flores-Segura and Torres, 1997) The lower enthalpy of amine reflects lower heat duties but with higher absorption rates. The amine blends can reach very low heat duty and moderate absorption rates with optimized combination ratios.

**Table 3.1** Major solvent improvement methods in amine blend in CO<sub>2</sub> absorption.

System	Use of reagent	Time
<b>MEA based blended amine</b>	MEA+R3N	Since 2005
<b>PZ based blended amine</b>	PZ+K <sub>2</sub> CO <sub>3</sub> , PZ+R3N	Since 2005
<b>AMP based blended amine</b>	AMP+DETA , AMP+EAE , AMP+DETA+PZ	Since 2016
<b>The selection rules developed based on structure -performance correlation</b>	MDEA,DEEA, 1DMA-2P, 3DMA-1P	Since 2016
<b>The “absorption-desorption parameter” studies of single and blended amines</b>	BEA, AMP, BEA+AMP	Since 2017
<b>The “coordinative effect” of MEA+RR’NH of single amine</b>	MEA(activator)+ DEA(domiant)	Since 2018

Based on literature review, Table 3.1 plotted 5 famous branches of solvent improvement / blended amine solution, along with the most recent 6<sup>th</sup> one: tri-blends containing coordinative effects. The 1<sup>st</sup> branch was famous and common, which is blending MEA with various tertiary amines MEA+R<sub>3</sub>N (5+0~2 mol/L) since 2005.(Decardi-Nelson et al., 2017; Gao et al., 2017; Liao et al., 2017; Liu, H. et al., 2017; Raphael Idem et al., 2006; Roongrat Sakwattanapong et al., 2005; Sema et al., 2012; Shi et al., 2014b; Srisang et al., 2018; Zhang, P. et al., 2019) Several typical examples were MEA+MDEA, MEA+DEAB, MEA+DEEA and etc.(Decardi-Nelson et al., 2017; Gao et al., 2017; Liao et al., 2017; Liu, H. et al., 2017; Raphael Idem et al., 2006; Roongrat Sakwattanapong et al., 2005; Sema et al., 2012; Srisang et al., 2018; Vega et al., 2020; Zhang, P. et al., 2019) It integrated the advantages of MEA (quick CO<sub>2</sub> absorption reaction rates) with tertiary amines (lower energy cost and larger cyclic capacity) and offset the disadvantage of MEA (higher energy cost of desorption and smaller cyclic capacity) with tertiary amine (slower absorption rates). For example, Zhang et al. used MEA (5M), MEA MDEA (5:1 molar ratio, total content 6M) and MEA-1DMA2P (5:1 molar ratio, total content 6M) as blended amine solution. The results show that as an additive in MEA, 1DMA2P has better potential than MDEA to generate bicarbonate ions under the condition of poor CO<sub>2</sub> load and reduce the regeneration energy.(Zhang, R. et al., 2016) The 2<sup>nd</sup> branch was mixing piperazine (PZ) with various types of tertiary amines PZ+R<sub>3</sub>N or K<sub>2</sub>CO<sub>3</sub>, etc.(Brüder et al., 2011; Cullinane and Rochelle, 2004; Gao, H. et al., 2018; Li et al., 2014; Zhao, B. et al., 2017) The concept integrates the advantage of PZ (faster absorption rate) with tertiary amine (lower energy cost and larger cyclic capacity) and offsets the disadvantage of PZ (easy to precipitate and poison to human life) and tertiary amine (lower absorption rates).

The 3<sup>rd</sup> branch was blending AMP based amine with either bi- amine blends or tri- amine blends, which fully exerted the advantage of AMP (higher desorption performance with moderate absorption performance). The carbamate of AMP was unstable, which was easy to hydrolyze under heat.(Ciftja et al., 2014) After 2016, a large number of studies involved tri-solvents of MEA+AMP+PZ,(Nwaoha et al., 2017; Nwaoha et al., 2016b) MDEA+DETA+AMP(Nwaoha et al., 2016a) and bi-solvents: AMP+PZ,(Brüder et al., 2011) and AMP+DETA,(Wai et al., 2018). Zhang et al. studied the regeneration behavior of 6M MEA-AMP-PZ (monoethanolamine, 2-amino-2-methyl-1-propanol and piperazine) tri-solvent mixtures loaded with CO<sub>2</sub> with different AMP/PZ molar ratios and blank mixtures at 96 °C. For non-catalytic operation, the results show that compared with 5M MEA, all three solvent mixed amines greatly increase the CO<sub>2</sub> desorption rate, and cycle capacity and reduce the relative heat load. C-13 NMR analysis showed that 3M MEA-2.5M AMP-0.5M PZ blend with the highest AMP/PZ ratio produced the largest amount of bicarbonate and less carbamate, which led to the best desorption performance.(Zhang, X. et al., 2018c)

The 4<sup>th</sup> branch started to investigate the chemical property of amines by their molecular structure (hindrance), kinetics ( $k_2$ ) and basicity (pKa), and correlate the performance with its CO<sub>2</sub> absorption and

desorption performance such as absorption rates, equilibrium CO<sub>2</sub> solubility ( $\alpha_{eq}$ ), heat duty (H), etc.(Singto et al., 2016) Several studies developed various selection rules of tertiary amines (R<sub>3</sub>N),(Xiao et al., 2016) which is named as “fast screen method” in 2016.(Xiao et al., 2016) Other studies(Singto et al., 2016),(Luo, X. et al., 2016; Muchan et al., 2017) also reported the selection rules of different amines based on “structure-activity correlations” based on equilibrium solubility, pKa analysis, and absorption rates after 2016-2017.

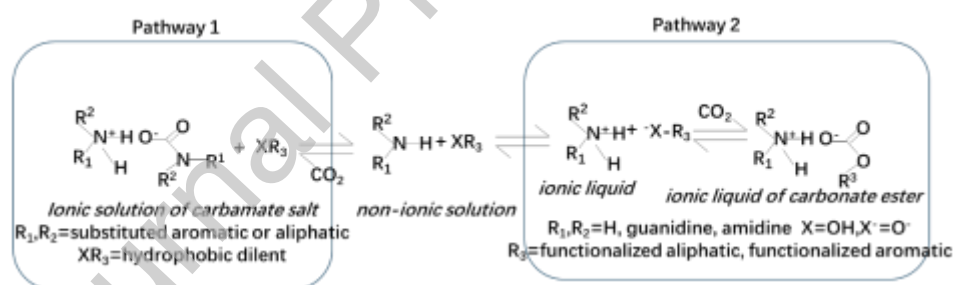
The 5<sup>th</sup> branch developed a set of comprehensive “absorption-desorption” parameters of various single amines, such as primary, secondary and tertiary amines in order to compare various single amines at a consistent level. Later on, these sets of parameters were extended to a blended amine solution.(Shi et al., 2018) The absorption and desorption parameters integrated the initial absorption rates, equilibrium CO<sub>2</sub> solubility, initial desorption rates, heat duty and cyclic capacity, etc. into two equations. That study discovered that BEA and AMP possessed optimised absorption parameters and desorption parameters.(Narku-Tetteh et al., 2017) AMP had a very high desorption parameter with a relatively adequate absorption parameter, while BEA had a very high absorption parameter with relatively good desorption parameter.(Narku-Tetteh et al., 2017) Based on intensive analysis, the 2+2 mol/L BEA+AMP blended amine solvents were prepared, and tested with heterogeneous catalysts in both absorber and desorber in a batch process and bench scale pilot plant study.(Afari et al., 2018; Narku-Tetteh et al., 2018; Natewong et al., 2019; Prasongthum et al., 2019) After studies of these 5 branches, the methodologies of liquid amine solutions were upgraded to highly accurate quantitative analysis. The preparation method was developed from “combination of the advantage of two amine blends” since 2005,(Roongrat Sakwattanapong et al., 2005) to “structure-activity correlation” since 2016(Singto et al., 2016) and “absorption-desorption parameter analyses” since 2017.(Narku-Tetteh et al., 2017) The research focus was always at “heat duty oriented analysis” (energy efficient and low cost) by analyzing the individual energy contribution: such as absorption enthalpy, sensible heat, and heat of vaporization.(Narku-Tetteh et al., 2018; Nwaoha et al., 2017)

The 6<sup>th</sup> branch was developed in 2018. It is the application of “coordinative effect” onto “bi-solvents” or “tri-solvents”, together with absorption-desorption parameters analysis(Narku-Tetteh et al., 2017) of the 5<sup>th</sup> branch to analyze the performance of amine solution comprehensively. Firstly, Liu et al.<sup>31</sup> and Shi et al.(Shi, H. et al., 2020; Shi et al., 2018) discovered “coordinative effect” of MEA+RR’NH, which could facilitate CO<sub>2</sub> absorption(Shi, Huancong et al., 2022) and desorption(Shi, H. et al., 2020; Shi et al., 2018) simultaneously. This performance was contradictive to the general rule that MEA enhance CO<sub>2</sub> absorption performance and weakens desorption performance.(Nwaoha et al., 2017) The coordinative effect was already verified to exist within MEA+DEA(RR’NH) bi-solvent at the ratio of 0~0.5/2(Shi, H. et al., 2020) and MEA+BEA(RR’NH)+AMP tri-solvent at 0.1~0.5+2+2 mol/L<sup>34</sup>. Experimental results confirmed that their absorption and desorption performance was better than that of BEA+AMP 2+2 mol/L simultaneously.(Hsa et al.) Recently, other similar tri-solvents with the

coordinative effect of MEA+EAE+AMP(Shi, H. et al., 2022; Zhang, B. et al., 2022) MEA+BEA+DEEA(Shi, Huancong et al., 2022) were also studied by Shi et al. and exhibited higher absorption desorption performance.

### 3.1.1.2 Non-aqueous amine solution

It has been well understood that energy consumption was the main factor affecting the efficiency of power plants when employing the CO<sub>2</sub> capture process.(Chakma, 1995; Oexmann and Kather, 2010; Tan et al., 2011) Water evaporation in conventional aqueous amine solutions is the major reason for the high energy consumption.(Guo et al., 2014; Leites, 1998; Li, J. et al., 2012) Using organic solvents instead of water provides significant advantages. For example, it can reduce decomposition at high temperature and energy cost in the regeneration step due to their low heat of vaporization and high boiling temperature.(Barzagli et al., 2013; Yu et al., 2013) Recently, non-aqueous amine solutions have been extensively investigated. Lail et al.(Lail et al., 2014) developed improved RILs called "non aqueous solvents" (NASs). These solvents are composed of hydrophobic, steric, carbamate forming amine (with low water solubility) and an unspecified amount of low vapor pressure organic diluents to produce NASs with minimum foaming, viscosity reduction and water accumulation. Two families of promising NASs have been discovered and the general reaction pathways with CO<sub>2</sub> are depicted in Figure 3.1.



**Figure 3.1.** Reaction pathways for RTI's NASs.

David et al.(Barraga et al., 2022) found that dilute water solvents have unique thermodynamic and physical properties that can be used to improve efficiency Water-poor solvents have shown water resistance. The reboiler load is lower and the mass transfer rate is higher than expected, but the increase of intrinsic viscosity must be balanced. David et al.(Heldebrant et al., 2017) also studied the comprehensive examination of GAP/TEG solvent system at a molecular level to slow down hydrolysis and reduce viscosity. This discovery makes it possible to design one-component silicone-free diamine derivatives, which can reduce viscosity by adding selective chemical groups at specific positions, direct placement and directional hydrogen bonding. Compared with the original GAP/TEG formulation, the viscosity is reduced by 98%. Chen et al.(Chen, S. et al., 2015) studied that compared with the use of triethylene glycol (TEG) or diethylene glycol (DEG) cosolvent, the CO<sub>2</sub> capture formula produced by

ethyl monoethanolamine (EMEA) solution in tertiary ethanolamine cosolvent (such as diethylethanolamine (DEEA) or MDEA) has higher equilibrium solubility and high cycle capture capacity. DEEA participates in chemical absorption by extracting protons from EMEA carbamate intermediates. Moreover, using tertiary amine DEEA in non-aqueous solvent has better performance than using alcohol and glyco.(Chen, S. et al., 2016)

Sada et al. studied the kinetics of CO<sub>2</sub> absorption with mono- and diethanolamine in non-aqueous solvents, such as methanol, ethanol and 2-propanol.(Sada et al., 1985) Versteeg et al. developed a CO<sub>2</sub> absorption system of MDEA in ethanol and concluded that in non-aqueous solutions, no reaction, even no alkylcarbonate formation, occurred between CO<sub>2</sub> and tertiary alkanolamines.(Versteeg and van Swaaij, 1988) Sami et al. observed the pseudo-first-order rate constant value for the reaction of aniline/cyclohexamine/hexamine with carbon dioxide in ethanol and the results favored the zwitterion intermediate mechanism.(Ali et al., 2000) Park et al. measured the chemical absorption rate of CO<sub>2</sub> with DEA, DIPA, TEA and MDEA in non-aqueous solvents, such as methanol, ethanol, n-propanol, n-butanol (NBA), ethylene glycol, propylene glycol, and propylene carbonate.(Hwang et al., 2010; Park, S.-W. et al., 2006; Park et al., 2005; Park, S.W. et al., 2006) Tan et al. explored the CO<sub>2</sub> capture process with a mixture composed of MEA and triethylene glycol (TEG).(Tan et al., 2011) Li et al. studied the mixed non-aqueous solutions of MEA, DEA, and diglycolamine (DGA) with polyethylene glycol (PEG) as non-aqueous solvent for CO<sub>2</sub> capture.(Li, J. et al., 2012) Zheng et al. examined the CO<sub>2</sub> solubility in the non-aqueous solutions of AMP–diethylene glycol (DEG) and AMP–triethylene glycol (TEG).(Zheng et al., 2012) Guo et al. investigated a mixture of 2-(2-aminoethyl)ethanol with benzylalcohol (BP) as absorbent for CO<sub>2</sub> capture.(Guo et al., 2014) Barpaga team(Cantu et al., 2020) developed and studied the aqueous diamine solvent N1-(2-ethoxyethyl)-N<sub>2</sub>, N<sub>2</sub>-diisopropylethane-1,2-diamine (2-EEDIPEDA).

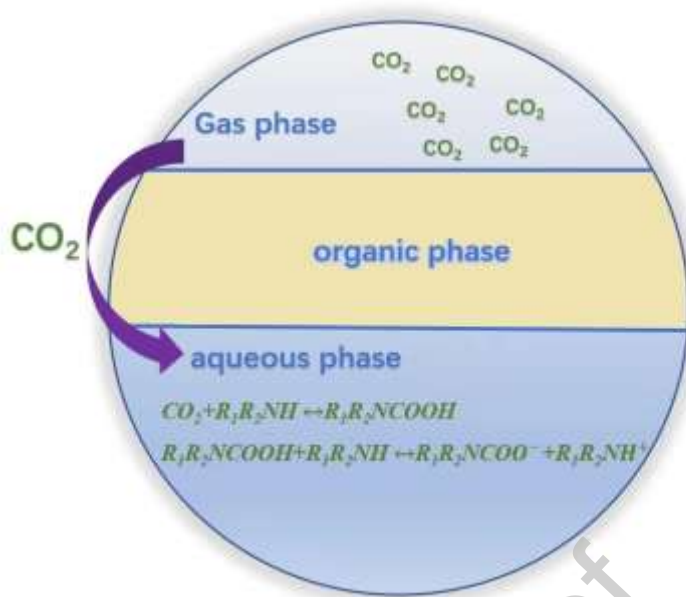
The CO<sub>2</sub> capture performance of the solvent was evaluated from the aspects of adsorption characterization such as vapor-liquid equilibrium adsorption kinetics and viscosity, and it was found that its performance was ahead of that of aqueous dilute amine solvent and its economic cost was as low as 46.8 USD/ton. The results of Fu et al. (Fu et al., 2020) showed that the viscosity of the three EHA non-aqueous solutions was smaller (<3 mPa·s) at the temperature range of 303.2 K ~ 323.2 K, which was conducive to the mass transfer and initial absorption rate of CO<sub>2</sub> absorption. These three non-aqueous adsorbents had good application potential in the process of CO<sub>2</sub> capture.

Zheng et al.(Zheng et al., 2016) studied the process mechanism of lean water CO<sub>2</sub> combined with organic liquid (CO<sub>2</sub>BOL) solvent platform and polar swing assisted regeneration (PSAR). From thermodynamics, dynamics and bench scale data, combined with Aspen Plus, the full-size process performance under three CO<sub>2</sub>BOL/PSAR conditions were predicted, the material performance was discussed, and the viscosity was determined as the key characteristic that most seriously limited the viability of the water-poor solvent platform.

The Water-poor solvents retain the chemical selectivity of water amine and utilise the lower specific heat of organic matter relative to water to reduce the load of the reboiler, that is, the energy required for the regeneration of solvent. In terms of time and cost, the dilute water solvent can be used as a drop-in solvent substitute that can use the first and second generation of water amine infrastructure. In addition to the characteristics of high boiling point, low specific heat and low evaporation enthalpy of organic solvent, the use of organic solvent instead of water to build an anhydrous absorbent system is expected to reduce the energy consumption of regeneration, and also reduce solvent loss and equipment corrosion. The future experimental work will focus on testing the new iteration of a similar amino-based dilute water solvent with different hydrophilicity to understand the impact on carbon dioxide capture while developing new configuration and process design to further improve the efficiency and cost of the solvent, and testing the use of lean water solvent for carbon dioxide capture after combustion with large-scale platform, testing its efficiency and calculating its cost.

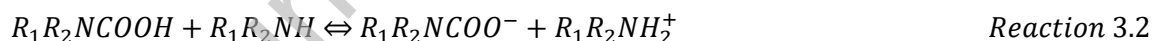
### 3.1.1.3 Phase-change amine solution

Recently, biphasic solvents, forming two immiscible phases (CO<sub>2</sub>-rich and CO<sub>2</sub>-lean phases) during the CO<sub>2</sub> capture process, have attracted increasing interest because the process only transports the CO<sub>2</sub>-rich phase into the desorption tower, which greatly reduces the volume of solution to be desorbed and regenerated and reduces the energy consumption for water evaporation and sensible heat, thus reducing the energy consumption for regeneration reduced. (Raynal et al., 2011; Zhou, X. et al., 2019) A biphasic solvent typically consists of active amines and a phase-separation agent. As shown in Figure 3.2, the active amine is a primary or secondary amine with a fast reaction rate, and the phase separation agent is a tertiary amine that cannot react directly with CO<sub>2</sub>, so it plays a role as a catalyst in the absorption process. (Ye et al., 2015)



**Figure 3.2** Phase separation schematic diagram of biphasic solvents.

The primary or secondary amine ( $R_1R_2NH$ ) can absorb  $CO_2$  and form a carbamate acid (Reaction 3.1), which can then be deprotonated by a base (Reaction 3.2) such as tertiary amine. The formation of the carbamate greatly increases the solvent polarity and changes the density. Phase separation occurs if the carbamate is immiscible with a phase-separation agent. Phase separation can occur, a phenomenon known as the salting-out effect.



Tertiary amines such as *N,N*-diethylethanolamine (DEEA), *N,N*-dimethylcyclohexylamine (DMCA), and pentamethyldiethylenetriamine (PMDTA) are used as phase-separation agent because of their low polarity, which allows the salting out of the carbamate to form aqueous and organic phase. (Liu, F. et al., 2019a; Liu, F. et al., 2019b; Pinto et al., 2014a; Pinto et al., 2014b; Ye et al., 2015; Zhang, S. et al., 2018) Pinto et al. proposed an aqueous biphasic solvent comprising 5 M DEEA mixed with 2 M *N*-methyl-1,3-diaminopropane (MAPA), compared with 5 M MEA, the DEEA-MAPA biphasic solvent requires lower heat to absorb, and can regenerate at high pressure or low temperature, which has a high cyclic absorption capacity ( $2 \text{ mol} \cdot \text{kg}^{-1}$ ) and a low regeneration energy consumption ( $2.2\text{--}2.4 \text{ GJ} \cdot \text{t}^{-1} \text{ CO}_2$ ). (Pinto et al., 2014b), Zhang et al. studied the phase change behavior of five different tertiary amines (DEEA, DMCA, PMDETA, 3-(diethylamino)-1,2-propanediol (DEAPD), and bis(2-dimethylaminoethyl)ether (BDMAEE)) on triethylenetetramine (TETA), total amine concentration is 4M, the molar ratio of DMCA and TETA is 3:1. and found that TETA-BDMAEE and TETA-PMDETA



were inferior to MEA in absorption capacity, TETA-DEAPD had the strongest absorption capacity, but due to the low hydrophobicity of DEAPD no phase separation occurred during absorption, TETA-DEEA formed a homogeneous phase at high CO<sub>2</sub> loading, and only TETA-DMCA showed high stability in absorption capacity and phase change behavior, the rate of CO<sub>2</sub> absorption into this biphasic solvent was comparable to that of the 5 M MEA solution, while the regeneration energy reduced by approximately 40 % compared with that achieved with MEA.(Zhang, S. et al., 2018) Zhou et al. explored a novel biphasic solvent comprising PMDTA and diethylenetriamine (DETA) with a CO<sub>2</sub>-absorption loading of 0.613 mol CO<sub>2</sub>·mol<sup>-1</sup> amine, in which 99.7 % of the absorbed CO<sub>2</sub> was distributed in the lower phase, accounting for 57 % of the total volume. The regeneration energy was reduced to 2.40 GJ·t<sup>-1</sup> CO<sub>2</sub>.(Lv et al., 2019; Zhou, X. et al., 2017)

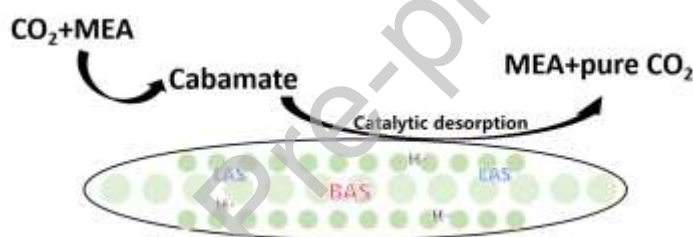
Organic physical solvents such as diethylene glycol dimethyl ether(DGM), diethylene glycol diethyl ether, 1-propanol, *N*-heptanol, and sulfone are often used as physical solvents and phase splitters.(Luo, W. et al., 2016; Wang, R. et al., 2019; Xu, M. et al., 2019) For example, Wang et al. used 1-propanol as a phase splitter mixed with an aqueous MEA solvent and triggered the liquid–liquid phase-change. Compared with pure MEA solution, the cycle capacity was increased from 1.01 mol/kg to 2.51 mol/kg after the addition of 1-propanol, and the biphasic solvent was able to reduce the energy consumption to 2.87 GJ·t<sup>-1</sup> CO<sub>2</sub>.(Wang, R. et al., 2019) Liu et al. developed 2-amino-2-methyl-1-propanol (AMP)/MEA blend-based biphasic solvents using diethylene glycol dimethyl ether and sulfolane as phase splitters, and shows that AMP/MEA blends with physical solvents have higher CO<sub>2</sub> absorption rate, with the most excellent being 69% higher CO<sub>2</sub>-absorption capacity and 36% lower regeneration energy than those achieved using 30 wt% MEA.(Liu, F. et al., 2019a) Hu et al. developed a biphasic solvent consisting of 2-(methylamino) ethanol (MAE), 3-(dimethylamino)propan-1-ol(3DMA1P), DGM and water with a CO<sub>2</sub> loading of 1.59 mol/kg, which is 74.2% higher compared to 30 wt% MEA, and demonstrated by simulation that the concentration of DGM has an effect on the absorption rate of CO<sub>2</sub>.(Hu, H.T. et al., 2022)

Non-aqueous solutions generally use organic reagents as solvents such as alcohols, polyethers, and alcohol.(Tao et al., 2018; Zhuang and Clements, 2018) However, precipitation often occurs when alcohols or polyethers are used as phase splitters, forming a solid–liquid biphasic solvent.(Chen, Z. et al., 2020) The liquid-solid biphasic solvents have significant advantages such as good absorption performance and low regeneration energy consumption, but the formation of solid products makes it difficult to transport to the resolution tower for desorption and regeneration. In addition, it can cause operational problems such as equipment fouling and plugging. Therefore, liquid–liquid biphasic solvents are more attractive. Zhou et al. proposed a novel non-aqueous liquid–liquid biphasic solvent composed of 2-((2-aminoethyl)-amino)ethanol (AEEA) as an active amine, dimethyl sulfoxide (DMSO) as a diluent, and *N, N, N', N'', N'''*-pentamethyldiethylenetriamine (PMDETA) as a phase splitter with a high CO<sub>2</sub>-absorption loading (1.75 mol·mol<sup>-1</sup>); 96.8 % of the absorbed CO<sub>2</sub> was in the lower phase. The

regeneration energy consumption could be reduced to  $1.66 \text{ GJ}\cdot\text{t}^{-1}\text{CO}_2$ . Moreover, the biphasic solvent in the  $\text{CO}_2$  saturated state did not exhibit corrosion behaviour on carbon steel.  $\text{CO}_2$  absorption products with high polarity are more willing to dissolve in the polar DMSO solvent rather than in the less polar PMDETA, resulting in phase-change behaviour. (Li, X. et al., 2021; Zhou, X. et al., 2020) Hence, phase-change behaviour can be obtained by modifying the solvent polarity. Note that the polarity of the phase-splitting agent should be lower than those of the active amine and diluent.

#### 3.1.1.4 Amine solution regeneration using catalysts

The addition of solid acid catalysts to  $\text{CO}_2$ -rich amine solution is considered as one of the potential methods to reduce the energy consumption for  $\text{CO}_2$  regeneration, as it can help decompose the carbamate by providing protons to increase the desorption rate and reduce the desorption temperature (Sun, Q. et al., 2021; Zhang, Xiaowen et al., 2019b). The principle of catalytic desorption with solid acid catalyst is shown in Figure 3.3.



**Figure 3.3** Principle of catalytic desorption with a solid acid catalyst (Xing, L. et al., 2021).

Domestic and international research based on solid acid catalysts has focused on metal oxides, zeolites, mesoporous silica, sulfated metal oxides, and composite catalysts (Alivand et al., 2020; Zhang, X. et al., 2019b). Metal oxides have a wide range of industrial applications as solid acid catalysts because of the acidic sites provided by surface defects (Lewis acidity, Brønsted acidity). The addition of  $\gamma\text{-Al}_2\text{O}_3$  as a catalyst to the rich solution was first proposed by Idem et al., and experimental data showed a 27% decrease in energy consumption for the regeneration of 5 M MEA aqueous solution (Shi et al., 2014a; Shi et al., 2014b). The catalytic properties of metal oxides ( $\text{TiO}_2$ ,  $\text{SiO}_2$ ) were investigated by Wang et al. and compared with  $\gamma\text{-Al}_2\text{O}_3$ . The result showed that  $\text{TiO}_2$  was the most effective and that the addition of  $\text{TiO}_2$  to MEA increased the desorption rate by more than 10% and reduced the desorption time by more than 40% compared to MEA with no catalysts (Wang, T. et al., 2016). Bhatti et al. systematically investigated the desorption kinetics of MEA aqueous solutions with metal oxide catalyse and found that  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$ ,  $\text{Ag}_2\text{O}$ , and  $\text{Nb}_2\text{O}_5$  exhibited better catalytic performance due to the presence of both Lewis and Brønsted acids on the surface (Bhatti et al., 2018a; Bhatti et al., 2017; Bhatti et al., 2018b). Ji et al. found that adding  $\text{ZrO}(\text{OH})_2$  and  $\text{FeOOH}$  to  $\text{CO}_2$ -rich amine solution can

reduce the desorption heat load by 45% and 47%, respectively (Ji et al.). Jiang et al. prepared metal hydroxyl oxide AlOOH and applied it to CO<sub>2</sub> desorption, and found that the addition of AlOOH increased the desorption rate by 560% and the amount of desorption by 251% (Jiang et al., 2022).

Previous studies have shown that the addition of synthetic zeolites (HZSM-5, HY, HB, SAPO-34) to the CO<sub>2</sub>-rich amine solutions can also improve CO<sub>2</sub> desorption performance. Xu et al. found that HZSM-5 could effectively promote CO<sub>2</sub> regeneration and reduce regeneration energy consumption by 23.9% (Xu, Y. et al., 2020). Bhatti et al. prepared a range of HZSM-5 with different properties and investigated its catalytic performance in CO<sub>2</sub>-rich amine solutions and found that optimally adjusted HZSM-5 could reduce the relative heat load by 62.7% (Bhatti et al., 2020). Zhang et al. found that HB with a larger mesoporous specific surface area and more Brønsted acid centers could improve CO<sub>2</sub> desorption performance by 1360.8% and reduce regeneration energy consumption by 66.1% (Zhang, X. et al., 2019a). Through their study, Srisang et al. found that the catalytic performance of HY in CO<sub>2</sub>-rich amine solutions was significantly inferior to HZSM-5 (Srisang et al., 2017). A commercial SAPO-34 had a similar surface area, average pore width and Brønsted to Lewis acid ratio to HZSM-5, but SAPO-34 showed a lower catalytic efficiency in CO<sub>2</sub>-rich amine solutions than HZSM-5 due to the lower number of total acid sites on SAPO-34 compared to HZSM-5 (Zhang, X. et al., 2018c). Natural zeolites are considered an ideal alternative to CO<sub>2</sub> desorption catalysts due to their unique advantages such as low price and high availability. However, only H-mordenite zeolite was reported to be applied as a catalyst for CO<sub>2</sub> desorption, showing similar catalytic performance to HZSM-5 (Zhang, Xiaowen et al., 2019a). Mesoporous silica such as MCM-41 and SBA-15 has also been used to catalyze CO<sub>2</sub> desorption due to their regular mesoporous structure and small amounts of Brønsted acid. However, their catalytic performance was inferior under the same conditions compared to that of HZSM-5 (Gao, Hongxia et al., 2020; Liu, H. et al., 2017; Zhang, X. et al., 2017).

Sulphated metal oxides exhibit more acidic sites due to the presence of sulphur atoms in their structure (Almeida et al., 2008; HINO and ARATA, 1979; López et al., 2000). As reported in previous years, the catalytic effects of sulfated zirconia (SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>), sulfated TiO<sub>2</sub> (SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>), and sulfated Fe<sub>2</sub>O<sub>3</sub> (SO<sub>4</sub><sup>2-</sup>/Fe<sub>2</sub>O<sub>3</sub>) was inferior to HZSM-5 and MCM-41 because of the lower number of Lewis and Brønsted acid sites and mesoporosity (Ali Saleh Bairq et al., 2019; Xing, Lei et al., 2021). Idem et al. investigated the preparation of solid super acid catalyst Ce(SO<sub>4</sub>)<sub>2</sub>/ZrO<sub>2</sub> and its catalytic effect on CO<sub>2</sub> desorption and found that Ce(SO<sub>4</sub>)<sub>2</sub>/ZrO<sub>2</sub> has a large number of Brønsted acid sites even well beyond HZSM-5 (Natewong et al., 2019; Prasongthum et al., 2019). Hybrid composite catalysts are usually composed of two materials with different properties, which combine the unique advantages of different materials to further reduce energy consumption for CO<sub>2</sub> regeneration.

For instance, composite amine catalyst  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/HZSM-5 is more effective in catalyzing desorption than  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or HZSM-5 alone (Liang et al., 2016b; Zhang, X. et al., 2018b). The catalysts were prepared by loading SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> onto mesoporous structures (e.g.,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SBA-15, and MCM-

41) and used to catalyse CO<sub>2</sub> desorption with a higher catalytic effect than HZSM-5 (Ali Saleh Bairq et al., 2019; Gao, Hongxia et al., 2020; Zhang, X. et al., 2018a; Zhang, X. et al., 2019b). Zhang et al. found that SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> significantly reduced the regeneration energy consumption of CO<sub>2</sub>-loaded MEA solution, while increasing the desorption rate by 33.3%<sup>[104]</sup>. Gao et al. synthesized composite catalyst SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>/SBA-15 and used it to reduce heat duty for the regeneration of CO<sub>2</sub>-loaded MEA solution. The results of the study showed that SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>/SBA-15 increased the desorption factor by 100-200% and reduced energy consumption for regeneration by 20-26.50% (Gao, H. et al., 2020). A series of composite catalysts (CMK-3-SiO<sub>2</sub>, CMK-3-MCM-41 and CMK-3-SBA-15) were prepared, and their catalytic performance was compared and analysed by Bairq et al. It was found that CMK-3-SiO<sub>2</sub> gave the best catalytic performance, being able to reduce the energy requirement by 37.41% and increase the desorption rate by 195% (Bairq et al., 2020).

### 3.1.1.5 Life cycle assessment of amine solutions based carbon capture

#### 3.1.1.5.1 Introduction

LCA is an important environmental management tool. The term “life cycle” refers to the whole process of an object from raw materials, through production and use, to abandonment (that is, from cradle to grave). The International Organization for Standardization (ISO) defines LCA as the assessment of environmental factors and potential impacts in the life cycle and mentions that LCA is generally carried out through four stages (target and scope definition, inventory analysis, impact assessment, and interpretation) to quantify the main potential environmental impacts associated with related products or services. Literature (Wang, Y. et al., 2022) introduces the four stages of LCA in detail:

1. Definition of objectives and scope: “clear objectives,” “determine the boundary,” “time span of evaluation,” and “specify the functional units of quantitative description.”

2. Inventory analysis: collect relevant data and prepare a list of inputs and outputs related to the environment and resources of the evaluated objects. When the data is missing or unclear, it needs to be analysed at the interpretation stage.

3. Impact assessment: The results of the inventory analysis are classified according to the type of impact, and the assessment method is selected and quantified for the resulting environmental impact.

4. Interpretation: analyse the results of the impact assessment phase, improve the data through sensitivity and uncertainty analysis, and draw conclusions.

In this paper, the life cycle impact of a part of the CCS system (the amine solution carbon capture system) is studied. The important problems involved in the LCA of an amine solution carbon capture system are analysed, and the limitations and shortcomings of the system are pointed out.

### 3.1.1.5.2 Life cycle assessment of amine solution carbon capture systems

#### ***Goals and Scope***

At present, the life cycle evaluation of carbon capture systems in amine solutions is very limited. Tim Grant et al. studied the life cycle evaluation of coal-fired power plants using MEA and potassium carbonate solution as absorbents (Grant et al., 2014). Ben Young et al. evaluated the life cycle of CCS in oil refineries, amine production plants, and coal-fired power plants in the United States (Young et al., 2019). There is extensive research on the life cycle evaluation of carbon capture systems, but there is a lack of research on amine-based carbon capture systems. The carbon capture system is a part of the CCS system, and the research on it can learn to a certain extent from the research experience of the CCS system life cycle. When the object of LCA is transferred from the CCS system to the ammonium solution carbon capture system, the focus of LCA should turn to the impact of the ammonium solution carbon capture system on the environment without considering the impact of the sequestration part on the environment.

In LCA, the definition of the functional unit should be based on its ability to serve as a reference for the impact of the evaluated system on the environment to facilitate the comparison between different studied systems. In general, functional units need to be defined in terms of research objectives, and the defined functional units need to be consistent with the goals of the overall system. Most research has focused on the environmental burden of CCS systems using different absorbents. Since most studies are based on coal-fired power plants, the LCA of CCS systems usually uses a functional unit based on power generation without capturing a certain amount of CO<sub>2</sub> as a functional unit. For example, Letitia Petrescu et al. (2017) selected 1 MWh of net generation as a functional unit in the LCA of a supercritical pulverised coal power plant with post-combustion carbon capture and storage (Petrescu et al., 2017). Francois Saunier et al. (2019) selected "separation of 1 tonne of CO<sub>2</sub> from smoke streams from a 550 MW coal-fired power plant in the Midwest of the United States in 2017" as a functional unit in a study on bio-catalysing and facilitating a comparison of the LCA of a K<sub>2</sub> carbonate process with amine-based carbon capture technologies (Saunier et al., 2019). The purpose of defining functional units in this way is to compare the environmental impacts of different CO<sub>2</sub> separation methods. In future studies, more consideration should be given to defining CO<sub>2</sub>-based functional units to make better comparisons between different studies.

The whole amine solution carbon capture system is a relatively complete process in the CCS system, which connects all devices in series by absorbing and desorbing carbon dioxide. By determining system boundaries, relevant processes can be included in the LCA of the target system, performing a full life cycle evaluation or a partial life cycle evaluation on the target system. In general, the boundaries of the target system should encompass the entire process from cradle to grave. For example, the boundaries

of the life cycle evaluation of CCS systems for sub-critical coal-fired power plants include the entire chain of CCS systems, i.e., the entire process from generation to CO<sub>2</sub> storage (Lorena Giordano 2018)(Giordano et al., 2018). Generally, the boundary of the target system should be selected according to different research purposes. When defining the system boundary, we can purposefully simplify the system boundary according to the research focus, which helps us better study the relatively complex system. However, the boundary of the target system should be simplified in line with the actual situation rather than arbitrarily. In particular, processes with less than 1% environmental impact are considered negligible. Kristina Zakuciova et al. (2020) defined the system boundary as the operation part of the power plant and the activated carbon production, emission treatment, carbon dioxide capture process, and waste generation in the life cycle evaluation of coal-fired power plants and carbon capture systems based on activated carbon(Zakuciová et al., 2020). However, the definition of the system boundary does not need to consider the operation part of the power plant or the production of activated carbon. Instead, it needs to focus on the production and deterioration processes of the amine solution. Since this paper only takes the carbon capture system as the object, carbon dioxide compression, transport, and oil displacement are excluded from the system boundary. When comparing amine solution carbon capture systems applied to different combustion power generation plants, it should be fully considered that the different coal-fired power plants may have an impact on the life cycle evaluation of amine solution carbon capture systems.

### ***Inventory analysis***

The rationality, timeliness, and accuracy of the required data can affect the final evaluation results to a large extent. When the available data cannot support the research, a variety of assumptions need to be added to the target system, which may affect the accuracy of the evaluation to some extent, and the relevant database cannot provide comprehensive life cycle inventory (LCI) data. Real data, rather than average or average data, should be used as far as possible for LCA, as many aspects, such as average data in geographical space, time span, and technical level, may lead to large errors in LCA. The improvement of the accuracy and timeliness of the data involved in the studied system can provide more experience for the construction of various carbon capture systems. Usually, researchers are faced with the problem of limited available data, so they will use relevant average data for research, which will reduce the accuracy of the results. It is particularly important to reduce the difficulty and improve the accuracy of data collection. In addition, with the continuous innovation of target system technology, researchers need more and more types of data, so they should pay more attention to data collection.

Most of the information used in this study is taken from published works, studies by international and national agencies (such as the IEA, IPCC, and Global CCS Institute), and a number of commercial databases (like Ecoinvent, Environmental Footprint, and Impact World+). In the areas of agriculture, building, chemical manufacture, power generation, fishing, metals, refineries, textiles, tourism, transportation, waste treatment and recycling, water supply, etc., the Ecoinvent database includes 140

nations. Due to the openness, depth, and dependability of its data, it is frequently utilised by businesses and has more than 18,000 data for roughly 3,200 items. The geographic variability of the data can be reduced in the IMPACT World Plus database, which provides country- or region-specific characterisation parameters.

### *Impact assessment*

Two accepted approaches to life cycle impact assessment are problem-oriented midpoint impacts and damage-oriented end effects. The former was chosen in most LCA studies of amine-based carbon capture systems. Selecting appropriate impact categories is the first and most significant step for the first method. The selection of impact categories usually depends on the purpose of the study, the time span considered in the study, and the geographical location of the object of study (Wang, Y. et al., 2022). The role of carbon capture systems is to reduce greenhouse gas emissions by separating CO<sub>2</sub> from fixed emission sources, which include cement, steel production, hydrogen production from fossil fuels, waste incineration, power generation, and other industries. However, the construction and operation of the infrastructure for carbon capture systems, as well as the production, regeneration, and degradation of amine solutions, will cause certain negative environmental impacts. Therefore, we should not only select the “global warming potential” (GWP) as the impact category but also select other impact categories for comprehensive analysis and assessment in the LCA studies of amine-based carbon capture systems. The table 3.2 lists the impact categories selected in the LCA study of the amine-based carbon capture system.

**Table 3.2** Selected impact categories for LCA studies on carbon capture in amine solutions

Study	GWP	AP	EP	PCOP	ADP	HTP	ETP	ODP	PMFP
Kathrin Volkart (2013)				√		√			√
Longlong Tang (2014)	√	√	√	√	√	√	√		
Tim Grant (2014)	√	√	√	√	√	√	√		
Utrecht University (2014)		√	√	√		√		√	√
Xiangping Zhang (2014)	√	√	√	√		√	√	√	√
M.A. Morales Mora (2016)	√								
Stefanie Troy (2016)	√	√	√	√	√	√	√		√
Tang Daqing (2016)	√	√	√	√	√	√	√	√	√
Letitia Petrescu (2017)	√	√	√	√	√	√	√	√	
Lorena Giordano (2018)	√	√	√	√	√	√	√	√	
Ben Young (2019)	√	√		√	√				√
Yi-Ming Wei (2019)	√	√	√	√	√	√	√	√	
Albert Ratner (2020)	√	√	√			√		√	
Alireza Aslani (2022)	√	√	√		√	√	√	√	√
Andrea Mio (2022)		√	√	√	√	√	√	√	

GWP = Global Warming Potential; AP = Acidification Potential; EP = Eutrophication Potential; PCOP = Photochemical Oxidation Potential; ADP = Abiotic Depletion Potential; HTP = Human Toxicity Potential; ETP = Ecotoxicity Potential;

ODP = Ozone Depletion Potential; PMFO = Particulate Matter Formation

### ***Interpretation***

There is a certain gap between the results of the LCA and the actual situation, so we need to analyse the cause of this gap. In the process of LCA, the evaluation is not accurate due to the data (such as the gap in the application of existing databases and some data caused by the integration of heterogeneous data sets). Furthermore, the emission trends of small-scale-related emissions have expanded to large-scale applications with factors that cause large errors and other factors that make the results of the life cycle subject to a certain degree of uncertainty. Therefore, we need to analyse the life cycle results and uncertainty to optimise the results of the parameters. Therefore, we should solve these uncertain issues in future research (Gibon et al., 2015).

### ***Sensitivity and uncertainty analysis***

The application of the CCS system can reduce the GWP indicator of the coal power generation system, but it will also affect some other environmental indicators to a certain extent. In the literature (Petrescu and Cormos, 2017), the condition of the IGCC power plant without CCS is compared with the IGCC power plant with calcium circulation for the carbon dioxide capture before burning. The results showed that the GWP of the CCS coal-fired power plant was 917.25 kg CO<sub>2</sub>-EQ/MWH, and the GWP was 373.09 kg CO<sub>2</sub>-EQ/MWH under CCS. The use of CCS reduced GWP by more than 50%. However, other environmental indicators have increased. The AP index of the power plant system that has not been used in CCS technology was 0.49 kg SO<sub>2</sub>-EQ/MWH. After using the CCS technology, the AP index increased to 1.47 kg SO<sub>2</sub>-EQ/MWH. The literature (Petrescu et al., 2017) compared the SC pulverised coal power plant without CCS with the SC pulverised coal power plant using amine-based (MDEA) combustion CCS. The GWP value of an SC pulverised coal power plant without CCS is 970.37 kg CO<sub>2</sub> equiv./MWh, and the total GWP value of an SC pulverised coal power plant using amine (MDEA) combustion was 495.93 kg CO<sub>2</sub> equiv./MWh. However, after the application of amine-based combustion, the AP environmental index has reached 4.57 kg SO<sub>2</sub> eq/MWh, while the AP index of pulverised coal power plants without CCS is 0.49 kg SO<sub>2</sub> eq/MWh, with an increase of about 9 times. Not only that, EP, ADP, and other relevant environmental indicators have also increased to varying degrees. According to the analysis, the MDEA production process and the upstream and downstream processes of CCS have made great contributions to these growth indicators. Therefore, the reduction of CO<sub>2</sub> emission in the power generation system can not only focus on the emissions of the power plant itself but also combine the whole process to analyse the environmental benefits of the system



comprehensively. In addition, the cost of establishing the emission reduction system should also be considered.

The fate of some other harmful substances other than carbon dioxide is also an important uncertainty. The amine solution absorbent may absorb other harmful substances besides carbon dioxide during the actual absorption process, which may make the whole system have better environmental performance. If the power plant system can effectively treat these substances, some environmental assessment indicators will be greatly reduced, and the environmental impact of the entire system will be smaller (Pehnt and Henkel, 2009). In addition, the energy efficiency of the system itself has an important impact on LCA. The literature (Young et al., 2019) indicated that in ammonia production systems and petroleum production systems, when the energy efficiency of the system was improved, almost the entire life cycle impact was reduced by 20%–30%, and the photochemical smoke formation potential (PSFP) in ammonia production systems reduced by 60%. The PSFP effect of CO<sub>2</sub> reduction per unit equivalent ammonia production system was greatest, while the increase in PSFP was minimal when energy efficiency was sensitive. Therefore, when a more energy-efficient carbon capture system is used, the environmental impact of the entire system can be significantly improved.

#### 3.1.1.5.3 Environmental impact of amine solution carbon capture systems

After the application of a carbon capture system to a coal-fired power plant, its direct CO<sub>2</sub> emissions decrease, but other negative environmental impacts increase. It was pointed out (Young et al., 2019) that the operation of carbon capture systems and the degradation of amine solutions caused negative impacts on the environment, such as abiotic depletion, acidification, and eutrophication. In another literature (Volkart et al., 2013), LCA was performed on a coal-fired power plant with a carbon capture system. The results showed that the plant was superior to the plant without a carbon capture system in terms of the impact categories of GWP and AP but had greater negative impacts on other impact categories (such as HTP, PMFP, ETP, ADP, etc.).

To justify whether the carbon capture system reduces the environmental burden, it is necessary to understand whether the environmental benefits generated by the system are higher than the environmental damage it brings. As a result, the method of a damage-oriented end impact assessment must be introduced for further analysis. For example, the end-point impact assessment method was applied for human health, and ecological environment damage was used to conduct an LCA for biomass co-fired power plants combined with CO<sub>2</sub> capture systems (Schakel et al., 2014). The results showed that the overall environmental performance of the power plant was improved, even though the CO<sub>2</sub> capture system itself produced various negative environmental impacts.

In the carbon capture system, the production and degradation of chemical absorbents are one of the main factors that cause negative environmental impacts, and different absorbents have different impacts

on the environment. In the literature (Barbera et al., 2022) and (Grant et al., 2014), carbon capture systems with different absorbents (monoethanolamine (MEA) and potassium carbonate) were compared. The results showed that in the natural gas power plant with a carbon capture system, the GWP of MEA was lower than that of potassium carbonate, but its ETP and HTP were higher than those of potassium carbonate. In the lignite power plant with a carbon capture system, the potassium carbonate process showed less environmental impact than MEA on the basic environmental indicators such as GWP, ETP, HTP, and ADP. It can be seen that the selection of absorbents depends on CO<sub>2</sub> emission sources, and selecting different absorbents for different CO<sub>2</sub> emission sources can improve the overall environmental performance. In addition, LCA was carried out on two carbon capture systems with MEA and strong hydroxide as absorbents (Zahedi et al., 2022). The results showed that except for eutrophication and nonbiological resource consumption, MEA had less impact on the environment than strong hydroxide in other impact categories. In addition to chemical absorbent separation, CO<sub>2</sub> capture systems can also use membrane separation methods to separate CO<sub>2</sub>. Compared with MEA, membrane separation not only consumes less energy but also has a lower negative environmental impact (Giordano et al., 2018; Zhang, X. et al., 2014).

The energy consumption of the CO<sub>2</sub> capture system can be reduced by using clean energy to supply energy to the MEA regeneration system. It was found that the temperature range of the solar collector had a good match with the regeneration temperature of MEA; thus solar energy can be used to supply heat for the MEA regeneration system. Junyao Wang et al. (Wang, J. et al., 2017) analysed the solar-assisted coal-fired power plant with a CO<sub>2</sub> capture system by using the LCA method. The results showed that when the CO<sub>2</sub> capture rate was 90%, in terms of GHG reduction performance, the implementation of CCS reduced the life cycle GHG emissions by 67.1% and 73.7% for coal-fired power plants with an amine-based CO<sub>2</sub> capture system and solar-assisted repowering of coal-fired power plants, respectively. This was because solar energy reduced greenhouse gases for carbon capture power plants more than the greenhouse gases emitted by the construction and operation of solar heat collection systems. Therefore, the application of solar heat collection systems is conducive to reducing the negative environmental impact of coal-fired power plants with CO<sub>2</sub> capture systems.

According to the LCA findings, carbon capture systems based on amine solutions can increase environmental performance while lowering greenhouse gas emissions and CO<sub>2</sub> levels. Additionally, it can be shown from a comparison of amine solution and other chemical absorbents that there is a small difference between the pros and cons of each absorbent. However, amine-based carbon capture technology is currently more advanced. Therefore, the primary technique for reducing CO<sub>2</sub> can be an amine solution carbon capture device. According to a life cycle study, reducing the running energy usage of a carbon capture system can greatly increase the total environmental benefits of the whole system.

#### 3.1.1.5.4 Disadvantages and limitations

##### *Accuracy of results*

Although the CCS system has attracted much attention in recent years, its application has been greatly hindered due to the constraints of cost and economy, the legal and regulatory framework, social acceptability, uncertainty, and scalability. The application popularity of CCS overall technology is extremely low, among which the application of amine solution carbon capture systems is less popular, which leads to the very limited data required. The enterprise application of amine solution carbon capture systems is only to reduce CO<sub>2</sub> emissions and pay little attention to other data collection related to the environment, resulting in extremely low accuracy of the required data. Because the required data is very limited and the accuracy is low, the LCA analysis of the amine solution carbon capture system often uses the average value and makes a series of assumptions, resulting in inaccurate LCA results.

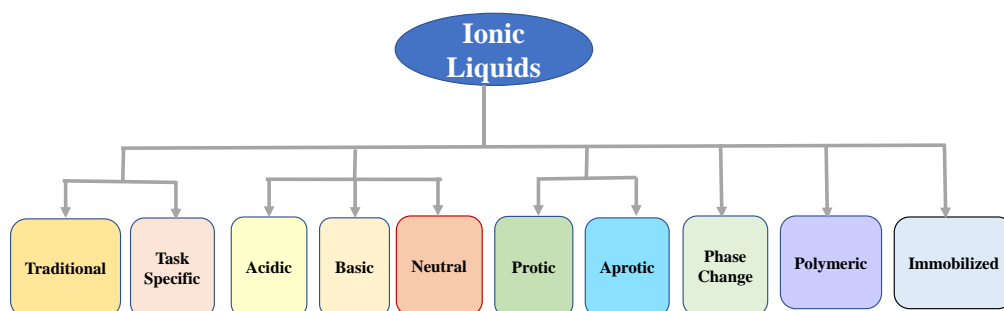
##### *Interdisciplinary and large-scale implementation assessment*

At present, most of the research on CCS systems focuses on the analysis of applications. Few researchers have studied the potential impact of CCS systems on the environment, and there are few studies on the CCS system (the amine solution carbon capture system). The amine solution carbon capture system employs both the LCA and the technical-economic assessment (TEA) methods for CCS evaluation (Wang, Y. et al., 2022). In this section, the LCA of an amine solution carbon capture system is carried out, but it is not combined with TEA or other methods for a comprehensive evaluation. It is limited to the study of a single discipline, which makes the evaluation results unreasonable. At present, there is no mature integrated method for the comprehensive evaluation of an amine solution carbon capture system, and even the comprehensive evaluation method for a CCS system is not mature. Therefore, the large-scale deployment of amine solution carbon capture systems is normally carried out without comprehensive evaluation of their economic and environmental benefits. Future research on amine solution carbon capture systems should focus on the interdisciplinary evaluation of environmental impact, economic cost, and geographical factors. A high level of evaluation combined with a variety of effective disciplines is conducive to better decision-making by decision-makers and helps make decisions more convincing and credible.

#### **3.1.2 Ionic liquids in CO<sub>2</sub> Capture**

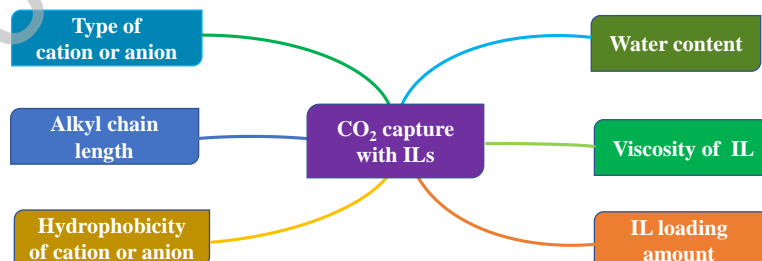
Ionic liquids (ILs), a class of room temperature molten salt composed of cations and anions, have been intensively investigated as novel solvents and soft functional materials for CO<sub>2</sub> capture, owing to their low vapor pressure, high thermal stability, superior solvation ability and designable structures (Gao, W. et al., 2020). Brennecke et al. (L.A. Blanchard, 1999) first reported that CO<sub>2</sub> has a high solubility in ILs. Subsequently, research demonstrated the application possibility of ILs in CO<sub>2</sub> absorption at room

temperature. Classification of ILs apart from the hybrid ILs can be broadly done, as indicated in the diagram (Figure 3.4). In this part, we mainly review novel IL-based materials and hybrid ILs-based materials for CO<sub>2</sub> capture.



**Figure 3.4 Classification of ILs.**

Although the CO<sub>2</sub> solubility in traditional ILs is relatively low compared to amine-based absorbents, the ILs properties can be improved by functionalization of cations or anions to increase the physical and chemical interactions between ILs and CO<sub>2</sub>. Effects of CO<sub>2</sub> solubility in ILs have been widely investigated to increase CO<sub>2</sub> capture performance, and the factors affecting CO<sub>2</sub> capture through ILs are listed in Figure 3.5. The longer alkyl chains on cation and fluorinated anions are profitable to facilitate the CO<sub>2</sub> capture process(Almantariotis et al., 2010; Zheng et al., 2020). The hydrophobic nature of the cation or anion can enhance the interaction between ILs and CO<sub>2</sub>. Water content in ILs also has a positive effect on fluidity and CO<sub>2</sub> absorption(Hu, H. et al., 2014). From the viewpoint of industrial practice, the high viscosity of ILs is one of the main reasons that cause slow gas diffusion(Hussain et al., 2021). In addition, ILs can be combined with numerous types of materials to form hybrid materials. However, doping an excessive amount of ILs may cause pore-blocking, there could be detrimental for immobilized ILs to capture CO<sub>2</sub>(Lian et al., 2021).



**Figure 3.5 Factors affecting the CO<sub>2</sub> absorption with ILs.**

### 3.1.2.1 Amino ILs

On the basis of the chemical reaction of CO<sub>2</sub> with the amino group, a large number of amino functionalized ionic liquids were developed as absorbents. Studies have found that more amino groups

in ILs lead to higher CO<sub>2</sub> absorption capacity, and water content has a great influence on CO<sub>2</sub> absorption capacity. When the moisture content increased from 0% to 40%, the absorption capacity of poly-amino-based ionic liquids [TETAH][BF<sub>4</sub>] increased from 0.96 mol CO<sub>2</sub>/mol IL to 2.04 mol CO<sub>2</sub>/mol IL (Hu, H. et al., 2014). A bifunctional ionic liquid [APmim][Gly] consisting of amine and amino acid has the advantages of high efficiency and high CO<sub>2</sub> capacity, which was as high as 1.23 mol CO<sub>2</sub>/mol IL (Lv et al., 2016a). A polyamine functionalized ionic liquid [APmim][Lys] by introducing amine and lysine functionalization groups into imidazole ILs was reported and its absorption load was 1.80 mol CO<sub>2</sub>/mol IL (Zhou, Z. et al., 2016). A novel hydrophilic amino acid ILs ([C<sub>2</sub>OHmim][Gly]) was designed and the level of capture capacity reached 0.575 mol CO<sub>2</sub>/mol IL (Lv et al., 2016b), which makes it has great potential to make up for the deficiency of water-based MEA and is beneficial to industrial application.

However, the formation of intermolecular hydrogen bonds in ILs-CO<sub>2</sub> complex may lead to a sharp increase in viscosity after absorbing CO<sub>2</sub>, thus affecting mass transfer performance and limiting the application of amine ILs (Cui et al., 2016). Bhattacharyya and Shah (Bhattacharyya and Shah, 2016) synthesized the ether functionalized choline amino acid ILs [N<sub>1,1,6,204</sub>][Lys] with low viscosity and high CO<sub>2</sub> sorption capacity. Luo et al. (Luo, X.Y. et al., 2016) introduced hydrogen receptors such as N or O atoms into amino-functionalized ILs, and showed that ILs such as [P<sub>66614</sub>][4NH<sub>2</sub>-NC], [P<sub>66614</sub>][Ac-Gly], [P<sub>66614</sub>][Me-Gly], [P<sub>66614</sub>][Ac-PhO] and [P<sub>66614</sub>][MA-Tetz] have two active sites for CO<sub>2</sub> on an amine group through the formation of intramolecular hydrogen bonds and proton transfer processes, and the viscosity of these amino-functionalized ILs slightly increased or even decreased during CO<sub>2</sub> capture.

In order to achieve low regenerative energy consumption and low viscosity, a novel CO<sub>2</sub> capture method for [TEPAH][2-MI] combined with organic solvents was proposed (Liu, F. et al., 2020). The absorption load of [TEPAH][2-MI]/N-propanol/ethylene glycol was 1.72 mol CO<sub>2</sub>/mol IL, which was much higher than MEA/water. The regeneration efficiency remained at 90.7% after the fifth regeneration cycle, and the viscosity of the solution before and after absorption was only 3.66 and 7.65 mPa·s.

### 3.1.2.2 Protic ILs

Protic Ionic Liquids (PILs) generally include proton donor and proton acceptor, and a hydrogen bond network can be formed in the structure with strong polarity (Cohen et al., 2019; Er et al., 2019; Sun et al., 2014), which not only has typical ILs properties, but also builds the hydrogen bond network due to the proton that can migrate in its structure. In general, PILs have high viscosity, which is a result of strong interactions between the ions through, mainly, the hydrogen bonds of hydroxyl groups and protic ion-ion interactions. Therefore, when PILs are used to absorb CO<sub>2</sub>, it is generally mixed with water, methanol, ethanol and other solvents and then used in its two-phase system.

The viscosity of PILs is an important property in studying its application range. The structure of anions in PILs has a great influence on the viscosity, and the anions such as F(HF)<sub>n</sub><sup>-</sup>, N(CN)<sub>2</sub><sup>-</sup>, N(CN)<sub>3</sub><sup>-</sup> have relatively low viscosity (Ignat'ev et al., 2015; Seki et al., 2010). Weak intermolecular interactions (such

as van der Waals forces and hydrogen bonds) have a certain effect on the viscosity of PILs. The stronger the intermolecular interaction, the greater the viscosity of PILs. Delocalization of charges on anions in PILs (e.g. fluorination) can weaken hydrogen bond interactions and reduce viscosity.

Zheng et al. (Zheng et al., 2017) determined the solubility of CO<sub>2</sub> in the cation PILs 3-(dimethyl amino)-1-propylamine (DMAPA) and different anions, and the results showed that the solubility of CO<sub>2</sub> in [DMAPAH][F] aqueous solution reached 3.62 mol/kg at 0.1 MPa and 35.2 °C. A series of etoxyacetic anionic PILs containing three different amine cations were designed (Wei et al., 2020), and the CO<sub>2</sub> solubility in [3-(dimethylamino)-1-propylamine][ethanol amine]([DMAPAH][EOAc]) was as high as 2.44 mol/kg. An anionic functionalized PIL synthesized by superbase 1,8-diazabicyclo [5.4.0]-undec-7-ene (DBU) and imidazole was synthesized (Zhu, X. et al., 2017), which can reversibly capture CO<sub>2</sub> with a capacity of 1 mol CO<sub>2</sub>/mol IL. In addition, there are many studies on fluorine substituents. Dimethyl-1,3-malon-2,3,5-difluorophenol salt ([DMAPAH][3,5F-PhO]) was synthesized, and its optimal absorption capacity was 3.99 mol CO<sub>2</sub>/kg IL (0.86 mol CO<sub>2</sub>/mol IL) (Zhao, T.X. et al., 2018).

As for the influence of cations and anions of PILs on CO<sub>2</sub> absorption, other researchers have given their own ideas. Ma et al. (Ma, J. et al., 2021) found that the absorption path by the anion of dimethylethylenediamine 4-fluorophenolate([DMEDAH][4-F-Pho]) was favorable in kinetics, while the absorption path by the cation was thermodynamically beneficial. Moreover, dimethylethylenediamine acetate ([DMEDAH][OAc]) only showed the possibility of cation absorption.

For the application of PILs in CO<sub>2</sub> capture, in addition to their CO<sub>2</sub> absorption performance, selectivity should also be considered as an important performance. Alcantara et al. (Alcantara et al., 2018) measured the phase equilibria data of low viscous diethylammonium butanoate [Bu] with CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> from 30 °C to 60 °C and up to 20 MPa. The results were shown that this PIL presented moderate to low CO<sub>2</sub> solubility, but it would display higher CO<sub>2</sub>/CH<sub>4</sub> selectivity than most ILs studied at high pressures. Swati et al. (Swati, I. K. et al., 2021) synthesized several ionic liquids, namely, 1-butylsulfonate-3-methylimidazolium P-toluene sulfonate ([BSmim][tos]), 1-butylsulfonate pyridine P-toluene sulfonate ([BSmpy][tos]), 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and 1-butylpyridine chloride ([Bpy]Cl) for the separation of CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> by supported ionic liquid membranes (SILMs). It was found that the presence of sulfonic group in proton ionic liquid would increase Lewis acid-base force and enhance the affinity of CO<sub>2</sub> to ILs, resulting in PILs having certain advantages in selectivity. The selectivity of [BSmim][tos] and [BSmpy][tos] to pure CO<sub>2</sub>/CH<sub>4</sub> was 47.4 and 40.7, respectively.

### 3.1.2.3 Phase change ILs

CO<sub>2</sub> capture using phase change ILs has attracted increased interest for the potential to reduce the cost of energy consumption. Upon CO<sub>2</sub> absorption, phase change ILs form a two-phase system, namely a CO<sub>2</sub>-enriched phase and a CO<sub>2</sub>-lean phase. The CO<sub>2</sub>-lean phase is a liquid phase and the CO<sub>2</sub>-enriched

phase is either a liquid or solid phase. Only the CO<sub>2</sub>-enriched liquid phase is used for solvent regeneration; thus, the heat required to regenerate the solvent is reduced. Recently, the research on PILs has been mainly focused on ionic liquid-amine composite and pure ionic liquids systems (Lv et al., 2020; Tiwari et al., 2021; Wu, J. et al., 2019; Zalewski et al., 2021).

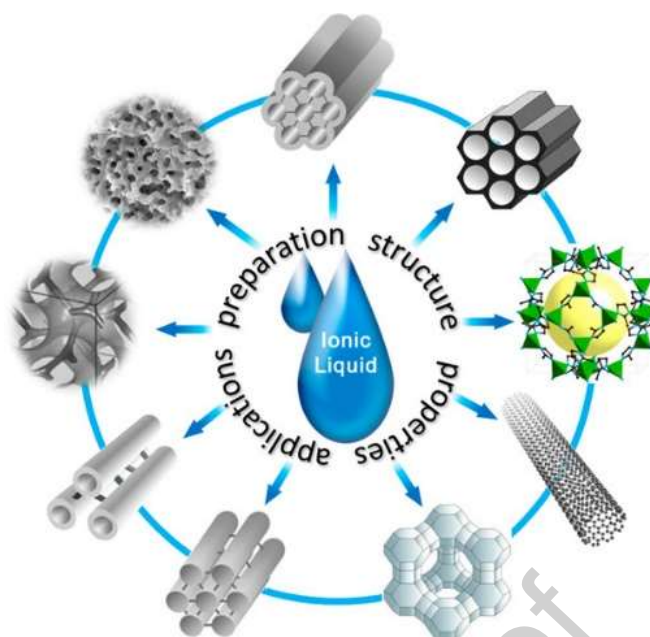
The blends of diethanolamine (DEA) with one of three IL, [EMIM][Tf<sub>2</sub>N], [BMIM][Tf<sub>2</sub>N] and [HMIM][Tf<sub>2</sub>N], were able to form a solid phase during CO<sub>2</sub> absorption (Hasib-ur-Rahman and Larachi, 2013; Hasib-ur-Rahman et al., 2012; Iliuta, Ion et al., 2014). The solid products of this IL-amine composite system are mainly carbamates and alkyl carbonates, and more than 99% are concentrated in the CO<sub>2</sub> rich phase. The precipitation of the carbamate product allowed CO<sub>2</sub> absorption to proceed beyond the equilibrium limitation exerted on a liquid phase system.

To enhance CO<sub>2</sub> capture capacities, some researchers investigated functionalized ILs in such phase change systems. Triethylenetetramine L-lysine ([TETAH][Lys]) was dissolved in ethanol-water solvent to form a phase change solvent, and the CO<sub>2</sub> capacity reached 2.35 mol CO<sub>2</sub>/mol IL as well as the volume ratio of the CO<sub>2</sub>-rich phase was 66% (Huang, Q. et al., 2018). At the same time, the regeneration energy consumption (1.29 GJ/t CO<sub>2</sub>) and solvent loss during the regeneration process are also reduced. The CO<sub>2</sub> capacity of triethylenetetramine hydrobromide [TETA]Br-PMDETA-H<sub>2</sub>O phase change system was high to 2.631 mol CO<sub>2</sub>/L at 30 °C and 0.1 MPa, and the regeneration efficiency remained above 95% after four cycles at 150 °C (Zhou, H.C. et al., 2020).

Recently, an amino-azolyl dual-functional IL/ethanol/water system ([DETAH][Im]-CH<sub>3</sub>CH<sub>2</sub>OH-H<sub>2</sub>O) for CO<sub>2</sub> capture was constructed via dissolution of a diethylenetriamine-imidazole functionalized ionic liquid ([DETAH][Im]) in the mixed ethanol-water solvent and the CO<sub>2</sub> loading was reported to be 1.548 mol CO<sub>2</sub>/mol absorbent whereas the volume only accounted for 32% (Lü B, 2021). As shown in **Figure 3.6**, in the process of absorption, [DETAH][Im] as the main absorbent, cations can react with CO<sub>2</sub> to form carbamates (RN<sup>+</sup>COO<sup>-</sup>), whileazolyl anions can react with CO<sub>2</sub> to form HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>, which ensures the efficient CO<sub>2</sub> trapping ability of the system. At the same time, [Im]-H and ethanol can promote the decomposition of carbamate (RN<sup>+</sup>COO<sup>-</sup>) and produce easily decomposed HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> and ethyl carbonate products, while leads to the high regeneration efficiency of the rich liquid.



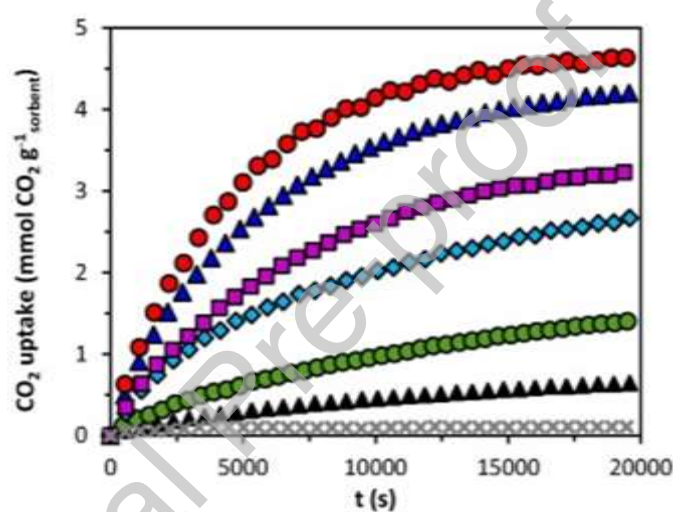




**Figure 3.7 Concept of ILs immobilized by various porous solid matrices(Zhang, S. et al., 2017)**

Porous silica and zeolite are the preferred matrices for ILs considering their porosity, nontoxicity and facile synthesis. The interaction between the pore wall and ILs plays a key role in affecting the properties of the corresponding SILs or ENILs, which depends on both silica surface properties and the functional groups of ILs. The surface of silica and zeolite mainly contains Si, Al, Si-O groups and Si-OH groups, which serve as interaction sites for the supported ILs (Wang, Q. et al., 2011; Zhang, S. et al., 2017). For example, Zhu et al. (Zhu, J. et al., 2018) immobilized imidazolium and phosphonium ILs into porous silica supports and suggested that the CO<sub>2</sub> adsorption through the porous nature of the silica dominated the adsorption behavior of the hybrid adsorbent. Pohako-Esko et al. (Pohako-Esko et al., 2016) prepared the ENILs by encapsulating chitosan containing ILs with nanoporous fumed silica. The results showed that dissolution chitosan in ILs increased the CO<sub>2</sub> adsorption capacity of chitosan about 10 times. In addition, functional groups usually increase the interaction between ILs and CO<sub>2</sub>, resulting in increased CO<sub>2</sub> capacity. Zhang et al. (Zhang, W. et al., 2019) prepared multi-amino functionalized IL adsorbent supported on SBA-15, which exhibited a high CO<sub>2</sub> capacity of 2.15 mmolCO<sub>2</sub>/g-adsorbent under 60 °C and 0.015 MPa. Arellano et al. (Arellano et al., 2015) reported the SBA-15 supported metal-based zinc-functionalized ILs. It was shown that an excellent CO<sub>2</sub> capacity of 4.70 mmolCO<sub>2</sub>/g-adsorbent was achieved under 40 °C and 0.015 MPa after incorporating EZT3 into SBA-15. As displayed in **Figure 3.8**, the CO<sub>2</sub> capacity of EZT3@SBA-15 is 600% and 250% of the pristine ILs and SBA-15, owing to the creation of abundantly accessible CO<sub>2</sub> adsorption sites and the elimination of the viscosity-imposed limitation on mass transfer. Yu et al. (Yu, Yinghao et al., 2014) applied NaY zeolite as support to encapsulate [C<sub>n</sub>mim][Br] (n = 4, 6, 8, 10). It was shown that the encapsulated [C<sub>n</sub>mim][Br]@NaY was more thermal stable than the neat one. Moreover, the results showed that the CO<sub>2</sub> capacity under 35 °C and 0.015 MPa increased with decreasing length of the side chain on the

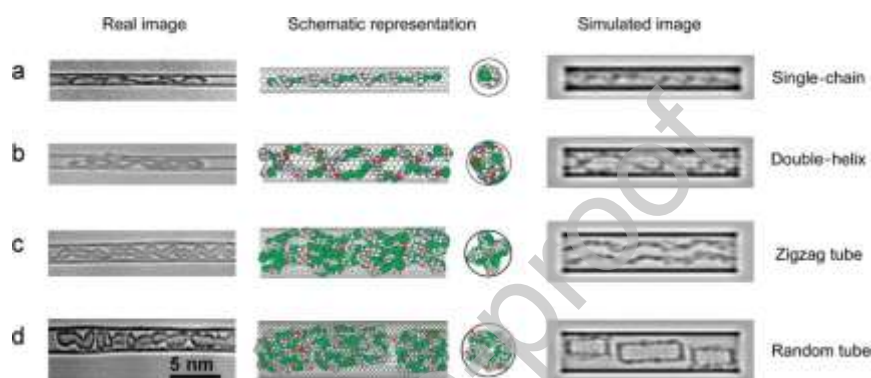
cation. Besides, immobilization methods affect the performance of the SILs a lot. Zhu et al. (Zhu, J. et al., 2018) studied the effect of immobilization methods (impregnation and grafting) on the CO<sub>2</sub> selectivity of silica-supported ILs. They found that compared with the impregnated adsorbent, grafting ILs on the support surface caused a weak loss of microporosity, leading to a slight decrease in CO<sub>2</sub> adsorption capacity, and had better recycling. The grafted silica exhibited diffusivities faster than those of the impregnated one, indicating that excessive filling of with ILs was unfavorable for CO<sub>2</sub> diffusion. According to Yin's report (Yin et al., 2018), the CO<sub>2</sub> capacity of [C<sub>4</sub>mim][BF<sub>4</sub>]@SBA-15 synthesized by supercritical fluid method (0.79 mmol CO<sub>2</sub>/g-adsorbent) is higher than that of the impregnation method (0.63 mmolCO<sub>2</sub>/g-adsorbent) under 25 °C and 0.003 MPa. The authors proposed that the supercritical fluid method could make ILs more homogeneously distributed on the support and increase the loading amount of ILs, resulting in the increased CO<sub>2</sub> adsorption capacity.



**Figure 3.8** Dynamic CO<sub>2</sub> uptake capacity for SBA-15 (green), nonfunctionalized IL ET (grey), E2T3 (black), and E2T3@SBA-15 with different IL loadings: 10 wt% (cyan), 25 wt% (dark blue), 50 wt% (red), and 80 wt% (pink) (Arellano et al., 2015).

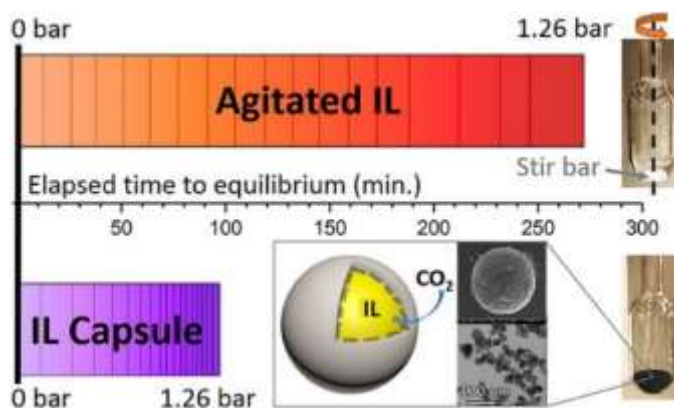
CO<sub>2</sub> adsorption on pristine carbon materials is physical and weak, thus, the adsorption is sensitive to the reaction temperature and CO<sub>2</sub> selectivity is very low (Wang, Q. et al., 2011). Immobilizing ILs on carbon materials, such as activated carbons (AC) and carbon nanotubes (CNT), is particularly interesting to overcome the drawbacks of both pristine carbon materials and ILs, and combine their respective advantages. CNTs are investigated the most since their initially empty channel could spontaneously be filled with surrounding ILs in the container to achieve a saturated state. **Figure 3.9** displays one of the typical ENILs, where the [Me<sub>3</sub>NC<sub>2</sub>H<sub>4</sub>OH][ZnCl<sub>3</sub>] is encapsulated inside CNTs with different diameters (Chen, S. et al., 2009). Maurya et al. (Maurya and Singh, 2019) compared the CO<sub>2</sub> adsorption capacity of MOFs (InOF-1, UiO-66 and ZIF-8), COFs (COF-108 and COF-300) and carbon based materials (single-wall carbon nanotube SWCNT), and the results showed that SWCNT had the highest CO<sub>2</sub> adsorption capacity. Moreover, the CO<sub>2</sub> adsorption capacity and selectivity further

improved by impregnating with ILs. Zeng et al. (Zeng, Y. et al., 2018) synthesized a series of ENILs using carbon nanotube (CNT) as shell material, including  $[\text{C}_4\text{mim}][\text{PF}_6]@\text{CNT}$ ,  $[\text{C}_4\text{mim}][\text{SCN}]\text{CNT}$  and  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]\text{CNT}$ , to study the effect of anions on the ENILs for  $\text{CO}_2$  capture. The results showed that  $[\text{C}_4\text{mim}][\text{PF}_6]@\text{CNT}$  exhibited the highest  $\text{CO}_2$  capacity of  $1.30 \text{ mmolCO}_2/\text{g-adsorbent}$  under  $30 \text{ }^\circ\text{C}$  and  $0.1 \text{ MPa}$ , because  $[\text{PF}_6]^-$  had a stronger interaction with  $\text{CO}_2$  than  $[\text{SCN}]^-$  and  $[\text{Tf}_2\text{N}]^-$ . As a consequence of the reduced pore volume by the larger anion inside CNT,  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]\text{CNT}$  showed the low  $\text{CO}_2$  capacity. In general, the  $\text{CO}_2$  selectivity of SILs and ENILs synthesized by impregnation method is higher than that of the grafting method.



**Figure 3.9 Images of  $[\text{Me}_3\text{NC}_2\text{H}_4\text{OH}][\text{ZnCl}_3]$  encapsulated inside SWCNTs with different diameters (Chen, S. et al., 2009).**

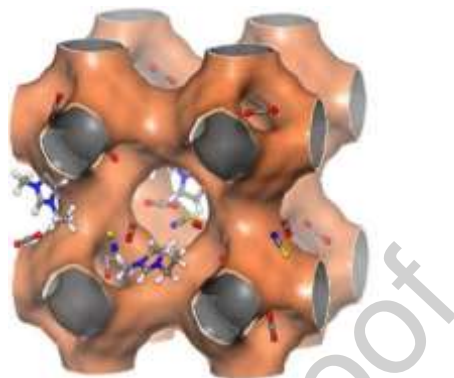
He et al. (Wang, W.J. et al., 2019a) incorporated the phosphonium ILs  $[(\text{EtO})_3\text{SiP}_{8883}][\text{Tf}_2\text{N}]$  into activated carbon (AC) by the grafting method and the impregnation method, respectively. The results showed that the  $\text{CO}_2/\text{N}_2$  selectivity of the adsorbent synthesized by the impregnation method is higher than that of the grafted one. This is because the thin film of ILs formed on the support after impregnation is beneficial for permitting the entry of  $\text{CO}_2$  but blocking  $\text{N}_2$  (Wang, W.J. et al., 2019a; Zhu, J. et al., 2018). Besides, Karousos et al. (Karousos et al., 2016) found that the  $\text{CO}_2/\text{SO}_2$  selectivity of the AC-impregnated  $[\text{C}_2\text{mim}][\text{OAc}]$  is much higher than that of the AC-grafted one under  $50 \text{ }^\circ\text{C}$  and  $0.1 \text{ MPa}$ . The similar conclusions for other supports (SBA-15 and MOF-177) were also obtained. Graphene oxide was also reported to construct ILs-based solid  $\text{CO}_2$  adsorbent. For example, Huang et al. (Huang, Q. et al., 2019) synthesized the encapsulated imidazolium-based ILs with alkylated graphene oxide as the shell with ILs loading of 80 wt%. The shell material was permeable to  $\text{CO}_2$  and allowed  $\text{CO}_2$  to reach the inner IL core effectively, resulting in the increased  $\text{CO}_2$  adsorption rate. As shown in **Figure 3.10**, the time to reach  $\text{CO}_2$  adsorption equilibrium for encapsulated ILs was shortened from 271 to 97 min compared with the agitated ILs. This result proves that the encapsulating ILs in special structure can increase the gas-liquid contact area and improves the mass transfer.



**Figure 3.10** The elapsed time to reach CO<sub>2</sub> adsorption equilibrium and schematic of encapsulated [C<sub>2</sub>mim][Tf<sub>2</sub>N] (Huang, Q. et al., 2019).

Metal-Organic Frameworks (MOFs) are constructed from transition metal ions and bridging organic ligands, which are a new family of porous materials. Impregnation of ILs on MOFs has been proposed as a promising alternative to traditional ILs, because they are non-volatile, non-flammable and thermal stable and therefore are categorized as green adsorbents. **Figure 3.11** shows the schematics of [C<sub>2</sub>mim][SCN] incorporated into Cu-BTC. Silva et al. (Silva et al., 2015) proposed MOF-supported ILs for CO<sub>2</sub> capture and proved that the incorporation of [C<sub>4</sub>mim][PF<sub>6</sub>] to Cu-BTC enhanced the CO<sub>2</sub> adsorption capacity compared with pristine MOFs. However, the CO<sub>2</sub> adsorption capacity of [C<sub>4</sub>mim][PF<sub>6</sub>]@Cu-BTC with 5 wt% ILs loading (1.2 mmol CO<sub>2</sub>/g-adsorbent) under 25 °C and 0.025 MPa was lower than pure Cu-BTC (1.3 mmol CO<sub>2</sub>/g-adsorbent). Besides, a further decrease in CO<sub>2</sub> adsorption capacity was observed as the ILs loading increased. This might be caused by channel jam after the incorporation of excessive ILs. Although loading conventional ILs suppressed the CO<sub>2</sub> adsorption capacity of MOFs, it is worth noting that the conventional ILs have a positive effect on CO<sub>2</sub> selectivity (Vicent-Luna et al., 2018). Kinik et al. (Kinik et al., 2016) incorporated [C<sub>4</sub>mim][PF<sub>6</sub>] into zeolitic imidazolate frameworks-8 (ZIF-8) and found that the CO<sub>2</sub> adsorption capacity of [C<sub>4</sub>mim][PF<sub>6</sub>]@ZIF-8 (0.10 mmol CO<sub>2</sub>/g-adsorbent) was twice as high as that of the pristine ZIF-8 under 25 °C and 0.00065 MPa. Furthermore, CO<sub>2</sub> selectivity in CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> was improved. Ferreira et al. (Ferreira et al., 2019) found that incorporating [C<sub>10</sub>mim][Tf<sub>2</sub>N]@ZIF-8 onto ZIF-8 enhanced the CO<sub>2</sub>/CH<sub>4</sub> selectivity of 3.1 under 0.05 MPa, which increased by 35% compared with the blank ZIF-8. Besides, the nonpolar and long side chain of [C<sub>10</sub>mim][Tf<sub>2</sub>N] strengthened its interaction with CO<sub>2</sub>, making [C<sub>10</sub>mim][Tf<sub>2</sub>N]@ZIF-8 show better CO<sub>2</sub> separation performance than other ILs@ZIF-8. The functional groups, like amino group and carboxyl group, also play a key role in CO<sub>2</sub> adsorption, considering their interaction with CO<sub>2</sub>. For instance, Mohamedali et al. (Mohamedali et al., 2018) incorporated the acetate-based ILs into ZIF-8, which enhanced the CO<sub>2</sub> capacity and CO<sub>2</sub>/N<sub>2</sub> selectivity. In comparison with the pristine ZIF-8, the CO<sub>2</sub> uptake of [C<sub>4</sub>mim][OAc]@ZIF-8 was increased by more than seven times, and the CO<sub>2</sub>/N<sub>2</sub> selectivity reached 18 times. By increasing the ILs loading to 83.04 wt%, Wang et al. (Wang, Xue et al., 2019) prepared a [C<sub>4</sub>Py][Tf<sub>2</sub>N]@ZIF-8 adsorbent

with 1.36 mmolCO<sub>2</sub>/g-adsorbent under 30 °C and 1.8 MPa, which increased by 24% compared with pristine ILs. Mohamed et al. (Mohamed et al., 2019) investigated six ENILs with different ILs and the same ZIF-8 support via Monte Carlo simulations. The results showed that the encapsulation of [C<sub>4</sub>mim][B(CN)<sub>4</sub>] and [C<sub>4</sub>mim][TCM] into ZIF-8 can achieve higher CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivity than that of [C<sub>4</sub>mim][Tf<sub>2</sub>N]@ZIF-8. For explanation, the authors proposed that more ILs pairs in ZIF-8 cages provided more CO<sub>2</sub> adsorption sites, consequently the higher CO<sub>2</sub> selectivity.

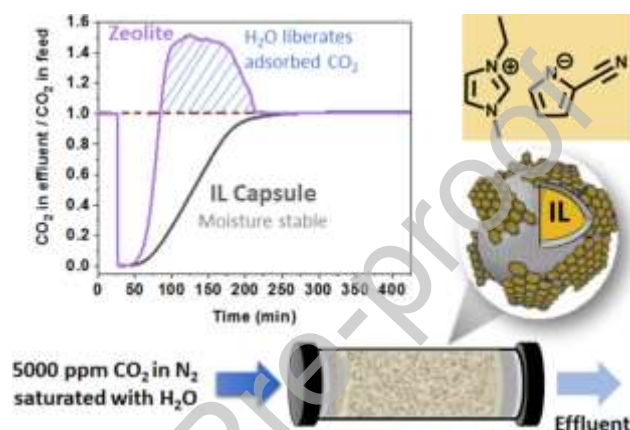


**Figure 3.11 Schematics of [C<sub>2</sub>mim][SCN]@Cu-BTC (Manuel Vicent-Luna et al., 2013).**

In addition to the intensively studied rigid inorganic matrices, ILs could also be confined into organic polymer matrices. The application of polymers as porous hosts for ILs gives rise to the easy and convenient formation of flexible membranes, although this system often experiences a loss of mechanical when the loading of immobilized ILs is too high. Polymer-immobilized ILs are usually prepared by either in situ polymerization of monomers in ILs (Guyomard-Lack et al., 2015) or a solvent casting method (Tang et al., 2015; Yang, J. et al., 2015). Several polymers have been explored for supporting ILs, such as polymethyl methacrylate (PMMA) (Uehara et al., 2018; Wang, X. et al., 2013), fluorinated copolymer poly-(vinylidene fluoride-co-chlorotrifluoroethylene) (P(VDF-CTFE)) (Yang, J. et al., 2015), biopolymers (Guyomard-Lack et al., 2015; Trivedi et al., 2015), and epoxy resins (Matsumoto and Endo, 2008). Ren et al. (Ren et al., 2018) synthesized a series of SILs by impregnating tetramethylammonium glycinate ([N<sub>1111</sub>][Gly]) into four supports, including polymethyl methacrylate (PMMA), titanium oxide (P25), MCM-41 and silica gel (SG). Among them, PMMA-[N<sub>1111</sub>][Gly] displayed the best CO<sub>2</sub> adsorption behavior in terms of adsorption capacity and rate. The CO<sub>2</sub> adsorption capacity reached up to 2.14 mmolCO<sub>2</sub>/g-adsorbent at 35 °C. Pristine ILs and supported ILs might exhibit opposite behavior. For instance, Uehara et al. (Uehara et al., 2018) synthesized a series of polymethyl methacrylate (PMMA) supported ILs, including [C<sub>2</sub>mim][Lys]@PMMA, [C<sub>2</sub>mim](Chen, S. et al.)@PMMA, [C<sub>2</sub>mim][Gly]@PMMA, [P<sub>4444</sub>][Lys]@PMMA, [P<sub>4444</sub>](Chen, S. et al.)@PMMA and [P<sub>4444</sub>][Gly]@PMMA. It was found that the [Lys]<sup>-</sup> and (Chen, S. et al.)<sup>-</sup> exhibited higher CO<sub>2</sub> capacity than [Gly]<sup>-</sup>. However, the CO<sub>2</sub> capacity was the opposite when these ILs were supported on PMMA. The [C<sub>2</sub>mim][Gly]@PMMA had a higher CO<sub>2</sub> capacity (0.88 mmolCO<sub>2</sub>/g-adsorbent) than [C<sub>2</sub>mim](Chen, S. et al.)@PMMA (0.63 mmolCO<sub>2</sub>/g-adsorbent) under 30 °C and 0.0023 MPa. This was



because the side chains with amino groups in (Chen, S. et al.) blocked the pore structure of PMMA, which inhibited the entry of CO<sub>2</sub> and thus reduced CO<sub>2</sub> capacity. Lee et al.(Lee, Y.-Y. et al., 2020) combined [C2mim][2-CNpyr] with polyurethane and graphene oxide nanosheet shells to prepare the reactive ENILs. As shown in **Figure 3.12**, the CO<sub>2</sub> capacity of this adsorbent was 1.30 mmolCO<sub>2</sub>/g-adsorbent under 25 °C and 0.0005 MPa. In comparison with the most advanced zeolite 13X, these ENILs had better stability, recyclability and higher CO<sub>2</sub> capacity. Kaviani et al.(Kaviani et al., 2018) investigated the feasibility of ILs encapsulation within a polymeric shell and evaluated the hybrid adsorbent in CO<sub>2</sub> absorption. The proper choice of chemistry for the polymeric matrix allows the ENILs to outperform the pristine ILs. The improvement was ascribed to the synergistic effect between the fluorine-containing polymer and ILs on the CO<sub>2</sub> adsorption of the ENILs.



**Figure 3.12** Schematics of encapsulated [C<sub>2</sub>mim][2-CNpyr] with polyurethane and graphene oxide nanosheet shells (Lee, Y.-Y. et al., 2020).

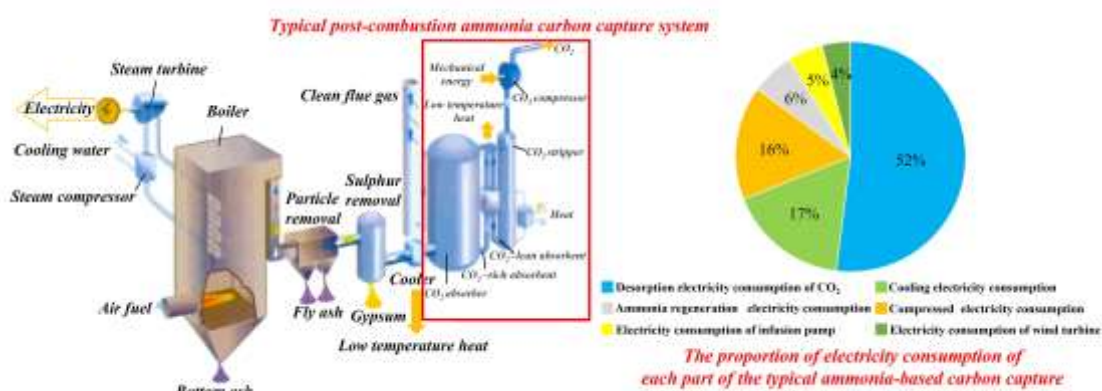
### 3.1.3 New ammonia-based CO<sub>2</sub> capture

As the most feasible post-combustion CO<sub>2</sub> capture technology, the chemical absorption method shows great prospects for industrial applications. Currently, the main industrial method is alcohol-amine solution-ethanolamine (MEA) absorption. However, there are many problems in the practical application, such as high regeneration energy consumption, serious equipment corrosion, and easy solvent volatilization and decomposition(Liang et al., 2016a). Therefore, ammonia-based carbon capture technology may become the main theme of CO<sub>2</sub> capture technology, but its ammonia escape problem is serious. The advent of additives brings a turnaround, and ammonia and additives can promote each other to some extent to improve the CO<sub>2</sub> absorption rate of ammonia. Ethanol as an additive excels in all aspects, and a new ammonia-based carbon capture technology (ammonia-ethanol hybrid absorber) (Zhang, Y. et al., 2019) was born. Due to the high corrosiveness of MEA and regeneration problems, ammonia-based CO<sub>2</sub> capture is a viable carbon capture technology over conventional amine-based CO<sub>2</sub> capture technology, technically and economically.

### 3.1.3.1 Ammonia-based CO<sub>2</sub> capture technology

Reliable absorbents for low concentration CO<sub>2</sub> capture are amine- and amino-based CO<sub>2</sub> capture technologies. The thermochemistry of CO<sub>2</sub>-NH<sub>3</sub>-H<sub>2</sub>O systems with ammonia as an alternative to amine-based absorbers is reasonably well understood, including vapor-liquid-solid equilibria, species formation, absorption heat, reaction kinetics, and thermodynamic model development. Many thermodynamic models based on CO<sub>2</sub>-NH<sub>3</sub>-H<sub>2</sub>O systems were developed by Thomsen, Rasmussen(Thomsen and Rasmussen, 1999), and Que and Chen(Que and Chen, 2011), which accurately predicted the gas-liquid-solid phase equilibrium. Figure 3.1 shows the typical post-combustion ammonia carbon capture system and the proportion of electricity consumption of each part of the process. The existing typical processes of this technology are as follows: Alstom refrigerated ammonia process, Powerspan ECO<sub>2</sub> process, CSIRO ammonia process of Australian Federal Science and Industry Commission, RIST ammonia process of Korea Industrial Science and Technology Research Center, etc.

During CO<sub>2</sub> capture, ammonia reacts with carbon dioxide (aq) to form carbamate, which is immediately deprotonated to give carbamate. Due to the reversal of the equilibrium as the pH changes with continued CO<sub>2</sub> uptake, the carbamate eventually decomposes to produce protonated ammonia and bicarbonate. The carbamate equilibrium constant of MEA is much higher than that of ammonia, indicating that the yield of ammonia-derived carbamate is lower than that of the equivalent monoethanolic ammonium carbamate ammonia possesses a higher CO<sub>2</sub> capture capacity compared to MEA. Based on equilibrium calculations(Darde et al., 2009), the cold ammonia method resulted in significantly lower energy consumption in the regeneration step than the amine-based method. Table 3 shows a qualitative comparison between amine and ammonia as CO<sub>2</sub> capture absorbents. Ammonia-based CO<sub>2</sub> capture technology outperforms conventional amine-based CO<sub>2</sub> capture technology in terms of technical and economic advantages, with high CO<sub>2</sub> absorption capacity, low heat of absorption reaction, and less susceptibility to downgrading by O<sub>2</sub> in the flue gas, low corrosiveness, and low feedstock prices(Darde et al., 2009; Pellegrini et al., 2010).



**Figure 3.1 Typical post-combustion ammonia-based carbon capture system and the proportion of electricity consumption of each part of the process diagram (Yu and Wang, 2015).**

**Table 3.3 Qualitative comparison between amines and ammonia as CO<sub>2</sub> absorbers**

Characteristics	Amines	Ammonia
CO <sub>2</sub> capture capacity	0.5 mol- CO <sub>2</sub> /mol-MEA	1.0 mol- CO <sub>2</sub> /mol-NH <sub>3</sub>
Regeneration energy (GJ/tCO <sub>2</sub> )	4.2 (MEA)	< 2.5
Absorption rate	Fast	Slow
Corrosiveness	Severe	Mild
Volatility	Low	High
Absorbent cost	Expensive	Cheap
Advantages	Fast reaction kinetics and high absorption capacity	Absorption at high loading, low corrosion, and degradation, easy regeneration
Disadvantages	High regeneration energy, high corrosion rate, easily oxidized and degraded	Ammonia escape, secondary pollution

### 3.1.3.2 Ammonia escape

While ammonia solution as a CO<sub>2</sub> absorber has the above-mentioned significant advantages, there are also common shortcomings and deficiencies in the current application.

1) Low CO<sub>2</sub> absorption rate, the reaction rate of CO<sub>2</sub> absorption by ammonia at the same temperature is about an order of magnitude lower than that of MEA.

2) Serious ammonia escape, the concentration of escaped ammonia during CO<sub>2</sub> absorption can be as high as 2 vol.%, and the concentration of escaped ammonia during rich liquid regeneration reach 10-20 vol.%; with 14% ammonia, for example, the total ammonia loss is as high as 43.1%(Jilvero et al., 2015).

3) High energy consumption for desorption and regeneration and up to 4-4.2 MJ/kgCO<sub>2</sub> for regeneration in the pilot experiment of ammonia decarbonization(Yu, 2018).





Figure 3.2 Schematic diagram of ammonia escape.

The main drawbacks of ammonia-based CO<sub>2</sub> capture technology are slower absorption kinetics and higher volatility than amine solutions. The ammonia escape mechanism is shown in Figure 3.2, and the ammonia escape problem is becoming one of the most critical technical and economic challenges in the commercial application of ammonia-based CO<sub>2</sub> capture technology. A high NH<sub>3</sub> escape rate also reduces the concentration of NH<sub>3</sub> in the solution, thus reducing the CO<sub>2</sub> uptake capacity (Wang, F. et al., 2018). In addition, ammonia can leak into the air, thus causing serious secondary pollution. Therefore, it is imperative to develop effective methods to suppress ammonia leakage or recover the leaked ammonia. Optimizing process parameters through acid and aqueous washing, membrane technology, additives and accelerators, and applying cold ammonia processes and mixed salts are common strategies to control ammonia escapes.

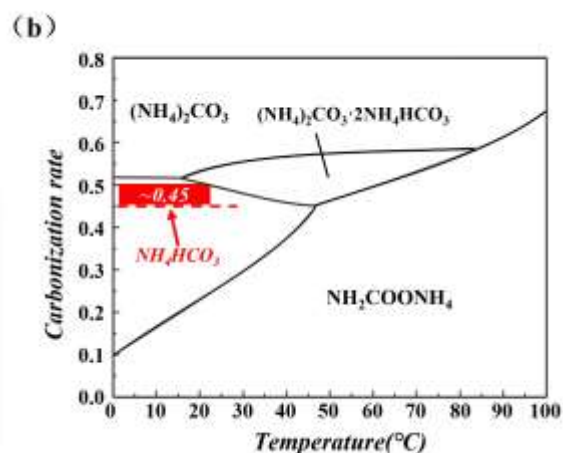
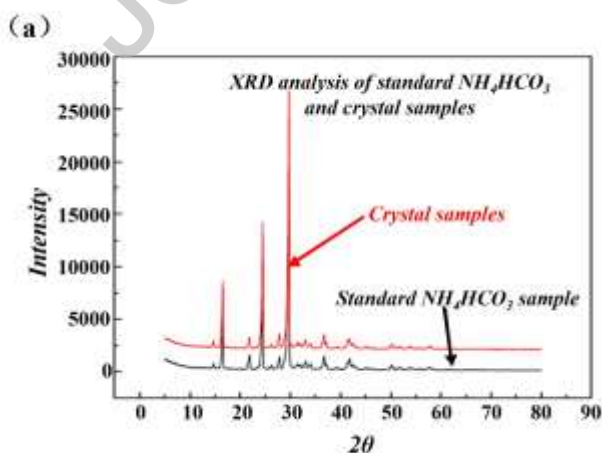
### 3.1.3.3 Ammonia-ethanol mixture absorber

To solve the ammonia escape problem, many scholars have proposed the modification of CO<sub>2</sub> absorption by ammonia solutions using additives, which inhibit not only NH<sub>3</sub> escape but also improve CO<sub>2</sub> absorption performance. 4 provides the results of studies on CO<sub>2</sub> capture by ammonia additive in the last five years. Gao and Zhang et al. (Gao et al., 2015; Zhang, Y. et al., 2019) have shown significant advantages of using ethanol as an additive in various aspects. Ammonia and ethanol can promote each other to improve the CO<sub>2</sub> absorption rate of ammonia (Yang, N. et al., 2014). However, there is a slight contradiction between the hybrid absorber increasing the absorption rate and inhibiting ammonia escape (Ma et al., 2016). The additive mainly binds the free ammonia in the ammonia solution through hydrogen bonding. It thus inhibits ammonia escape, but when the hybrid absorber absorbs CO<sub>2</sub>, the additive does not achieve effective ammonia release, thus decreasing the liquid-phase partial pressure of free ammonia, which adversely affects the absorption process. Ethanol as an additive does not show

significant differences in this regard. In addition, Pellegrini(Pellegrini et al., 2010) pointed out that partial replacement of water in chemical absorbents by ethanol solvents with a smaller specific heat can significantly reduce the regeneration energy consumption (the specific heat of anhydrous ethanol is  $2.4 \times 10^3 \text{ J}/(\text{kg}\cdot^\circ\text{C})$ , which is only 57% of that of water, i.e., the same mass of solvent can save nearly 40% of the heat by increasing the same temperature), which shows that "ammonia-ethanol mixture (i.e., the same mass of solvent can save nearly 40% of the heat by increasing the same temperature), which shows that the "ammonia-ethanol mixture" has significant advantages for  $\text{CO}_2$  absorption and capture (Zhang, Y. et al., 2019).

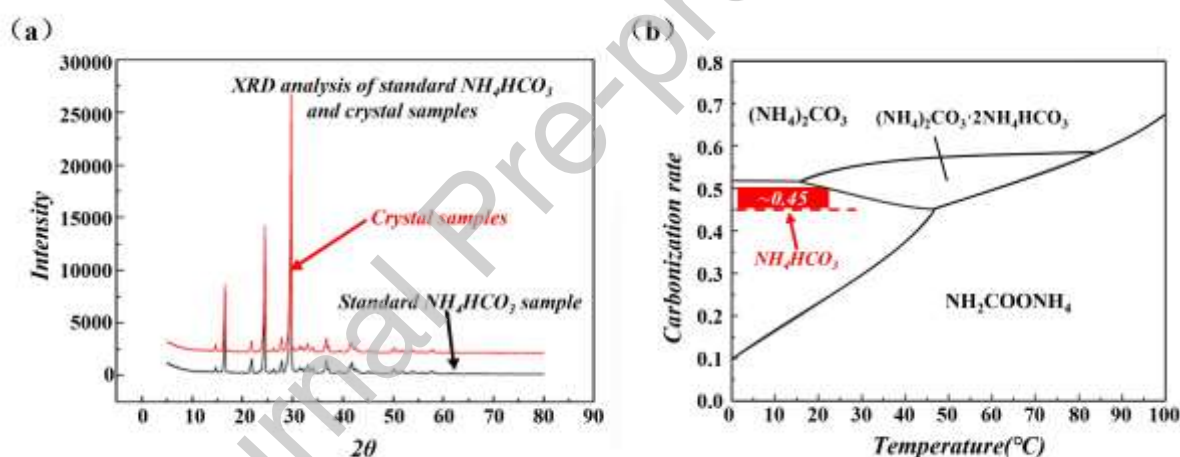
**Table 3.4 Comparison of ammonia  $\text{CO}_2$  capture performance with different additives**

Parameters	Additives	$\text{CO}_2$ loading (mol/mol)	$\text{CO}_2$ removal efficiency	Reference
8.22 mol $\text{NH}_3/\text{kg}$ $\text{H}_2\text{O}$ , $T=27^\circ\text{C}$	1.5 mol $\text{K}_2\text{CO}_3/\text{kg}$ $\text{H}_2\text{O}$	0.4	90%	(Pachitsas and Bonalumi, 2022)
6.31 mol $\text{NH}_3/\text{kg}$ $\text{H}_2\text{O}$ , $T=27^\circ\text{C}$	1.0 mol $\text{K}_2\text{CO}_3/\text{kg}$ $\text{H}_2\text{O}$	0.3	90%	
4 M $\text{NH}_3$ , $T = 25^\circ\text{C}$ , $\text{CO}_2 = 12 \text{ vol}\%$	0.25 mol Piperazine /kg $\text{H}_2\text{O}$	0.43	85.0%	(Jiang, K. et al., 2018)
2.5 M $\text{NH}_3$ , $T = 25^\circ\text{C}$	1.50 M $\text{K}_2\text{CO}_3$	0.35	>90%	(Lillia et al., 2019)
0.85 mol/L $\text{NH}_3$ , $T = 20^\circ\text{C}$	Ethanol	-	1.64kg/kg	(Gao et al., 2015)
3 mol/L $\text{NH}_3$ , $T = 26^\circ\text{C}$	Capacitive deionization	0.24	87.0%	(Ullah et al., 2017)
3.6 wt.% $\text{NH}_3$ , $T = 25^\circ\text{C}$	20 mL microalgae	-	76.8%	(Song et al., 2019a)
5 wt.% $\text{NH}_3$ , $T = 20^\circ\text{C}$ , $\text{CO}_2 = 15 \text{ vol}\%$	0.1 mol/L Piperazine /kg $\text{H}_2\text{O}$	-	60.0%	(Xu, Yin et al., 2019)
247 mg/L $\text{NH}_3$ , $T = 25^\circ\text{C}$ , $\text{CO}_2 = 5 \text{ vol}\%$	423 mg/L microalgae	17 mg/L	87.0%	(Song et al., 2019c)



**Figure 3.3 (a) Crystal and standard  $\text{NH}_4\text{HCO}_3$  sample analyzed by X-ray diffractometer (b) The effect of carbonization rate on the "carbon balance" of ammonia-based carbon capture system (Gao et al., 2015).**

The solubility of the products in the reaction process of  $\text{CO}_2$  absorption by ammonia is known. Ammonium carbamate is soluble in water and soluble in ethanol, and ammonium bicarbonate is soluble in water-insoluble in ethanol. As reported (Gao et al., 2015; Zhang, Y. et al., 2019), the ammonia carbon capture process could be controlled to a low carbonation degree ( $<0.5$ ) (Figure 3.15) to ensure the efficient carbon capture rate of the system and adopted a new decarbonization and regeneration process of "ammonia-ethanol mixed absorption leading to solvation crystallization and crystal regeneration instead of rich liquid regeneration." It has been proved that the ammonia-ethanol liquid-phase mixed absorption of the  $\text{CO}_2$  dissolution crystallization process is mainly precipitated by  $\text{NH}_4\text{HCO}_3$  crystals.



**Figure 3.3 the crystal sample after reaction (Gao et al., 2015).**

The regeneration tower only needs to heat the  $\text{NH}_4\text{HCO}_3$  crystal products, indicated in Figure 3.16.  $\text{NH}_4\text{HCO}_3$  crystals could be decomposed into  $\text{CO}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  above  $36^\circ\text{C}$  and completely decompose at  $60^\circ\text{C}$ . This can greatly reduce the system's energy consumption by eliminating the energy consumed by heating and vaporizing the solvent during conventional liquid-rich desorption.

#### 3.1.3.4 Applications and Outlook

The mainstream  $\text{CO}_2$  liquid-phase chemical absorption method is difficult to avoid high regeneration energy consumption, degradation problems, and high corrosiveness. The discovery of ethanol additives

has further improved the techno-economic of the amino CO<sub>2</sub> absorption system. The new ammonia carbon capture technology ("ammonia-ethanol hybrid absorber") shows great potential in carbon capture. With the rapid development of CO<sub>2</sub> solid-phase adsorption technology, biochar is considered the most promising solid CO<sub>2</sub> adsorbent for application (Creamer et al., 2014). Suppose biochar particles are used as modified materials to enhance the liquid-phase mass transfer characteristics. In that case, their stronger CO<sub>2</sub> diffusion characteristics can be fully utilized to improve the overall carbon-negative degree and CO<sub>2</sub> capture rate of the CO<sub>2</sub> capture system, enhance the solid-liquid two-phase mass transfer enhancement and suppress ammonia escape (Zhang, Yu et al., 2022). The high-quality rice husk nano-pore carbon was prepared using agricultural waste rice husk, combined with the new ammonia CO<sub>2</sub> capture technology to improve the overall performance of carbon dioxide capture. In addition, the intermediate product NH<sub>4</sub>HCO<sub>3</sub> from the new ammonia CO<sub>2</sub> capture and the intermediate product K<sub>2</sub>SiO<sub>3</sub> from the preparation of rice husk nano-pore carbon were used to prepare nanoscale silica through process regulation, which significantly solved the problems of CO<sub>2</sub> capture product dissipation, agricultural waste pollution, and high-value product preparation. The production of high-value products - rice husk nano-pore carbon and nano-grade silica - also helps form an integrated system of energy and product laddering and integrated removal of various pollutants, which provides a new idea for a CO<sub>2</sub> capture system.

### **3.2 Low-temperature solid sorbents**

#### **3.2.1 Cyclic adsorption processes for carbon capture**

Advanced sorbents, process design and swing technologies are the fundamentals for adsorptive carbon capture technologies. The adsorbents and their shaping and pellet sizes have been demonstrated to have a significant impact on the separation performances (Hedin et al., 2013; Zapata Ballesteros et al., 2022). Bed design such as multilayer packing has been employed to selectively pre-remove minor impurities including SO<sub>x</sub>, NO<sub>x</sub> and H<sub>2</sub>O, with part of the adsorbents being replaced by activated alumina, silica gel or zeolites (Hefti and Mazzotti, 2018).

One of the most challenging tasks in adsorption is the ranking of the performances of different adsorbents, in which isotherm based selectivity and working capacity are often unsatisfying (Khurana and Farooq, 2016a). Simplified cycles have been used for adsorbent screening, which provides rapid (seconds to minutes) solutions to pre-select suitable adsorbents for various functions (Ajenifuja et al., 2020; Gutierrez-Ortega et al., 2022; Maring and Webley, 2013b; Rajagopalan et al., 2016; Subramanian Balashankar et al., 2019; Wang, Jiajun et al., 2021). Moreover, efficient engineering processes are the key to the development of operable and economical adsorption technologies. The fine-tuning of both adsorbents and processes is crucial to commercializing adsorption technologies (Zanco et al., 2017).

Almost all adsorbents appear to have a strong affinity to CO<sub>2</sub> over other major components, i.e., N<sub>2</sub> and O<sub>2</sub>, due to the large quadrupole moment and high polarizability of CO<sub>2</sub>, which means CO<sub>2</sub> is always the heavy component that is adsorbed and regenerated from adsorbents. CO<sub>2</sub> selective adsorbents are also favored due to the low concentration of CO<sub>2</sub> in carbon capture applications, e.g. confined space (0.7%)(Zhan et al., 2020), air (0.04%), flue gas in natural gas fired (3–5%) and coal fired (10–15%) power plants. The target of these cycles is to recover the heavy product at high purities.

CO<sub>2</sub> capture using adsorption can be classified as temperature swing adsorption (TSA) and pressure swing adsorption (PSA) based on their dominant regeneration mechanism, i.e. increase in temperature or decrease in pressure(Webley, 2014). Other effects must also be taken into account, such as heat and mass transfer, pressure drop, and energy consumption, and there is still no straightforward way to design regenerative cycles for adsorption processes(Subramanian Balashankar et al., 2019).

### 3.2.1.1 Pressure/Vacuum Swing Adsorption (P/VSA)

P/VSA cycles have been developed over the last several decades through various applications, reported by Skarstrom(Skarstrom, 1960) for gas mixture separation, Sircar and Kratz(Sircar and Kratz, 1988) for hydrogen purification, Grande et al.(Grande et al., 2010) for propane/propylene separation. P/VSA is the most frequently studied for the adsorptive carbon capture process, with multiple pilot scale demonstrations reported(Cho et al., 2004; Krishnamurthy et al., 2014b; Wang, L. et al., 2013a, b). PSA cycles are the most suitable for pre-combustion conditions as the feed gas is often at high pressures, while VSA is more often used for post-combustion, where vacuum evacuation is employed for the regeneration of adsorbents. Adsorption at high pressure and regeneration under vacuum may also be considered to enhance the working capacity of adsorbents. A typical P/VSA cycle includes two necessary steps: adsorption at high pressure and desorption at low pressure, with a few modifications available to improve separation performances and process efficiencies, such as depressurization, purge, pressure equalization, repressurization.

The high flexibility of PSA makes it possible to meet the specifications of feed conditions and desired separation targets, through one or multiple stages. However, it seems a single stage PSA struggles to reach the > 95% CO<sub>2</sub> purity target with > 90% recovery from a 15% feed gas, which often requires extremely low vacuum conditions(Khurana and Farooq, 2016b; Ntiamoah et al., 2015; Yan et al., 2016). Another concern regarding P/VSA is that the energy consumption is often underestimated as high grade energy (electricity) must be used for pressure variation(Zhao, R. et al., 2017b), where a thermal energy conversion is necessary to compare its performance with the benchmark amine processes fairly.

Dual reflux pressure swing adsorption (DR-PSA), also known as duplex PSA, is a special format of PSA in which the feed position is not constrained to the end of an adsorption column. An adsorption column can then be divided into a rectifying section and an enriching section, and two high purity product streams can be achieved simultaneously(Diagne et al., 1994; Leavitt, 1992). DR-PSA cycles

consist of four fundamental steps, i.e., adsorption/feed, pressurization, purge and blowdown. It can be applied via four basic configurations, i.e., DR-PL-A, DR-PH-A, DR-PL-B and DR-PH-B, depending on the feed position and purged streams (Guo, Y. et al., 2021; Kearns and Webley, 2006a, b). Here, PL and PH refer to the feed injected into the high- and low-pressure column, respectively; A and B denote the types of the purged gas, adsorbate (heavy component) and less adsorbed component, respectively.

DR-PSA has been a rapidly developing process in the past two decades, with many researchers dedicated to providing process optimization methods, such as the Triangular Operating Zone (TOZ) (Rossi et al., 2020), Capacity Ratio (C) (May et al., 2017) and feed position ( $z_{\text{feed}}$ ) analysis (Guo, Y. et al., 2021). Zhang et al. achieved 99% CO<sub>2</sub> purity with 99% recovery from a 15% feed gas in a simulated work (Li, D. et al., 2016). In a pilot investigation, Wawrzyńczak et al. compared a 9-step DR-PSA with an 8-step PVSA cycle with a 4-bed system using 540 kg activated carbon as adsorbents (Wawrzyńczak et al., 2019). The DR-PSA cycle showed a 14% higher CO<sub>2</sub> purity and 28% higher energy costs, 29% lower CO<sub>2</sub> recovery and 30% lower productivity. This may be due to the cycles are not fully optimized, such as feed position, pressure ratio and purged quantity (Bhatt et al., 2017, 2018).

### 3.2.1.2 Temperature Swing Adsorption (TSA)

TSA cycles regenerate the adsorption via lifting the column temperature. The packed adsorption column also serves as a heat exchanger packed with adsorbents (Masuda et al., 2021). Researchers have explored multiple ways to heat the entire column to the desired temperature, via direct or indirect heating. TSA has drawn great interest in carbon capture from power plants, given that available waste heat reuse is an advantage. For example, the temperature of low grade heat in power plants, such as waste steam and flue gases, can be over 300 °C, which perfectly suits the regeneration of adsorbents (Leppänen et al., 2014; Zanco et al., 2017).

Direct heating often refers to the adsorbents in direct contact with heating media such as hot steam, air or CO<sub>2</sub>. As direct heating using nonadsorbing gases leads to the dilution of CO<sub>2</sub> products, hot steam or CO<sub>2</sub> product are preferred to serve as the heating sources (Ntiamoah et al., 2016). Indirect heating does not incur the dilution problem and refers to heating sources such as heating/cooling jacket and inner heating/cooling pipes, which often requires a less adsorbing sweep gas (N<sub>2</sub>, air or flue gases) to recover the desorbed CO<sub>2</sub>.

The basic step sequence of a TSA cycle is adsorption, heating and regeneration, and cooling, where CO<sub>2</sub> product purity can rarely reach the 95% target in carbon capture applications. Several novel design concepts have been employed to achieve better separation performances. For example, a purge using feed prior to adsorption can push the regenerated CO<sub>2</sub> out of bed to enhance recovery; a purge step using the CO<sub>2</sub> product prior to the heating and regeneration step can push the free gas out of bed to increase the product purity; other internal purge steps can also be used to integrate the heat and reduce

energy consumptions, e.g., a novel 5-step cycle consists of adsorption, heavy reflux using the light purged gas stream, desorption/heating, light purge, cooling (Joss et al., 2017). Mazzotti et al. compared four TSA cycles and concluded that the cycle with purge and recycle steps outperformed others, reaching the DOE target of 95% CO<sub>2</sub> purity with 90% recovery from flue gases containing 12% CO<sub>2</sub> (Joss et al., 2017; Peh et al., 2022). The major issue with TSA is the long time required for heating and cooling, resulting in the long cycle time ranging from minutes to days. Hence, the number of columns and the time schedule of TSA cycles are crucial in assessing their separation performances.

### 3.2.1.3 Pressure Temperature Swing Adsorption (PTSA)

Separation performance is extremely sensitive to the regeneration temperature and evacuation pressure, which is dependent on the properties of adsorbents (Plaza and Rubiera, 2019; Zhan et al., 2021). The productivity of conventional PSA cycles is often reduced due to the exothermic nature of adsorption, i.e., high bed temperature during adsorption and low bed temperature during desorption (Plaza and Rubiera, 2019). Hybrid cycles by combining the effects of temperature and pressure, i.e., pressure temperature swing adsorption (PTSA), may be capable of solving this problem and allowing for milder regeneration conditions which are easier to achieve for large scale CO<sub>2</sub> capture plants, i.e., lower regeneration temperature compared with TSA and higher desorption pressure than PSA (Wang, L. et al., 2012; Wurzbacher et al., 2011). Such lower temperature is easier to be integrated with waste heat in power plants than conventional TSA. Hence, PTSA possibly requires lower energy consumption and achieves higher process efficiency/productivity, although with higher cycle complexity (Su and Lu, 2012).

A simple PTSA process consists of the following steps: adsorption, heating and depressurization or evacuation, cooling and/or pressurization (Wang, Jiajun et al., 2021). More complex cycles are also reported, such as a 7-step cycle, including adsorption, pressure equalization, depressurization, vacuum heating, vacuum cooling, pressure equalization, and pressurization (Zhan et al., 2021). Cooling water may also be introduced to maintain the column temperature during the adsorption step to avoid the capacity drop due to the released heat of adsorption. Tsutsumi et al. reported a 40% energy penalty reduction via energy recovery measures such as pressure recovery through an expander and adsorption heat recovery through a chemical heat transformer (Song et al., 2016). Plaza and Rubiera simulated a PTSA carbon capture process in an 820 MWe power plant using a desorption temperature of 80 °C and pressure of 5 kPa. Results showed the energy penalty is 2.41 MJ (heating)/kg CO<sub>2</sub> and 1.15 MJ (evacuation)/kg CO<sub>2</sub>, which is mainly due to the extremely low desorption pressure (Plaza and Rubiera, 2019).

### 3.2.1.4 Electric Swing Adsorption (ESA)

ESA has been reported as commercially viable for volatile organic compounds (VOC) removal (Subrenat and Le Cloirec, 2006). Adsorptive carbon capture using ESA aims to solve the

lengthy heating time issue related to conventional TSA and improve the overall productivity of adsorbents(Zhao, Q. et al., 2019), in which rapid and homogeneous heating can be achieved via electrification by Joule effect (or Ohmic heating). The temperatures of adsorbents can be raised to 70 °C in 22 s at a potential of 24 V(Mendes et al., 2021) or 10 V(Pereira et al., 2022), 101 °C in 90 s at a potential of 60.5 V(Zhao, Q. et al., 2019), and 150 °C in less than 30 s at a potential of 8 V(Verougstraete et al., 2022). Even though the electric power for ESA is of a higher exergetic energy format than thermal energy required by TSA, such low voltage requirements in ESA cycles offer an opportunity to integrate with renewable electricity.

A simple operational ESA cycle consists of the following steps: adsorption, electrification, rinse/purge or evacuation, and cooling. More complex cycles have also been demonstrated for high CO<sub>2</sub> purity and recovery, with extra internal rinse, purge and depressurization steps(Grande et al., 2009); 89.7% purity and 72.0% recovery were achieved from 3.5% CO<sub>2</sub> flue gases.

ESA cycles require that adsorbents must be conductive, such as activated carbons, hybrid adsorbents combining zeolite and activated carbon, and uniform adsorbents to allow heat to be transferred homogeneously(Zhao, Q. et al., 2018). Uneven heating may lead to hot spots and damage the adsorbents due to partial overheating. Three-dimensional (3D) printing is an ideal methodology to replace conventional pelleting, which shows lower pressure drop, no fluidization and better heat transfer. This also provides a pathway to create hybrid adsorbents, which may combine the best properties of multiple adsorbents, CO<sub>2</sub> uptake capacity, CO<sub>2</sub>/N<sub>2</sub> selectivity and mass transfer coefficient. It should be noted that the cooling step still requires quite a significant time, which may be a major hurdle for its application. According to Grande et al., electric heating only accounts for 1.5% of the cycle time (2225 s)(Lillia et al., 2018), with enormous time put into the cooling of adsorbents.

### **3.2.1.5 Rapid pressure or temperature swing adsorption (RPSA/RTSA)**

A 600 MWe coal power plant emits 500 m<sup>3</sup>/s of flue gas with 13% CO<sub>2</sub>(Merkel, Tim C et al., 2010). Hence, it is critical to develop economical CO<sub>2</sub> separation technologies to handle flue gases with massive flow rates. Rapid swing adsorption shows its superiority as CO<sub>2</sub> capture from flue gases is often at a very large scale, and the structuring of adsorbents becomes crucial to allow a high flow rate and avoid sorbent pulverization. The cycle sequence in rapid swing adsorption is similar to conventional ones, with modifications in different aspects. In a reported rapid pressure swing adsorption process, the total cycle time is 18 s, which employs the same cycle as conventional PSA, i.e., adsorption (8 s), desorption (8 s), purge (1 s) and repressurization (1 s)(Luberti et al., 2017). The superficial velocity is as high as 1.6 m/s, which is much higher than conventional PSA cycles (0.1–0.5 m/s), resulting in a significant pressure drop of 16 kPa at the column length to diameter ratio of 1:1.

Rapid temperature swing adsorption (RTSA) can be achieved via direct heating using hot steam, which involves quick heating through the latent heat and adsorption competition between water vapor and



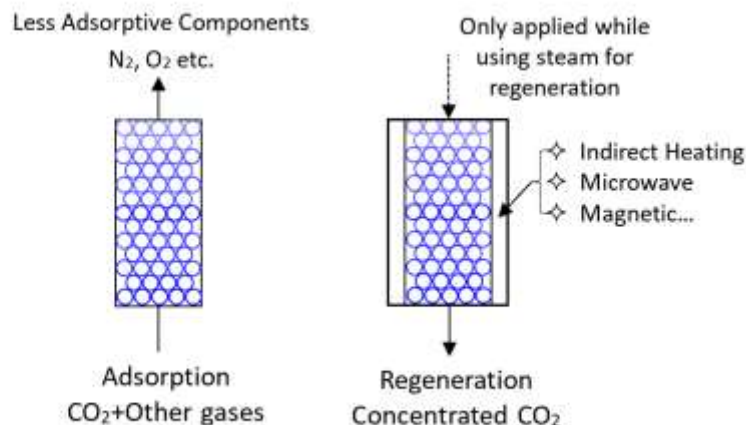
CO<sub>2</sub>. A hot air stream is essential to remove the condensed steam right after CO<sub>2</sub> regeneration (prior cooling) to avoid a significant capacity drop. The cycle time can also be reduced to 20–330 s, which is much lower than conventional TSA cycles ( $\geq 15$  min) (Verougstraete et al., 2020). RTSA may also be achieved using hybrid materials, which employ a hollow fiber embedded with porous adsorbents, as demonstrated by Lively et al. (Lively et al., 2009). Such hollow fiber adsorbent performs as both a heat exchanger and gas contactor (or “adsorbing heat exchangers”(Lively et al., 2010)), for which 90% adsorption occurs within the first 2 s (Lively et al., 2012), and thermal equilibrium can also be achieved within seconds. A high linear velocity of 1.6 m/s was also tested (Lively et al., 2012). This setup also enables internal cooling during adsorption so the adsorption enthalpy can be quickly removed to maintain a high CO<sub>2</sub> uptake capacity. The hollow fiber RTSA cycles have also been extended to air separation by integrating LiX zeolites on thermally stable polymers (Sujan et al., 2018).

Other novel design concepts are also seen in literature such as the rotary adsorption system for MOF based carbon capture systems (Lin, J.-B. et al., 2021), fin coil heat exchangers filled with an adsorbent that allows internal heating and cooling (Masuda et al., 2021, 2022) and structured honeycomb carbon monolith adsorbents which can tolerate high linear velocities of flue gases as high as 3.4 m/s (Verougstraete et al., 2020).

### 3.2.1.6 Other swing concepts

Hybrid cycles combining two or more of the above mentioned swing technologies have been widely investigated, such as those combining ESA and VSA, namely VESA (Zhao, Q. et al., 2019); ESA and TSA, namely TESA (Lillia et al., 2018); ESA and VSA, namely VESA (Zhao, Q. et al., 2019). Different adsorption column configurations are also considered including fixed beds, fluidized beds, moving beds and simulated moving beds to improve the separation performances (Yi et al., 2007). Fixed beds are still the most commonly used configuration due to their simplicity and low requirement in the mechanical strength of adsorbents.

Novel swing concepts are continuously proposed to improve the energy efficiency and separation performances of adsorptive carbon capture technologies. Microwave, commonly interpreted by three mechanisms, i.e. ionic conduction, dipolar rotation of polar molecules and dielectric polarization (Lee, E.J. et al., 2019), has been applied to the regeneration of adsorbents using a hybrid adsorbent of graphene oxide and MIL-91 (Muschi et al., 2021), in which desorption occurred faster and under lower temperature, i.e. 50 °C for 150 s using microwave versus 80 °C for 215 s using conventional electrical heating. High microwave absorption allows temperature increases through energy dissipation. Sound assisted adsorption/desorption is reported to enhance kinetics and cut overall energy consumption (Ammendola et al., 2015; Raganati et al., 2020). Magnetic induction swing adsorption (MISA) has also attracted interest due to its high energy efficiency (Bellusci et al., 2021; Li, H. et al., 2016a). However, these concepts are rather immature and needs more exploration.



**Figure 3.17** A simplified schematic adsorptive cycle. Adsorption occurs at high pressure and/or low temperatures. Regeneration occurs at low pressure and/or high temperatures, where the heating can be achieved by heat conduction, Joule effect, magnetic effect, microwave etc.

In summary, adsorptive swing technologies can be as simple as shown in Figure 3.17, which consists of an adsorption and a desorption step. The adsorption step occurs at high pressure and/or low temperatures. Regeneration occurs at low pressure and/or high temperatures. Any form of radiation may be used for adsorbents regeneration as long as the adsorbents can absorb the form of radiation, such as evacuation (PVSA), heating (TSA), Joule effect (ESA), magnetic effect (MSA), microwave (MCSA) etc. However, efficient processes, which can heavily impact the performance of cyclic adsorption processes, are much more complicated than the two-step cycles. There is yet no best way to design and optimize such processes.

### 3.2.2 MOF-based materials for CO<sub>2</sub> capture

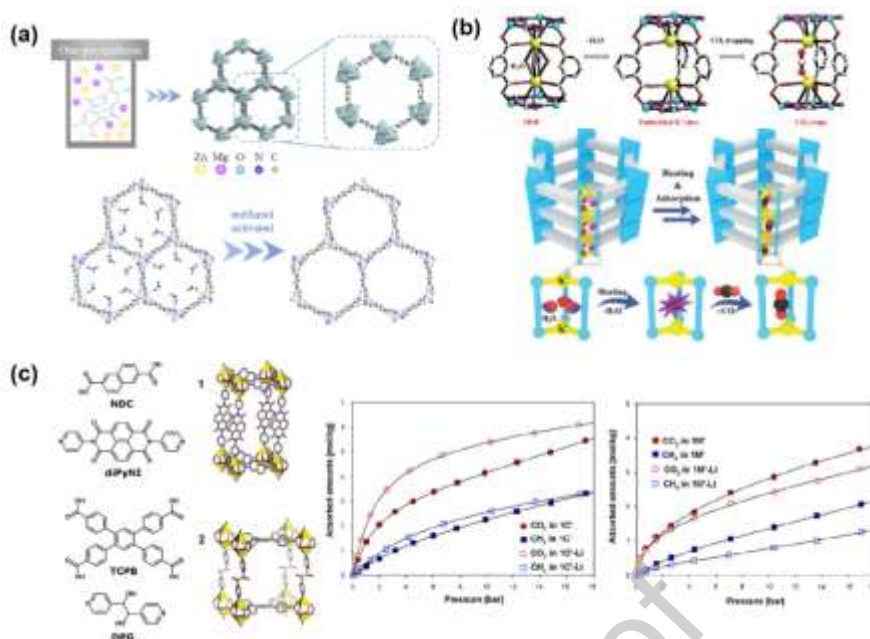
Metal organic frameworks (MOFs) are deemed to be the most promising materials for CO<sub>2</sub> adsorption due to their high porosity, large specific surface area, designability, tunability, rich spatial topology, and unsaturated metal sites. Zn(BDC) became the first reported MOFs material for CO<sub>2</sub> adsorption (Li et al., 1998), and then Yaghi synthesized a series of MOFs to systematically investigate the effects of structural and porous attributes on CO<sub>2</sub> adsorption performance (Millward and Yaghi, 2005). The results showed that the higher pressure and larger specific surface area were favorable for CO<sub>2</sub> adsorption, which opened the door to explore MOFs in the field of CO<sub>2</sub> adsorption capture and separation. Several MOFs have been prepared and commercialized on a large scale, such as MOF-177, HKUST-1, ZIF-8, UIO-66, and MIL-127 (Gargiulo et al., 2020).

### 3.2.2.1 Influence of pressure on CO<sub>2</sub> capture

The adsorption of gases can be divided into high and low pressure. For high pressure condition, CO<sub>2</sub> adsorption is generally related to the specific surface area and pore volume of MOFs. Hu et al. (Hu et al., 2013) studied the behavior of ZIF-8 for high pressure CO<sub>2</sub> adsorption using situ FTIR spectroscopy, the results showed that the chemical and mechanical robustness of the framework formed by the relatively stiffer metal centered tetrahedrons as joints but with flexible linkers makes ZIF-8 a promising agent for the storage of CO<sub>2</sub> at high pressure conditions. Arstad et al. (Arstad et al., 2008) synthesized USO-2 using Ni(NO<sub>3</sub>)<sub>2</sub> as a metal ion source and 1,4-phenylene terephthalic acid (1,4-H<sub>2</sub>BDC) as a ligand, which increased CO<sub>2</sub> adsorption at 25 atm compared to atmospheric pressure adsorption by 46%. Qasem et al. (Qasem et al., 2018) prepared MOF-177, which has excellent storage capacity at high pressure ( $\geq 10$  bar) and gradually increases its adsorption capacity with increasing external pressure, from 0.07 kg kg<sup>-1</sup> at 5 bar to 1.58 kg kg<sup>-1</sup> at 30 bar, with a 22-fold increase in its adsorption capacity. Llewellyn et al. (Llewellyn et al., 2008) prepared mesoporous MIL-101 and found a high adsorption capacity of 40 mmol g<sup>-1</sup> by activating it with ethanol and KF at 5 MPa and 303 K. To further increase the surface area of the adsorbent material, Farha et al. (Farha et al., 2010) designed a new MOF material (NU-100) with Cu<sup>2+</sup> as the metal center and hexatopic carboxylate as the organic ligand through calculation and simulation, and successfully prepared it through experiments. The MOF has a super high surface area of 6143 m<sup>2</sup> g<sup>-1</sup> and the total pore volume is 2.82 cm<sup>3</sup> g<sup>-1</sup>, and its CO<sub>2</sub> adsorption capacity reaches 2315 mg g<sup>-1</sup> at 40 bar and 298 K. Furukawa et al. (Furukawa et al., 2010) synthesized MOFs using Zn<sup>2+</sup> as the metal center and various carboxylate organic ligands, among which MOF-210 has a larger surface area (6240 m<sup>2</sup> g<sup>-1</sup>) and a large pore volume (3.6 cm<sup>3</sup> g<sup>-1</sup>), so that its adsorption capacity also reaches an impressive values of 2870 mg g<sup>-1</sup> at 50 bar and 298 K. In addition to the selection of ligands with longer molecular chains, the surface area of MOFs can also be increased by introducing defects. Wu et al. (Wu et al., 2013) adjusted the degree of defects by adding different concentrations of acetic acid to the UIO-66 system and setting different reaction times, and the porosity of UIO-66 increased dramatically with increasing dosage and longer reaction times, which results in an increase in pore volume from 0.44 cm<sup>3</sup> g<sup>-1</sup> to 1 cm<sup>3</sup> g<sup>-1</sup> and an increase in surface area from 1000 m<sup>2</sup> g<sup>-1</sup> to 1600 m<sup>2</sup> g<sup>-1</sup>. Moreover, the hydroxyl group on the surface of UIO-66 was found to contribute to the adsorption of CO<sub>2</sub> due to the presence of the Columbic interactions between the negatively charged O (of CO<sub>2</sub>) and the positively charged H (of the -OH group), making the CO<sub>2</sub> uptake in the hydroxylated MOF (2.50 mmol g<sup>-1</sup>) at 300 K and 1 bar is more than 50% higher than that in the dehydroxylated MOF (1.60 mmol g<sup>-1</sup>).

Compared with high-pressure adsorption, low-pressure adsorption is more common in industrial production and is mainly used to capture CO<sub>2</sub> from combustion exhaust gases. Low-pressure adsorption is mainly related to the heat of CO<sub>2</sub> adsorption, which can be improved by introducing unsaturated metal sites, ligand group modification, and introducing defects.

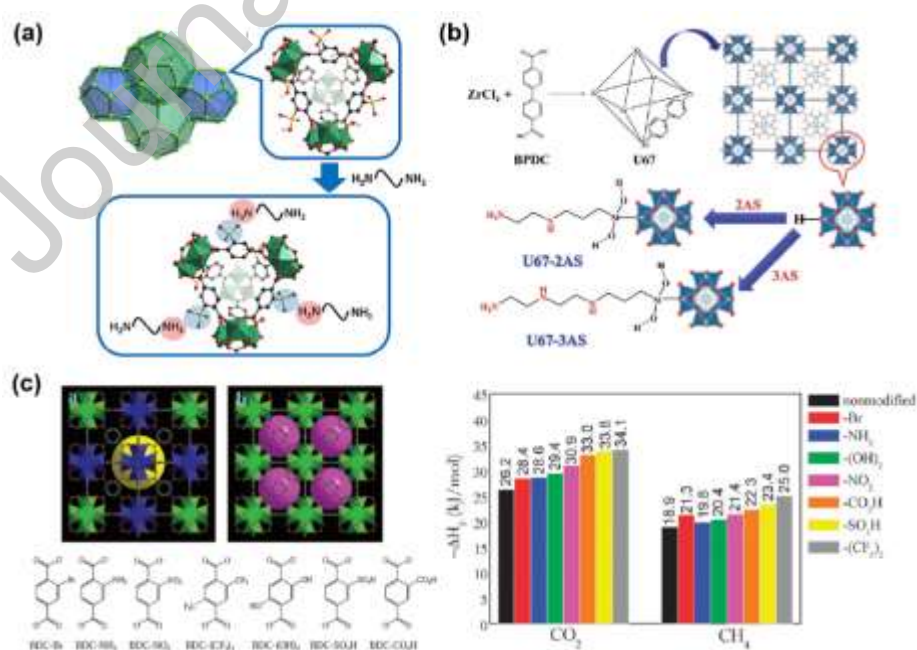
(i) Introduction of coordinated unsaturated metal sites and ion doping. During the preparation of MOFs, solvent molecules will be coordinated with metal sites, and the unsaturated metal sites are obtained by removing solvent molecules through the solvent exchange, vacuum heating, and freeze-drying to enhance the adsorption capacity of MOFs. MOF-74 is a common low-pressure CO<sub>2</sub> adsorption material, which is prepared from divalent metal ions (Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, etc.) and 2,5-dihydroxyterephthalic acid, where Mg-MOF-74 has excellent low-pressure CO<sub>2</sub> adsorption (8.6 mmol g<sup>-1</sup>) at 100 kPa and 298 K. This is due to the high density of open metal sites in MOF-74 and the presence of Mg-O bonds that improve the CO<sub>2</sub> adsorption capacity relative to the chemical bonds formed by other metal ions (Bahamon and Vega, 2016; Caskey et al., 2008). In addition to this, HKUST-1 is also a common material for low-pressure CO<sub>2</sub> adsorption, due to the high charge density of Cu<sup>2+</sup>, which allows a strong interaction with CO<sub>2</sub> (Hamon et al., 2010; Yazaydin et al., 2009). After treatment with ethanol and NH<sub>4</sub>Cl at 338 K, it also has a high adsorption capacity (11.6 mmol g<sup>-1</sup>) at 1 atm and 273 K (Yan et al., 2014). To further improve the adsorption performance, bimetallics can be introduced to the MOF framework as metal sites and optimal results have been obtained by adjusting the ratios, Gao et al. (Gao, Z. et al., 2021) prepared Zn<sub>0.75</sub>Mg<sub>0.25</sub>-MOF-74 by one-step hydrothermal synthesis (Figure 3.18a), due to the large surface area (667.6 m<sup>2</sup> g<sup>-1</sup>) and affinity for CO<sub>2</sub>, its CO<sub>2</sub> adsorption capacity of 128.3 cm<sup>3</sup> g<sup>-1</sup> at 1 bar and 273 K. Also, due to the multiple active sites of the unsaturated metal centers as active Lewis acid sites and O atoms from Zn-O and Mg-O as Lewis basic sites, conferring excellent catalytic properties. Kadi et al. (Kadi et al., 2020) prepared Cu<sub>1.5</sub>Mg<sub>1.5</sub>(BTC)<sub>2</sub> with a molar ratio of Cu to Mg of 1:1, and this MOF maintained the original crystalline shape of HKUST-1. The substitution of Cu of atomic radius 128 pm by larger ions of Mg of atomic radius 173 pm may lead to electrostatic unbalance in the surface of the MOF, which enhance the adsorption efficiency due to the created synergetic phenomenon, resulting in a significant increase in adsorption to 23.85 mmol g<sup>-1</sup>, which is much higher than Cu-BTC (5.95 mmol g<sup>-1</sup>) and Mg-BTC (4.57 mmol g<sup>-1</sup>). In addition to this, unsaturated alkali metal ions can be introduced into the framework of MOF to enhance the adsorption performance, for example, K<sup>+</sup> can be immobilized in NKU-521 through a tetrazole based motif and are effectively embedded in a trinuclear Co<sup>2+</sup>-tetrazole coordination motif (Figure 3.18b), resulting in a 24% increase in isosteric heat for CO<sub>2</sub>, with a CO<sub>2</sub> adsorption capacity of 139 cm<sup>3</sup> g<sup>-1</sup> at 273 K and 1 atm (Li, N. et al., 2019). Bae et al. (Bae et al., 2011) introduced Li<sup>+</sup> into Zn-MOF using different methods to enhance the adsorption performance, and after experimental analysis, it is known that the chain structure can be replaced and the pore capacity can be reduced by the chemical reduction method leading to improved adsorption, while the ion exchange method is due to the stronger interaction of the desolvated Li<sup>+</sup> with CO<sub>2</sub> (Figure 3.18c).



**Figure 3.18.** (a) facile one-pot method to synthesize bimetallic Zn/Mg-MOF-74, and 2D structure of original and methanol-activated Zn/Mg-MOF-74(Gao, Z. et al., 2021); (b) the structures of the framework of NKU-521 and Co-K MBB, and schematic illustration of the MOF featuring novel  $K^+$  binding sites for  $CO_2$ (Li, N. et al., 2019); (c) chemical structures of ligands, the crystal structure of MOFs and effect of chemical reduction on the  $CO_2$  and  $CH_4$  isotherms in 1C and 1M at 298 K(Bae et al., 2011).

(ii) Organic ligand selection and group modification. Since the acid-base and dipole-quadrupole interactions between N atoms and  $CO_2$  molecules induce dispersion and electrostatic forces between  $CO_2$  and MOFs, thus enhancing the adsorption capacity of MOFs, the current chemical modifications are mainly based on the selection of organic ligands containing N elements or the introduction of Lewis bases. The direct selection of ligands containing N element can eliminate the complex preparation process, such as nitrogen heterocycles, aromatic amines, adenine, triazole and so on. Hong et al.(Hong et al., 2017) used 4-(2-hydroxy-3-methoxy-benzylidene-hydrazinocarbonyl)-N-pyridin-4-yl-(benzamide) compounds as organic ligands for the synthesis of Cd-MOF, which has a heat of adsorption of  $26 \text{ kJ mol}^{-1}$  and an adsorption capacity of  $1.5 \text{ mmol g}^{-1}$  at 273 K and 1 bar. Maity et al.(Maity et al., 2019) chose  $Cu^{2+}$  and  $Zn^{2+}$  with adenine and terephthalic acid as organic ligands for the preparation of IISEPR-MOF26 and IISEPR-MOF27, which exhibited excellent cyclic stability with  $CO_2$  adsorption amounts of  $4.3 \text{ mmol g}^{-1}$  and  $3.8 \text{ mmol g}^{-1}$  at 273 K and 1 atm, respectively, due to the lower heat of adsorption and thus ease of desorption. In addition, the synthesized MOFs also have excellent water stability with no decay of adsorption properties in water as well as exposure to water vapor for more than 24 h. The above synthesized MOFs can be seen to only rely on nitrogen-containing ligands for  $CO_2$  adsorption, which has a low adsorption capacity. Therefore, post-modification of the MOFs by

introducing Lewis bases (amino acids, alkyl amines, etc.) is needed to further enhance the adsorption performance. Khan et al.(Khan et al., 2018) synthesized ZIF-8 nanoparticles with  $n_{Zn^{2+}}:n_{Hmim}=1:8$ . At the same time, a small amount of triethylamine was added to the synthesis process. Due to the introduction of N-H group, it helped to improve the adsorption capacity of  $CO_2$ , reaching  $22.43 \text{ mmol g}^{-1}$ . Li et al.(Li, H. et al., 2016b; Li, Hao et al., 2019) used Brønsted Acid-Base Reaction and solvent effect to access alkylamines to Cr-MIL-101 (Figure 3.19a), and the use of low-polar cyclohexane as dispersant could make higher chemical potential of alkylamine and enhanced driving force from cyclohexane to MOF, allowing for introduce more amino groups into the MOF and enhancing the adsorption capacity of  $CO_2$ , which was  $4.21 \text{ mmol g}^{-1}$  at 150 mbar and 298 K. Yoo et al.(Yoo and Jung, 2022) used aminosilanes for UIO-67 modification and by choosing different types and amounts of aminosilanes (Figure 3.19b), the heat of adsorption after treatment was found to be between  $35\text{-}50 \text{ kJ mol}^{-1}$ , due to the formation of a carbamate via the interaction between primary/secondary amino groups and  $CO_2$ , resulting in good adsorption of amino acids on  $CO_2$  at 298 K and 15 kPa, the highest adsorption capacity can reach  $0.58 \text{ mmol g}^{-1}$ . In addition, the experimental analysis revealed no major difference in the adsorption of  $CO_2$  between primary and secondary amino groups. Yang et al.(Yang et al., 2011) investigated the effect of different group modifications on the adsorption properties by means of simulated calculations (Figure 3.19c), and the heat of adsorption increased with increasing group polarity:  $-SO_3H > -CO_2H > -NH_2 > -OH > -NO_2 > -Br > -CF_3$ . Although the polarity of the  $-CF_3$  group is the lowest, the strongest  $CO_2$  adsorption mainly results from the highest confinement caused by the significant decrease of the accessible pore volume.

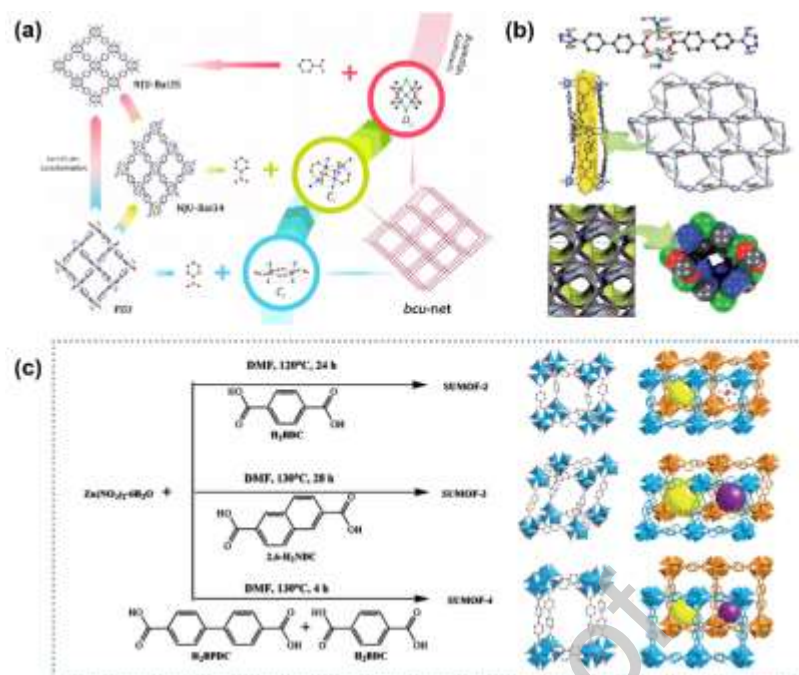


**Figure 3.19** (a) Cr-MIL-101-SO<sub>3</sub>H topology and illustration of electrostatic interaction between sulfonate groups and ammonium groups(Li, H. et al., 2016b); (b) a scheme to introduce amino groups

on the U67 MOF(Yoo and Jung, 2022); (c) illustration of the UIO-66(Zr) crystalline structure, including: octahedral cages, tetrahedral cages and functionalized ligands, calculated low-coverage adsorption enthalpies of pure CO<sub>2</sub> and CH<sub>4</sub> gases in the non-modified UIO-66(Zr) and its functionalized derivatives at 303 K(Yang et al., 2011).

(iii) Pore size tuning. The molecular size of CO<sub>2</sub> is between 0.3-0.4 nm, so tuning the pore size of MOFs and using the size effect for adsorption is also an effective way. Jiang et al.(Jiang, J. et al., 2018) synthesized highly symmetric NJU-Bai35 with Cu<sup>2+</sup> as metal sites and isonicotinic acid and [Cu(IN)<sub>2</sub>]<sub>∞</sub> as dual ligands (Figure 3.20a). Its internal space has homogeneous dimensions in the a, b, and c axis with dimensions of 3.6\*3.6, 3.4\*3.4, and 3.6\*3.6 Å<sup>2</sup>, respectively, which are close to those of CO<sub>2</sub>, resulting in CO<sub>2</sub> adsorption up to 7.2 wt.% at 298 K and 0.15 bar. Bao et al.(Bao et al., 2015) used biphenylcarboxylic acid derivatives as ligands to synthesize [Zn<sub>2</sub>L<sub>2</sub>]<sub>2</sub>DMF (Figure 3.20b), which has a high heat of adsorption (33 kJ mol<sup>-1</sup>) and a high adsorption capacity of 79.9 cm<sup>3</sup> cm<sup>-3</sup> at 298 K and 100 kPa due to the presence of N elements in the structure and a one-dimensional nanochannel with a diameter of 3.6 Å. By fine design of the pore size structure of MOFs, a size matching CO<sub>2</sub> can be obtained. However, the more complicated preparation process and the screening of organic ligands are not suitable for large-scale applications. Compared with directly designing MOFs with the size matching CO<sub>2</sub>, the intercalated structure is a more convenient method. Yao et al.(Yao et al., 2012) synthesized three SUMOFs with intercalated structures using Zn<sub>4</sub>O clusters and rigid dicarboxylate anions (Figure 3.20c), all of which have two different types of small pores and high pore volumes. Among them, MOF synthesized with terephthalic acid as a ligand has a structure closer to the molecular size of CO<sub>2</sub> (5.9 Å and 7.7 Å). In addition, with the aid of interpenetration in these MOFs, the electric field gradients in the small pores are increased, and therefore enhancing the interaction between CO<sub>2</sub> and the host framework. At 273 K and 100 kPa, The three MOFs synthesized have high low-pressure adsorption properties of 4.26, 3.44 and 3.6 mmol g<sup>-1</sup>, respectively. Pal et al.(Pal et al., 2017) added a flexible N-containing donor to the Zn<sup>2+</sup> and sulfonyldibenzoic acid system and synthesized {[Co<sub>2</sub>(SDB)<sub>2</sub>(L)]·(H<sub>2</sub>O)<sub>4</sub>·(DMF)}<sub>n</sub> with a double interpenetrating structure by hydrothermal method. The MOF material has a rhombic channel with a size of 3.4\*5.0 Å inside, and its adsorption heat is 23 kJ mol<sup>-1</sup>, the CO<sub>2</sub> adsorption capacity is 50.6 cm<sup>3</sup> g<sup>-1</sup> at 273 K and 1 bar.





**Figure 3.20** (a) isoreticular transformation of bcu-type MOF by symmetry-upgrading inorganic clusters(Jiang, J. et al., 2018); (b) the structure of NENU-520 obtained by Pore size design(Bao et al., 2015); (c) synthesis of the SUMOFs, non-interpenetrated models and crystal structures of the doubly interpenetrated frameworks(Yao et al., 2012).

Due to the structural limitations, MOFs suitable for high-pressure adsorption have low CO<sub>2</sub> adsorption performance under low pressure environment due to the larger pore size, which reduces the potential energy superposition between the pore walls and the interaction between CO<sub>2</sub> molecules and the material(Mason et al., 2011). MOFs suitable for low-pressure adsorption have lower surface area, which limits the performance of CO<sub>2</sub> adsorption. In contrast, MIL-53 has a unique double-cage structure that allows it to have a "breathing effect", which can achieve low-pressure adsorption in the internal small frame and high-pressure adsorption in the external large frame, giving the desired adsorption performance of CO<sub>2</sub> at different air pressures. Finsy et al.(Finsy et al., 2009) synthesized MIL-53 using Al<sup>3+</sup> as the metal site and found that at pressures below 5 bar, CO<sub>2</sub> adsorption led to the contraction of the framework and the formation of a narrow pore, while at high pressures, further adsorption of CO<sub>2</sub> reopened the framework, leading to a sudden increase in adsorption above 6 bar. Mahdipoor et al.(Mahdipoor et al., 2021) synthesized three MOFs (Fe-MIL-53, Fe-MIL-101, Fe-MIL-101-NH<sub>2</sub>) and investigated the adsorption capacity of CO<sub>2</sub> at different pressures (0-40 bar), compared to the other two, Fe-MIL-101-NH<sub>2</sub> has a larger specific surface area (915 m<sup>2</sup> g<sup>-1</sup>) and pore volume (0.4 cm<sup>3</sup> g<sup>-1</sup>) with heat of adsorption of 46.7 kJ mol<sup>-1</sup>. Moreover, the adsorption capacity increased sharply between 15-20 bar, and finally reached 13 mmol g<sup>-1</sup> at 298 K and 40 bar.



In addition, MOF materials are often combined with other materials to enhance the adsorption effect. Policicchio et al. (Policicchio et al., 2014) investigated the adsorption performance of urea-modified graphene oxide with Cu-BTC for CO<sub>2</sub> at different temperatures and pressures, and the surface area and total pore volume of the composites were 1367 m<sup>2</sup> g<sup>-1</sup> and 0.663 cm<sup>3</sup> g<sup>-1</sup>, respectively. Compared to MOF, the surface area and total pore volume of the composites were 1367 m<sup>2</sup> g<sup>-1</sup> and 0.663 cm<sup>3</sup> g<sup>-1</sup>, which were improved by 53.25% and 54.91%, respectively, and the heat of adsorption reached 30 kJ mol<sup>-1</sup> with 7.27 mmol g<sup>-1</sup> at low pressure (0.1 MPa) and 15 mmol g<sup>-1</sup> at high pressure (1.5 MPa) at 277 K. In addition, it also has a fully reversible adsorption process to recover its CO<sub>2</sub> adsorption capacity without heat treatment. Chakraborty et al. (Chakraborty and Maji, 2014) prepared composites for CO<sub>2</sub> adsorption at room temperature by immobilizing nanocrystals of Mg-MOF-74 in the mesopores of SBA-15 rods by in situ growth, and the CO<sub>2</sub> adsorption capacity was 88 ml g<sup>-1</sup> at 293 K and P/P<sub>0</sub>, the heat of adsorption was 30.3 kJ mol<sup>-1</sup>. Ghahramaninezhad et al. (Ghahramaninezhad et al., 2018) synthesized Li<sup>+</sup>-doped polyoxometalate ({Mo132})-coated ZIF-8 with a surface area of 237 m<sup>2</sup> g<sup>-1</sup> and a CO<sub>2</sub> adsorption of 16 mmol g<sup>-1</sup> at 298 K and 10 bar, and the composite also has excellent water stability. After being exposed to humid air for 7 months, the adsorption capacity of CO<sub>2</sub> has not changed significantly. Qasem et al. (Qasem et al., 2017) modified multi-walled carbon nanotubes with HNO<sub>3</sub> and grew Cr-MIL-101 in situ on their surface. Compared with Cr-MIL-101, the surface area and pore volume of the prepared composites were 4004 m<sup>2</sup> g<sup>-1</sup> and 2.07 cc g<sup>-1</sup>, which were increased by 6.92% and 4.62%, respectively. At 298 K and 20 kPa, the maximum adsorption capacity was 1.2 mmol g<sup>-1</sup>.

### 3.2.2.2 Surface chemistry of MOFs based CO<sub>2</sub> capture

The intrinsic capacity for CO<sub>2</sub> uptake by MOFs is influenced through either structural or functional routes.

(i) Structural route: it involves reducing the size of micropores in the 0.5-1.2 nm range by penetration or intercalation to encourage intermolecular interactions and achieve molecular sieving (Han et al., 2013). IRMOF-9, 13, and 15 have an interpenetrated MOF-5 scaffolding, however, it has less pore size than its parent framework (Eddaoudi et al., 2002). Transition metal interpenetrated Co<sub>2</sub>(ndc)<sub>2</sub>(bipym) having pore cross-section of 4.4 × 3.4 Å is another example of such strategy (Choi et al., 2004; Lee et al., 2003).

(ii) Functional route: it involves the creation of frameworks with coordinatively unsaturated metal sites acting like charge-binding sites for adsorption. These could be obtained by dissolving the material in a vacuum or at high temperatures (Bae et al., 2008; Moon et al., 2006). One of the examples of such material is [M<sub>2</sub>(DOBDC)(EG)<sub>2</sub>] (M = Mg, Co, Ni) frameworks, with open Mg(II), Co(II), and Ni(II) sites offering zero-loading enthalpies as 44.0, 35.0 and 62 kJ/mol, respectively (Kim, H. et al., 2019).

Apart from the above two approaches, MOFs can also be modified post-synthesis through heterogeneous chemical transformations of metal groups and ligands without disturbing the overall geometry of the structure (Demessence et al., 2009; Hoskins and Robson, 1990; Jones and Bauer, 2009; Wang and Cohen, 2007). Some MOFs have been post-synthetic functionalized with alkylamines like  $\text{HCu}[(\text{Cu}_4\text{Cl})_3(\text{BTri})_8]$  ( $\text{H}_3\text{BTri} = 1,3,5\text{-tris}(1H\text{-}1,2,3\text{-triazol-}4\text{-yl)benzene}$ ) and diamines like *N,N'*-dimethylenediamine (McDonald, 2011). Few MOFs undergoing this approach are ethylenediamine modified  $\text{Mg}_2(\text{dobdc})$  having unsaturated sites of Mg(II) (Choi, Sunho et al., 2012),  $\text{Mg}_2(\text{dobpdc})$ , and  $\text{Zn}_2(\text{dobpdc})$  (McDonald et al., 2012). The functionalization with ethylenediamine not only enhances the  $\text{CO}_2$  uptake capacity, but also improves the material regenerability. ZIF-68, -69, and -70 show excellent adsorption and  $\text{CO}_2/\text{CO}$  separation capacities after modification with alkaline/polar charges and N-functionalization with 4&5-azabenzimidazolate and purinate ligands (Bastin et al., 2008; Chen et al., 2008; Liu and Smit, 2010; McCarthy et al., 2010). Apart from this, ZIF-related compounds like  $\text{Zn}(\text{bdc})(4,4'\text{-bipy})_{0.5}$  showed improved  $\text{CO}_2$  separation from  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{CH}_4/\text{N}_2$  gas mixtures (Bastin et al., 2008).

Unsaturated metal sites can also be created in MOFs via post-synthesis treatment. One of the example is impregnated  $[\text{Zn}_3(\text{tcpt})_2(\text{HCOO})][\text{NH}_2(\text{CH}_3)_2]$  with  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  cations. This in return results in increased zero-loading  $\text{CO}_2$  uptake isosteric heat from 29.3 to 34.5-37.4  $\text{kJ mol}^{-1}$  in  $[\text{Zn}_3(\text{tcpt})_2(\text{HCOO})][\text{NH}_2(\text{CH}_3)_2]$  and cation-doped compounds, respectively (Park and Suh, 2013).

### 3.2.2.3 Effect of water on $\text{CO}_2$ adsorption

Contrary to zeolites, the adsorption capacity of MOFs can be highly affected by water due to weak metal-ligand bonds, which sometimes may result in structure collapse. Steam stability routs have been reported for MOFs over wide range of temperatures (Park and Suh, 2013). The most common example to hydrothermally unstable MOF is MOF-5. IRMOF series with Zn carboxylate clusters are also less hydrothermally stable due to quick hydrolysis of Zn-carboxylate bonds (Kaye et al., 2007; Li and Yang, 2007; Schröck et al., 2008). MIL family compounds show the highest hydrothermal stability, especially robust MIL-100 and M101 having clusters of Cr(III) (Férey et al., 2005; Férey et al., 2004; Küsgens et al., 2009), Zr(IV)-MOFs (i.e.,  $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$  (UiO-66) (Cavka et al., 2008), and  $\text{Ni}_3(\text{btp})_2$ -based on azolate linkers (Colombo et al., 2011).

Apart from hydrothermal stability, water also plays an important role in identifying  $\text{CO}_2$  over other gases and improve adsorption capacity. Half pore blockage by  $\text{H}_2\text{O}$  upon  $\text{CO}_2$  adsorption is also reported in rigid MOFs.  $\text{Mg}_2(\text{dobdc})$  shows a sturdy deactivation when  $\text{H}_2\text{O}$  is adsorbed via reduction of  $\text{CO}_2$  binding energy (Yu and Balbuena, 2013). However,  $\text{Co}_2\text{dobdc}$  and  $\text{Ni}_2(\text{dobdc})$  performed better after  $\text{H}_2\text{O}$  exposure and kept a stable  $\text{CO}_2$  adsorption (Kizzie et al., 2011; Liu et al., 2011). KHUST-1

impregnated with unsaturated Cu(II) showed reduction in CO<sub>2</sub> capacity after two H<sub>2</sub>O molecule coordinated at Cu sites (Liu, J. et al., 2010). However, when one H<sub>2</sub>O molecules coordinated, the framework showed a major improvement in CO<sub>2</sub> adsorption. This is due to the presence of selective electrostatic interactions among coordinated H<sub>2</sub>O molecule and CO<sub>2</sub> molecule (Yazaydin et al., 2009). On the other hand, in hydrated MIL-101, the terminal H<sub>2</sub>O molecules act as an extra binding set for CO<sub>2</sub> adsorption.

A very special type of property has been observed in flexible MOFs (such as the MIL-53 family) where H<sub>2</sub>O can promote reversible structural changes. Flexible MOFs can perform adsorption/desorption cycles but become less stable over time (Cheng et al., 2009). In pure MIL-53(Al)-NH<sub>2</sub>, water improves the stability of narrow pores and provides an excellent material for membrane design (Bureekaew et al., 2008). Since the flue gas contains 5-15% of water, the evaluation of MOF-based membranes in humid environment, and ternary breakthroughs tests for the mixture of CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O are needed. MOF adsorbents, particularly those with unoccupied Lewis acid sites, generally have reduced CO<sub>2</sub> adsorption capabilities when exposed to moisture due to the higher affinity of H<sub>2</sub>O compared to CO<sub>2</sub>. For instance, Mason et al. (Mason et al., 2015) proposed 83% decrease in total CO<sub>2</sub> adsorption (from 5.87 mmol g<sup>-1</sup> (Hu et al., 2017b) to 1 mmol g<sup>-1</sup>) for Mg-MOF-74 under wet condition. In the case of MOFs with small apertures, the same trend is followed as in the case of opt-UiO-66(Zr)-(OH)<sub>2</sub>, which shows 90% (from 2.47 mmol g<sup>-1</sup> to 0.7 mmol g<sup>-1</sup>) reduction in CO<sub>2</sub> adsorption capacity (Nguyen et al., 2014). The water-repellent characteristics of MOFs can be improved by either doping chemical functions like alkyl amines, or by boosting the hydrophobicity. For example, doping with hydrazine (N<sub>2</sub>H<sub>4</sub>), N,N'-dimethylethylenediamine (mmen), and 2,2-dimethyl-1,3-diaminopropane (dmpn) can result in 100% retention of CO<sub>2</sub> uptake. Nguyen et al. (Nguyen et al., 2014) developed a hydrophobic chabazite-type ZIF-300, capable of upholding constant CO<sub>2</sub> uptake capacity within 80% relative humidity. Furthermore, Hu et al. (Hu et al., 2017a) synthesized a triphasic hydrothermal approach for introducing ligands into parental UiO-66 structures and demonstrated that UiO-66(Zr)-NH<sub>2</sub>-F<sub>4</sub>-0.53 show a loss of only 30% in CO<sub>2</sub> capture capacity under 70 % relative humidity and CO<sub>2</sub>(15)/N<sub>2</sub>(85) mixture.

In summary, it can be seen that MOFs have made a big breakthrough in CO<sub>2</sub> adsorption due to their advantages such as designable chemical structure, adjustable pore size, and high chemisorption capacity. However, there are still problems that need to be solved. Firstly, we should continue to improve the adsorption capacity of MOFs, especially under atmospheric pressure, and conduct in-depth research on the adsorption mechanism; secondly, we should improve the environmental stability of MOFs, so that they have high thermal stability, water stability, and high selective adsorption; thirdly, the current research mainly focuses on the adsorption of CO<sub>2</sub>, and in the future, we can focus on the desorption, enrichment, and conversion of CO<sub>2</sub>; fourthly, the ligands used in MOFs are mainly derived from chemical materials, which is not conducive to sustainable development, the use of biomass materials

(e.g., lignin derivatives, furandicarboxylic acid, etc.) as ligands and their structure and adsorption properties can be explored.

### 3.2.3 Carbon materials (biochar and activated carbon) for CO<sub>2</sub> capture

#### 3.2.3.1 Biochar for CO<sub>2</sub> adsorption

##### 3.2.3.1.1 Introduction of biochar and its properties

Biochar is an eco-friendly adsorbent that is produced from different kinds of biomass and organic wastes. Although many carbon-based porous materials are available on the market, biomass-derived adsorbents seem attractive for biomass and waste management. Biochars and activated biochars might be used as adsorbents for carbon dioxide capturing thanks to their developed porous structure, noticeable carbon dioxide adsorption capacities (Singh et al., 2019) and also high thermal, chemical and mechanical resistance (Amer et al., 2022). Biochars are also about ten times cheaper than other CO<sub>2</sub> adsorbents due to the wide availability of biomass on the market and relatively simple and cheap synthesis methods. Additionally, to minimize the cost of the adsorbent, waste materials are used as a raw feedstock in a pure state or as a mixture with biomass, usually woody or lignocellulosic (Ibrahim et al.; Igalavithana, A. D. et al., 2020; Liu, 2019; Xu, X.Y. et al., 2016).

The physicochemical properties of biochar are greatly affected by the pyrolysis operating parameters (e.g., temperature, retention time, carrier gas flow rate, and heating rate) (Foong et al., 2020). For instance, slow pyrolysis was reported to produce biochar with a larger pore volume and surface area. This is because a longer reaction time/slow heating rate enhanced the release of volatile organic matter from the feedstock, thus creating a more porous structure on the surface of biochar (Foong et al., 2020).

Pristine biochar obtained through pyrolysis was reported to have a low total pore volume (0.016–0.083 cm<sup>3</sup>/g) and surface area (8–132 m<sup>2</sup>/g). The pore size of the pristine biochar is contributed mainly by micropores (12.1–58.0%) and mesopores (18.9–31.7%), which is within pore size of < 50 nm (Leng et al., 2021). Sajjadi et al. (2019a) also reported that cellulose-rich biomass produces highly microporous biochar while lignin-rich biomass produces highly macroporous biochar. Besides that, high pyrolysis temperature and activation temperature enhanced the formation of larger surface area and pore size on the biochar (Feng et al., 2017; Lam et al., 2018). However, micropores are highly desired in CO<sub>2</sub> capture for sorption and storage of the gas molecules via the micropores' diffusional activation energy (Ghanbari and Kamath, 2019; Lahijani et al., 2018). Thus, pyrolysis or activation at lower temperatures is preferable to avoid excess widening of the pores that lead to a decrease in CO<sub>2</sub> adsorption capacities.

The physicochemical properties of biochar have been shown to affect CO<sub>2</sub> adsorption capacities. These properties include microporosity, total pore volume, specific surface area, surface chemistry, and pore

size. Microporosity and specific surface area are interrelated. A high volume of micropores contributes to a larger surface area, which in turn promotes CO<sub>2</sub> adsorption capacities (Durá et al., 2016; Serafin et al., 2017). Besides that, the CO<sub>2</sub> adsorption capacity in micropores is dependent on the adsorption pressure and temperature. The CO<sub>2</sub> adsorption at temperature and pressure of 0 °C and < 0.1 bar as well as 25 °C and < 1 bar is governed by the pore size of < 0.7 nm (ultra-micropore) and < 1 nm (micropore), respectively (Adeniran and Mokaya, 2016; Presser et al., 2011).

Surface chemistry plays an important role in CO<sub>2</sub> capture. For instance, an increase in the N-containing functional group (e.g., amino group) on the biochar surface facilitates the adsorption of CO<sub>2</sub> *via* interactions such as H-bonding, dipole-dipole interaction, and covalent bonding (Shafeeyan et al., 2010). The presence of O-containing functional groups (e.g., phenols, carboxylic acids, carbonyl) on the biochar surface was shown to affect CO<sub>2</sub> adsorption as most of them are acidic. The O-containing functional group and N-containing functional group are removed *via* pyrolysis at a temperature higher than 100 °C and 400 °C, respectively (Sajjadi et al., 2019a). S-doped on biochar surfaces also plays an important role in CO<sub>2</sub> adsorption. The S-containing functional group present on the biochar surface is basic in nature, thus facilitating the adsorption of weak acidic CO<sub>2</sub> *via* acid-base interaction (Seema et al., 2014). A strong pole-pole interaction is also present between the polar sites of S functional groups and the large quadrupole moment of CO<sub>2</sub> thus enhancing the adsorption of CO<sub>2</sub> onto the biochar surface (Xia et al., 2012).

Hydrophobicity and polarity of biochar were reported to influence the CO<sub>2</sub> capture performance. It can be determined through the content of oxygen (O), hydrogen (H), nitrogen (N), and sulphur (S) as well as the aromaticity of the biochar. Low content of O, H, the ratio of (O+N)/C and (O+N+S)/C contributed to high hydrophobicity and low polarity, thus limiting the adsorption of polar molecules (e.g., H<sub>2</sub>O) and enhancing the adsorption of non-polar molecules (e.g., CO<sub>2</sub>) (Shafawi, Anis Natasha et al., 2021; Shen et al., 2016). The presence of alkali (e.g., K, Na) and alkaline earth metals (e.g., Ca, Mg) in the biochar was also reported to affect the CO<sub>2</sub> adsorption through chemisorption, as the presence of metal can improve the basicity of biochar (Xu, X. et al., 2016). For instance, Lahijani et al. (2018) reported that the introduction of Mg to biochar (82.0 mg/g) improved the CO<sub>2</sub> adsorption capacities as compared to pristine biochar (72.6 mg/g) due to the enhancement of basicity of the modified biochar. In another research, Xu, X. et al. (2016) reported that biochar prepared from pig manure is highly basic (pH=10.4), which showed high CO<sub>2</sub> adsorption capacities (23.5 mg/g) as compared to biochar prepared from sewage sludge (18.2 mg/g) with lower pH (pH=8.44).

Over the few decades, various types of activation methods and advanced pyrolysis techniques have been introduced to improve the porous characteristics of biochar used in CO<sub>2</sub> capture. The activation methods include chemical activation (e.g., KOH, NaOH, HCl) (Liew et al., 2018; Sakhiya et al., 2021) and physical activation (e.g. CO<sub>2</sub>, steam) (Sangon et al., 2018), while advanced pyrolysis techniques

include microwave pyrolysis (Huang, Y.-F. et al., 2015), catalytic pyrolysis (Jalalabadi et al., 2019), CO<sub>2</sub> pyrolysis (Kwon, Gihoon et al., 2019), and co-pyrolysis (Igalavithana, Avanthi Deshani et al., 2020a). These methods were introduced to resolve the limitation of pristine biochar in CO<sub>2</sub> adsorption as pristine biochar possesses low surface area, porosity, limited surface functional group, and low basicity (Shafawi, Anis Natasha et al., 2021). Pristine biochar is tuned via these methods to produce “engineered biochar” with optimum characteristics for CO<sub>2</sub> capture (high basicity, surface area, pore volume, pore size, and high hydrophobicity).

Among them, co-pyrolysis shows the potential to produce biochar with higher CO<sub>2</sub> adsorption capacities, as shown in 5. Besides that, the ratio of feedstock selected during co-pyrolysis plays an important role as it may change the surface chemistry and porous structure of the biochar produced, which in turn affects the CO<sub>2</sub> adsorption capacities. As reported by Igalavithana, Avanthi Deshani et al. (2020a), an increased ratio of food waste during co-pyrolysis produced biochar with reduced amounts of N%, S%, and C%, as well as micropores on the surface, thus lowering the CO<sub>2</sub> adsorption capacities. Interestingly, there is positive synergy by adding wood waste to the co-pyrolysis, as it can help to reduce the moisture content contributed by the food waste in the gasifier and increase the C% in the biochar produced. Igalavithana, Avanthi Deshani et al. (2020a) also modified the co-pyrolyzed biochar from food and wood waste with KOH and reported an increase in microporous structure, thus increasing the CO<sub>2</sub> adsorption (148 mg/g) compared to that without activation (115 mg/g). Another research by Liu, S.-H. and Huang, Y.-Y. (2018) converted coffee ground into biochar via pyrolysis, then performed ammoxidation, followed by KOH activation to produce engineered biochar with higher surface area ranging from 990 m<sup>2</sup>/g to 1684 m<sup>2</sup>/g compared to those without KOH activation (0.8 – 402 m<sup>2</sup>/g) and pristine biochar (34 m<sup>2</sup>/g). The CO<sub>2</sub> adsorption capacities of the engineered biochar is higher (89.8 – 117.5 mg/g) compared to biochar without KOH activation (18.0 – 37.4 mg/g) and pristine biochar (6.2 mg/g). The research reported that N-doped ammoxidation and KOH activation had significant effects on CO<sub>2</sub> adsorption by improving the biochar basicity and amount of microporosity. Although previous research reported promising result on using biochar in CCT, however, limited research is performed for optimization of different methods as well as combination of these methods, where the synergy presence in the processes still remain unknown. CO<sub>2</sub> adsorption test should also be performed with larger scale or in real industry to identify the feasibility of using biochar for CO<sub>2</sub> capture. 5 summarizes the production of biochar from various techniques.

**Table 3.5 Summary of biochar as CO<sub>2</sub> adsorbent.**

Feedstock	Preparation and modification of biochar	Biochar porous characteristic				CO <sub>2</sub> adsorption capacity (mg/g) (adsorption temperature)	Ref.
		BET surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Average pore width (nm)	pore		
Taihu blue algae	Conventional pyrolysis Temp: 500 °C	29.18	0.02	18.8		89.8 (0 °C) 62.9 (25 °C)	(Wang, H. et al., 2021)
Rice straw	Microwave pyrolysis Power: 200 W Temp: 300 °C Time: 20 min	122.2	0.08	5.0		86.2 (20 °C)	(Huang, Y.-F. et al., 2015)
Chicken manure	CO <sub>2</sub> pyrolysis Temp: 700 °C	13.59	-	9.3		-	(Kwon, Gihoon et al., 2019)
Sewage sludge	Slow pyrolysis Temp: 500 °C Time: 4 h	10.12	0.02	-		18.2 (25 °C)	(Xu, X. et al., 2016)
Pig manure	Slow pyrolysis Temp: 500 °C Time: 4 h	31.57	0.04	-		23.5 (25 °C)	(Xu, X. et al., 2016)
Walnut shell	Slow pyrolysis Temp: 900 °C Time: 90 min Modification: Mg	292.0	0.16	2.15		82.0 (25 °C)	(Lahijani et al., 2018)
Coffee ground	Fast pyrolysis Temp: 400 °C Time: 60 min	34.0	0.18	-		6.2 (35 °C)	(Liu, S.-H. and Huang, Y.-Y., 2018)
Coffee ground	Fast pyrolysis Temp: 400 °C Time: 60 min Modification: Ammoxidation	0.8 – 402	0.01 – 0.22	-		18.0 – 37.4 (35 °C)	(Liu, S.-H. and Huang, Y.-Y., 2018)
Coffee ground	Fast pyrolysis Temp: 400 °C Time: 60 min Modification: Ammoxidation followed by KOH activation	990 - 1684	0.55 – 0.94	-		89.8 – 117.5 (35 °C)	(Liu, S.-H. and Huang, Y.-Y., 2018)

<b>Food waste (20%) + wood waste (80%)</b>	Gasification Temp: 800-1000 °C	294.7	0.05	2.3	115.1 (25 °C)	(Igalavithana, Avanthi Deshani et al., 2020a)
<b>Food waste (40%) + wood waste (60%)</b>	Gasification Temp: 800-1000 °C Activation: KOH	841.3	0.36	2.9	148.0 (25 °C)	(Igalavithana, Avanthi Deshani et al., 2020a)

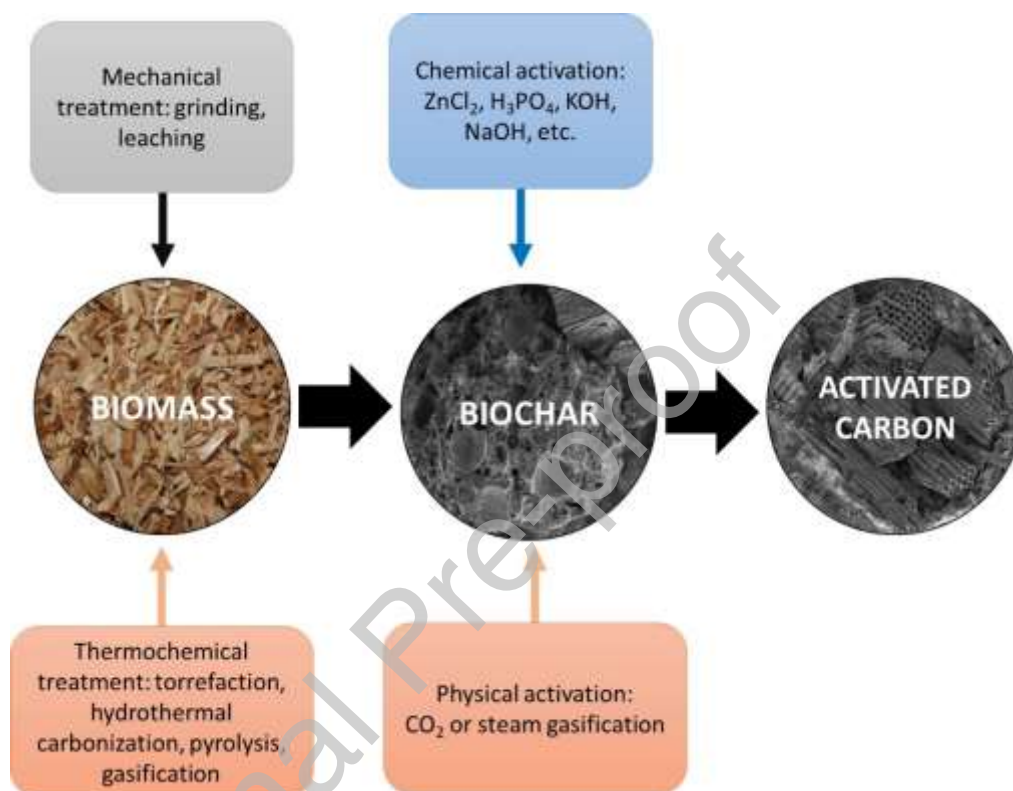
“Temp” denoted temperature.

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### 3.2.3.1.2 Biochar activation

Activated carbons are obtained through several processes, starting from carbonization under inert atmosphere. Initially, the raw biochar product does not have a developed porous structure; therefore, its activation is carried out through physical processes such as high-temperature carbon dioxide or steam gasification or by chemical treatment. A general concept of biochar and activated carbon synthesis is presented in Figure 3.21.



**Figure 3.21** Biochar and activated carbon synthesis methods, based on (Karimi et al., 2022)

Several modification methods were also implemented to enhance the adsorption properties of the biochar-derived activated carbons (Dissanayake et al., 2020). In terms of gaseous species, adsorption capacity and selectivity of the carbonaceous material are important factors (Ben Petrovic, 2022) for CO<sub>2</sub> adsorption selectivity toward nitrogen, and the presence of steam is another key factor (Manya et al., 2018). Specific properties of the materials are adjusted to the end-user requirements by proper modifications of production method and process conditions, raw material kind, its properties and additional post modifications (impregnation, doping etc.) (Xie et al., 2022). In addition, CO<sub>2</sub> adsorption using biochar-based materials is favourable at low-temperature adsorption; normally, its adsorption capacity increases with a temperature decrease (Cao et al., 2022).

The physical and chemical properties of biochars depend on the origin of biomass. Lignocellulosic biomass cell walls (e.g. woody, agriculture, food waste) are composed of three main components: two

polysaccharides (hemicellulose -  $(C_5H_8O_4)_m$ , cellulose -  $(C_6H_{10}O_5)_n$ ) and an aromatic polymer (lignin -  $[C_9H_{10}O_3(OCH_3)_{0.9-1.7}]_x$ ) and also other organic components (with acetyl groups, phenolic compounds) and mineral matter (Ashokkumar et al., 2022; Nahak et al., 2022). The content of each fiber component in biomass feedstocks is different: 6 – 38% of hemicellulose, 10- 50% of cellulose, and 6-46% of lignin (Saravanan et al., 2022). Cellulose is a polymer built with glucose monomers connected by glycosidic bonds, whereas hemicellulose is not a homogeneous polymer. It consists of glucose, mannose, arabinose, rhamnose, and other sugars. Because of their similar structure and nature, cellulose and hemicellulose make the stability of the matrix of biomass cell walls (Nagarajan et al., 2017). Lignin is a hydrophobic polymer built by aliphatic and aromatic hydrocarbons with a developed structure. Lignin plays the binding role between cellulose and hemicellulose, providing strong mechanical support to increase the recalcitrance of lignocellulosic biomass (Afzal et al., 2022). On the other side, lignin has a negative impact on cellulose conversion during conversion of thermochemical conversion of biomass (Zoghlami and Paes, 2019). It should be emphasised that lignocellulosic biomass was found as a good feedstock for biochar and activated carbon (AC) production (Duan et al., 2021; Kiełbasa et al., 2022). For biochar and AC production, the content of particular fiber components and mineral content are crucial because they determine the properties of obtained products. H. Tian et al. found that biochar derived from the highest content of lignin in biomass characterized the highest reactivity, whereas cellulose biochar had a rich porous structure (Tian et al., 2022). The literature revealed that cellulose could be obtained the activated carbon with a surface area of more than  $1000 \text{ m}^2/\text{g}$  (Suhas et al., 2016). Cellulose can also be used to produce nanofibrils and cellulose nanocrystals, which after modification, have a large surface area and high selectivity towards  $\text{CO}_2$  and high  $\text{CO}_2$  capacity (Ho and Leo, 2021).

The most suitable activated carbon synthesis method in the case of biomass is thermochemical treatment and chemical activation. Biochars obtained from pyrolysis or hydrothermal carbonisation of lignocellulosic biomass can be successfully activated to produce active carbon with a very high specific area (Shen et al., 2021). Cao et al. (Cao et al., 2022) proved that high adsorbent properties for  $\text{CO}_2$  capture and good reusability characterised biochar produced from woody and straw biomass. As well as biochar from palm biochar is a porous carbon-based material with high  $\text{CO}_2$  adsorption capacity through physisorption and chemisorption processes (Ben Salem et al., 2021a), whereas biochar from rice straw produced by using microwave pyrolysis was characterised by  $\text{CO}_2$  adsorption ability (Huang, Y.F. et al., 2015). Pyrolysis and further chemical activation using KOH of carbonaceous material of sugar cane bagasse resulted in the formation of phenolic and carboxylic functional groups with high affinity to  $\text{CO}_2$  (Peres et al., 2022). During biochar synthesis, a pyrolysis process temperature favours the development of porous structure, which directly affects the  $\text{CO}_2$  adsorption capacity of the material (Mukherjee et al., 2021). The development of the microporous structure of biochar is directly associated with the adsorption capacity of the carbonaceous material at low pressures in the range of 5 -15 kPa (Manya et al., 2020). The main mechanism of  $\text{CO}_2$  adsorption with biochar is a physical method

(physisorption) through van der Waals forces which adsorb CO<sub>2</sub> molecules (Zhang, Y. et al., 2022). According to the literature, specific surface area and pore size are the main factors affecting the process of CO<sub>2</sub> physical adsorption (Majchrzak-Kuceba and Soltysik, 2020; Xu, X.Y. et al., 2016).

Synthesis of adsorbents from biowaste is an important challenge nowadays. Constant economic progress, urbanization and industrialization are leading to a significant increase of the amount of municipal waste, food waste, bio-waste and sewage sludge. Therefore, the most important challenges for people are related to the reduction of waste generation and waste utilization in the circular economy concept bringing effective solutions (where re-materials generation, which can be returned into production processes) and environmental benefits for humans. One of the possibilities to reduce the use of natural resources is, in line with the waste management hierarchy, the use of waste to produce new products through material or energy recovery. The use of waste fuels, such as industrial non-hazardous waste, municipal waste, sewage sludge or the solid fraction after anaerobic digestion of the organic fraction of municipal waste in thermal conversion processes enables the production of valuable products, including gaseous energy carriers and solid products used in adsorption processes. The results presented by M. Karimi et al. in (Karimi et al., 2020) show that compost from municipal solid wastes might be a valuable resource for adsorbent synthesis through chemical activation using sulfuric acid and activation at 800 °C. The results of carbon dioxide capture were comparable to those obtained for commercial samples (Karimi et al., 2020). Biowaste, as a mixture of food waste and wood waste, was also a potential material for microporous activated carbon synthesis through gasification; combining with chemical activation using KOH gives better results of porosity of the material (Igalavithana, A. D. et al., 2020).

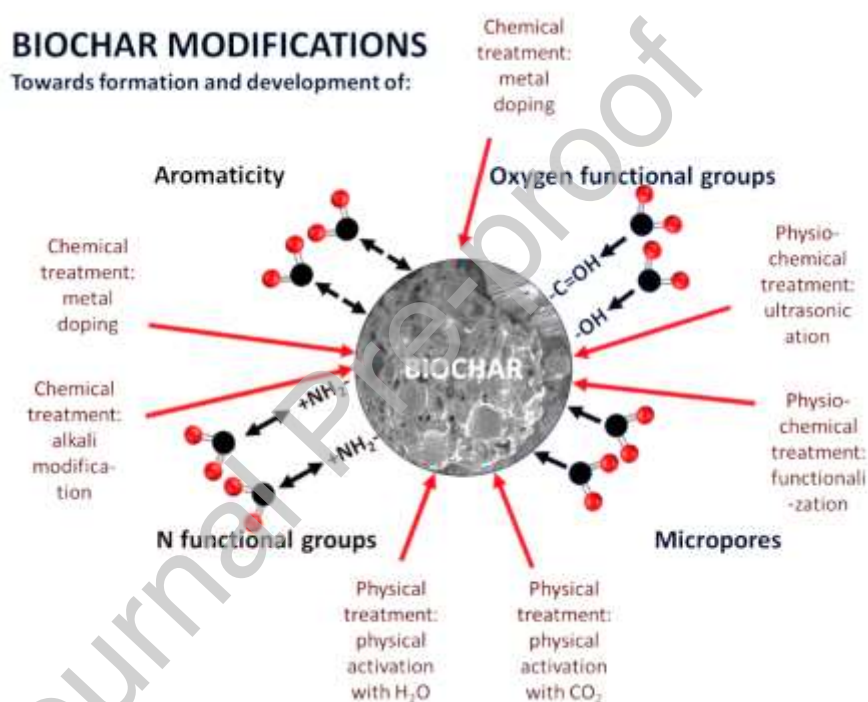
A mixture of sewage sludge and leucaena wood was tested as a precursor of biochar synthesis through microwave co-torrefaction. The results show that the adsorption capacity of pure leucaena wood biochar was almost four times higher than that of pure sewage sludge biochar (Huang, Y.F. et al., 2019). Biochar-derived carbons prepared from coffee grounds were studied by L. Shou-Heng (Liu, S.H. and Huang, Y.Y., 2018). The activated carbons were obtained through carbonisation, ammoxidation and KOH activation. A highly developed microporous structure resulted in high CO<sub>2</sub> adsorption capacity. Peanut shells were tested as a potential raw material for the synthesis of biochar through catalytic pyrolysis in the molten salt of ZnCl<sub>2</sub>, giving a high capacity of CO<sub>2</sub> and selectivity over other gases. It was reported by Manaya et al. [28] that chemical activation of vine shoots results in 20 – 30% higher CO<sub>2</sub> adsorption capacity of produced biochars compared with physical activation with CO<sub>2</sub>.

Due to the chemical reactions of mineral matter components to form carbonates, an enhanced process of CO<sub>2</sub> adsorption was observed. Mineral matter components, especially Mg, Al, Fe, Ni and Ca promote the chemical sorption of carbon dioxide. Additionally, high temperature and water vapor content in the gas stream enhance chemisorption (Xu, X.Y. et al., 2016). Mineral matter also influences the activation process and gases released during the process. For example, during the activation process of chicken

manure, which is a fuel rich in  $\text{CaCO}_3$ , an enhanced generation of CO and suppressed dehydrogenation was observed (Kwon, G. et al., 2019).

### 3.2.3.1.3 Modifications enhancing carbon dioxide capture

To enhance the  $\text{CO}_2$  adsorption capacity of carbonaceous materials, it is possible to introduce different modifications, increasing the role of the chemisorption mechanism in the process of adsorption. An overview of modification methods to enhance the porous structure and enhance the adsorption capacity of biochar towards carbon dioxide adsorption, using both chemical and physical methods, is presented in Figure 3.22.



**Figure 3.22** Biochar modification methods towards enhanced  $\text{CO}_2$  adsorption capacity, based on (Kumar et al., 2022; Shafawi, A. N. et al., 2021).

It was proved that the adsorption capacity of biochar towards  $\text{CO}_2$  might be enhanced by increasing the alkalinity of the material surface (Dissanayake et al., 2020). It is possible to enhance  $\text{CO}_2$  adsorption on carbon-based material by incorporating chemisorption and modifying biochar with metal oxides and amine-containing materials (Ben Salem et al., 2021a). Especially in the case of waste materials, such modifications are implemented, as organic waste usually contains smaller amounts of carbon, which directly affects the material's adsorption capacity. More advanced procedures are implemented and described in the literature to enhance biochars' adsorption capacity, for both physically and chemically

activated samples. For example, A. Igalavithana et al. defined modification of biochars through hetero atoms doping as a promising strategy to further increase CO<sub>2</sub> adsorption (Igalavithana, A. D. et al., 2020). A nitrogen doped biochar derived from chicken manure possessed a well-developed porous structure of above 300 m<sup>2</sup>/g, resulting in very high adsorption capacity and selectivity (Nguyen and Lee, 2016). Anaerobic digestion solid residue might also be a raw material for biochar-based sorbent synthesis. It was observed that nitrogen-functionalised porous carbon synthesised in a one-step process using urea seems to be effective in improving the uptake of CO<sub>2</sub> (Qiao et al., 2020). However, modifications before the chemical treatment of sawdust biochar by a simple impregnation method resulted in pores clogging and reduction of sample adsorption capacity (Madzaki et al., 2016). Pore blockage was also observed after K<sub>2</sub>CO<sub>3</sub> impregnation of conocarpus biochar (Al-Wabel et al., 2019).

A biochar dedicated to biogas treatment and capturing CO<sub>2</sub> and H<sub>2</sub>S was produced from sawdust biochar treated with urea phosphate to improve the porosity and surface N-containing functional groups of biochars (Ma, Q.X. et al., 2021). An enhanced adsorption process of CO<sub>2</sub> was observed on metalized-biochar in the sequence of metals: Mg > Al > Fe > Ni > Ca (Lahijani et al., 2018), due to a change of physical mechanism to the chemical reaction between e.g., iron oxyhydroxides and carbon dioxide (Xu, X.Y. et al., 2020). Sorption properties might also be enhanced using mechanical treatment e.g. using ball mining (Xu, X.Y. et al., 2020).

Biochars, on the example of coconut shell biochar, might be used for a simultaneous NO/CO<sub>2</sub> removal system which uses biochar and calcined limestone in the calcium looping process (Zhang, W. et al., 2020b). To further enhance adsorption properties, Cu-modification of biochar was proposed together with CaO in the carbonation stage of calcium looping (Zhang, W. et al., 2020a).

In 6, the review of adsorption capacities toward carbon dioxide of biomass-derived adsorbents was shown. Biochars are produced from a wide range of feedstocks characterizing different CO<sub>2</sub> adsorption capacities.

**Table 3.6 CO<sub>2</sub> adsorption capacities of biomass-derived adsorbents**

No.	Sample	CO <sub>2</sub> adsorption capacity, mmol/g	Adsorption parameters	process	Reference
1	Biochar-derived carbons from coffee grounds	2.04 - 2.67	Ambient pressure, 35 °C		(Liu, S.H. and Huang, Y.Y., 2018)
2	Biochar from compost from municipal solid wastes	2.5	2.5 bar and 40 °C		(Karimi et al., 2020)
3	Biochar prepared by catalytic pyrolysis of waste roasted peanut shell in the molten salt of ZnCl <sub>2</sub>	3.8	100 kPa and 0 °C		(Guo, T.X. et al., 2018)
4	Carbonaceous material of sugar cane bagasse	1.22	Ambient pressure, 25 °C		(Peres et al., 2022)
5	Biochar derived from chicken manure chemically treated with HNO <sub>3</sub> and NH <sub>3</sub> at 450 °C	10.15	Ambient pressure (1bar), 20 °C		(Nguyen and Lee, 2016)

6	Leucaena wood biochar	1.20	Ambient pressure (1bar)	(Huang, Y.F. et al., 2019)
7	Vine shoots-derived biochar using both chemical and physical methods	0.92-2.42	15 kPa, 0 °C	(Manya et al., 2018)
8	pine cone biochars activated with KOH	3.64	1 bar, 25 °C	(Kaya and Uzun, 2021)
9	Pecan nut shell biochar obtained through microwave pyrolysis	2.5 (2.0)	1 bar, 0 °C (25 °C)	(Duran-Jimenez et al., 2021)
10	Vine shoots biochar obtained at 600 °C and activated with CO <sub>2</sub> (at 0.1 MPa and 800 °C)	2.35-2.67	1 bar, 25 °C	(Manya et al., 2020)
11	Wheat straw biochar obtained at 500 and activated with CO <sub>2</sub> (at 0.1 MPa and 800 °C)	2.44-2.63	1 bar, 25 °C	(Manya et al., 2020)
12	Sawdust biochar activated using urea phosphate at 700 °C	2.42	1 bar, 25 °C	(Ma, Q.X. et al., 2021)
13	Bamboo chips biochar modified by ZIF-8 grafting	1.8	1 bar, 30 °C	(Zhang, J.J. et al., 2022)
14	Anaerobic digestion solid residue biochar modified by urea	1.22	1 bar, 25 °C	(Qiao et al., 2020)
15	Lignin impregnated with sodium lignosulfonate	2.34	1 bar, 25 °C	(Zhang, X.Y. et al., 2022)
16	Rape straw, soybean straw, corn stalk, wheat straw, walnut shell, hickory wood, and pine wood biochar obtained at 600 °C	0.69-1.02	1 bar, 25 °C	(Cao et al., 2022)
17	Conocarpus biochar obtained at 400 °C	4.47	1 bar, 25 °C	(Al-Wabel et al., 2019)
18	Date palm waste biochar obtained at 500 °C	0.38	1 bar, 25 °C	(Ben Salem et al., 2021b)
19	Biocarbon	0.6	30 mbar, 30 °C	(Majchrzak-Kuceba and Soltysik, 2020)
20	Walnut shell biochar (Mg metalized)	1.65 (1.86)	Ambient pressure, 25 °C	(Lahijani et al., 2018)
21	biochar/Fe oxyhydroxide composite	3.63	Ambient pressure, 25 °C	(Xu, X.Y. et al., 2020)
22	Spent coffee grounds obtained at 600 °C	2.8	1 bar, 25 °C	(Mukherjee et al., 2021)
23	Pig manure biochar obtained at 500 °C	0.53	1 bar, 25 °C	(Xu, X.Y. et al., 2016)
24	Wheat straw biochar obtained at 500 °C	0.78	1 bar, 25 °C	(Xu, X.Y. et al., 2016)
25	Peanut shell derived activated carbon with KOH	7.06 (4.61)	1 bar, 0 °C (25 °C)	(Deng et al., 2015)
26	Rambutan peel-derived KOH-activated hydrochar using KOH:HC ratio of 2:1 at 850 °C for 120 min with the involvement of water-soaking pretreatment	2.78	1 bar, 30 °C	(Zubabri et al., 2021)
27	Sugarcane bagasse biochar produced at 600 °C	1.67	1 bar, 25 °C	(Creamer et al., 2014)

28	Argan fruits shells obtained through dry physical mixing with KOH	5.63	1 bar, 25 °C	(Boujibar et al., 2018)
29	Rice straw biochar produced by microwave pyrolysis (200 W and 300 °C)	1.75	1 bar, 20 °C	(Huang, Y.F. et al., 2015)
30	Rambutan peel biochar impregnated with magnesium nitrate (raw biochar)	1.71 (1.56)	1 bar, 30 °C	(Zubbri et al., 2020)

### 3.2.3.2 Sewage sludge char for CO<sub>2</sub> adsorption

#### 3.2.3.2.1 Composition and main characteristics of sewage sludge derived biochar

The biochar product of sewage sludge pyrolysis is a carbon-like material that contains sulphur, nitrogen and oxygen-containing compounds, polycyclic aromatic hydrocarbons, valuable nutrients for the soil (e.g. N, P, K, Ca, Fe, Mg, Cu, Zn) and heavy metals (e.g. As, Cd, Cr, Ni, Pb, Se). Depending on the raw material and the reaction parameters, the yield of biochar is usually between 20 and 70% (Table 3.7). The amount of ash, fixed carbon and volatile compounds is 29-86%, 7-64%, 1-39%, respectively (Chen, R. et al., 2021; Hossain et al., 2011; Moško et al., 2021; Stylianou et al., 2020; Tong et al., 2021). It is also known, that the ash content of sewage sludge derived biochar is generally higher, than that of based on biomass, which can be attributed to the higher mineral content of sewage sludge (Li, M. et al., 2018). The properties of biomass and sewage sludge derived bio-carbons should be different depending on the composition of raw materials and process parameters (Li, M. et al., 2018; Zhang, M. et al., 2019).

The sewage sludge derived biochar can be used for many purposes, e.g. as a sorbent, catalyst and soil amendment. The application is determined by the physico-chemical properties (e.g. specific surface area, pore volume, average pore diameter), the relative proportions of volatile compounds, fixed carbon and ash in the biochar (Yuan et al., 2015). Biochar obtained at higher pyrolysis temperature ( $T > 450^{\circ}\text{C}$ ) has higher specific surface area and increased adsorption capacity (Peng et al., 2011; Yuan et al., 2015).

As it was mentioned earlier, sewage sludge derived biochar also contains heavy metals, that accumulate in the carbonaceous residue; e.g. Pb, Zn, Ni, Cd, As, Cu or Cr. Their concentrations should be significant ( $>5000\text{ppm}$ ) and it can be increased as function of temperature (Cao and Harris, 2010; Xiong et al., 2021; Yin et al., 2021; Zheng et al., 2013).

**Table 3.7** Yields, composition and main characteristics of biochar products of sewage sludge pyrolysis

Raw material	Pyrolysis conditions	Biochar yield, %	Properties, elemental composition, %								Other properties				Ref.
			Ash	Volatile compounds	Fixed carbon	C	H	N	S	O	HHV, MJ/kg	BET surface area, m <sup>2</sup> /g	Pore volume, cm <sup>3</sup> /g	Average pore diameter, nm	
Sewage sludge (100 g)	T=400-800°C, τ=2 h, He atmosphere (150 ml/min) quartz reactor	46.3-61.7	67.9-80.8	0.9-21.5	10.6-18.3	17.2-23.1	0.3-1.6	0.9-3.0	0.8-0.8	<3.6	8.0-9.5	14.9-85.7	<0.1	-	(Moško et al., 2021)
Sewage sludge (10 g)	T=300-500°C, 10°C/min heating rate, N <sub>2</sub> atmosphere (100 ml/perc), quartz reactor	55-68	50.7-62.5	24.4-39.0	9.9-13.1	21.5-29.6	1.4-5.3	2.8-5.1	0.6-1.3	12.3-24.4	8.2-12.5	-	-	-	(Chen, R. et al., 2021)
Sewage sludge+rice husk (5 g)	Hydrothermal treatment, T=600°C, τ=0.5 h, N <sub>2</sub> atmosphere (200 ml/min) high pressure autoclave	24.4-62.4	28.8-86.1	5.6-9.5	8.2-63.6	2.5-62.1	0.9-2.2	0.7-0.8	0.1-0.2	6.2-8.4	3.9-23.0	13.7-211.9	0.1-0.3	2.5-17.5	(Tong et al., 2021)
Sewage sludge (kb. 250 g)	T=300-700°C, N <sub>2</sub> atmosphere (50 ml/min) Horizontal fixed-bed reactor	52.4-72.3	52.8-72.5	15.8-33.8	6.8-9.1	20.2-25.6	0.5-2.6	1.2-3.3	-	<8.3	-	-	-	-	(Hossain et al., 2011)
Sewage sludge, cattle manure, used coffee grounds (20-24 kg)	T=550°C, N <sub>2</sub> atmosphere, τ=1.5 h	21.2-41.6	-	-	-	28.5-87.4	0.9-2.4	1.6-5.7	0.3-0.5	-	-	1.5-14.0	<0.1	3.9-60.4	(Stylianou et al., 2020)



For sequestering CO<sub>2</sub>, many technologies (e.g. absorption, adsorption, membrane separation, chemical or Ca looping, pre- and post-combustion and oxy-fuel) have been developed (Osman et al., 2021). Among the variety of routes, adsorption technologies seem to be the most promising. Based on this fact, different types of porous solid sorbents such as synthetic or natural zeolites, mesoporous silica, metal organic frameworks, active carbon, etc. have already been studied for CO<sub>2</sub> removal (Creamer et al., 2014; Lahijani et al., 2018; McEwen et al., 2013). Although the listed sorbents have high adsorption capacity, the application of metal organic frameworks and zeolites is limited (Ahmed, E. et al., 2016). In case of metal organic frameworks, the instability should be mentioned (Guo, S. et al., 2022), and in the case of zeolites, the fast deactivation, the irreversible adsorption, the steric hindrance of the heavy compounds and the high regeneration temperature are the main disadvantages (Perot and Guisnet, 1990). Biochar can also be an excellent CO<sub>2</sub> sequestering sorbent (Singh et al., 2022). However, before its usage, it is inevitable to create the appropriate pore structure, alkalinity and surface functional groups with different modification methods (Guo, S. et al., 2022; Miricioiu et al., 2021).

#### 3.2.3.2.2 Modification of sewage sludge derived biochar for CO<sub>2</sub> reduction

In order to create the appropriate pore structure, alkalinity and surface functional groups, physical, chemical, physical-chemical modification of the biochar and co-pyrolysis of sewage sludge and biomass have been proposed in the literature (Shafawi, Anis Natasha et al., 2021; Xiao, Y. et al., 2022). The reason for the latter is that biomass also contains alkali elements and alkali earth metals and thus enabling the alkalinity and CO<sub>2</sub> adsorption capacity of the produced biochar to be increased (Huang, H.-j. et al., 2017).

The modification processes have three types. One of them is physical modification, which involves two steps: (i) carbonization carried out at low temperature (T=400-750°C) in the presence of physical agents, heat, gases (e.g. CO<sub>2</sub>/He/N<sub>2</sub>) or steam and (ii) activation in gas atmosphere at a relatively high temperature (T=800-1200°C) in order to further increase the porosity (Singh et al., 2020). The process that takes place is slow oxidation, which leads not only to the formation of new pores, but also to an increase in the diameter of the existing pores (Wang, S. et al., 2017).

Physical treatment has already been studied by several research groups, especially in the case of biomass derived bio-carbons (González et al., 2013; Plaza et al., 2011; Plaza et al., 2010; Shahkarami et al., 2015; Xiong et al., 2013). In these cases, a CO<sub>2</sub> adsorption capacity of even more than 100 mg/g can be achieved. In an interesting way, considerably less information is available about physical modification of sewage sludge derived bio-carbons. Despite the fact, that Tinnirello and co-workers (Tinnirello et al., 2020) observed a CO<sub>2</sub> adsorption capacity of 103 mg/g (temperature=600°C, dwell time=2 h, nitrogen flow rate=300 Nml/min) when they studied the physical activation of the anaerobically digested sewage sludge derived biochar. It is important to note that the reported value (2.3 mmol/g) is consistent with the adsorption capacity of activated carbon (2.6 mmol/g) (Siriwardane et al., 2001).

In addition to nitrogen, steam and CO<sub>2</sub> can also be used for biochar activation. According to Pallaréz et al. (Pallarés et al., 2018) CO<sub>2</sub> activation is more beneficial than steam modification, because CO<sub>2</sub> activation allows the formation of the desired micropores. The beneficial temperature of CO<sub>2</sub> activation is about 600-650°C and the resulting biochar has basic/alkaline character. In those cases, when nitrogen is used as activating agent the temperature should be around 700°C or even higher (Gao et al., 2014).

To increase the CO<sub>2</sub> sequestration capacity, chemical modification can also be used. This type of modification can be done in two ways: (i) impregnation of sewage sludge or biomass sample with the chemical agent and thermal treatment, (ii) impregnation of sewage sludge or biomass based biochar with the chemical reagent and thermal treatment (Ahmed, M.B. et al., 2016; Sajjadi et al., 2019b). Increasing the CO<sub>2</sub> adsorption capacity, it may be beneficial to create nitrogen-containing functional groups (e.g. amide, imide, nitriles, etc.) on the surface of the biochar. For this purpose, ammonia, amines and nitric acid are the most widely used compounds (Shen and Fan, 2013). In case of ammonia treatment/ammonification the most commonly used temperature is between 600 and 900°C, where ammonia first decomposes to free NH<sub>2</sub>, NH radicals, atomic hydrogen and nitrogen and then the nitrogen containing functional groups are formed from the reaction of the resulting radicals and the carbon (Stöhr et al., 1991). Between the functional groups and the ammonification temperature correlations have been observed (Mangun et al., 2001). It was found that amides, imides, imines, amines and nitriles are the most dominating functional groups below 600°C, while the thermally stable aromatic rings-like functionalities are dominated at higher temperatures (Plaza et al., 2009; Shafeeyan et al., 2010). It was also reported, that C-N and C=N chemical groups had been introduced into the char surface, by the using of 200-1000°C ammonification temperature till 2 hours (Przepiórski et al., 2004). In another study (Zhang, X. et al., 2016) soybean straw derived biochar and 500-900°C ammonification temperature was applied before the CO<sub>2</sub> adsorption capacity was determined. The resulting biochar had a micropore surface area of 311-461 m<sup>2</sup>/g and the adsorption capacities changed between 48 and 74 mg/g (CO<sub>2</sub> adsorption temperature=30°C). It was found that increasing the temperature is beneficial from the point of view of micropore production, but the ammonification temperature has a maximum (T=800°C) and above this value both the surface area and the adsorption capacity decreased.

The chemical treatment can also be conducted using alkaline solutions such as KOH and NaOH (Jin et al., 2014), but impregnation of biochar with metal salt solution can also be a promising option. In case of KOH and NaOH activation O-containing functional groups (e.g. carboxyl, hydroxyl etc.) are formed on the surface of the biochar and enhance the adsorption capacity for CO<sub>2</sub>. The reason for this is that carboxyl and hydroxyl groups led to intermolecular forces and dipole-dipole interaction with the molecule of CO<sub>2</sub> (Shafawi, Anis Natasha et al., 2021; Shafeeyan et al., 2012). As a result of this, the CO<sub>2</sub> adsorption capacity can be higher than 70 mg/g at ambient conditions, but in some cases it can be over 100 mg/g (Du et al., 2020; Manyà et al., 2018; Quan et al., 2020).

The literature results are also promising in the case of metal or metal oxide modification. In this case, aluminium chloride, magnesium chloride and iron chloride are the most widely used metal salts to

impregnate the biochar. The first step is impregnation, which is followed by a thermal treatment, where the metal salts are converted into metal oxides (Ahmed, M.B. et al., 2016; Jung and Ahn, 2016). Lahijani et al. (Lahijani et al., 2018) studied more individual metals (Mg, Al, Fe, Ni, Ca, Na) for the activation of biochar. It was found that Mg derived compounds have the highest CO<sub>2</sub> adsorption capacity (82 mg/g) and Na derived compounds are the least suitable for sequestering CO<sub>2</sub>. The latter had an even lower adsorption capacity than raw biochar. In Table 3.8 some of the results of chemical modification are summarized, particularly focusing on sewage sludge based bio-carbons.

**Table 3.8** Results of chemical modification of sewage sludge derived bio-carbons

Raw material	Conditions for biochar production	Chemical activation	BET surface area, m <sup>2</sup> /g	Micropore volume, cm <sup>3</sup> /g	Adsorption temperature (°C) and pressure	CO <sub>2</sub> adsorption capacity, mg/g (mmol/g)	Ref.
Chicken manure	400°C	KOH, activation under N <sub>2</sub> at 700°C for 1 h	22	N/A	25.1 bar	76.8	(Huang, H.-j. et al., 2017)
Chicken manure	400°C	HCl, activation under N <sub>2</sub> at 700°C for 1 h	137	N/A	25.1 bar	85.7	(Huang, H.-j. et al., 2017)
Sewage sludge	400°C	KOH, activation under N <sub>2</sub> in the temperature range of 500-900°C for 30 min	984	0.6	-	-	(Hunsom and Autthanit, 2013)

### 3.2.3.2.3 Mechanism of adsorption

The CO<sub>2</sub> reduction should be taken by physical and chemical adsorption at low temperature or even by chemical looping at high temperatures (Igalavithana, Avanthi Deshani et al., 2020b; Jung et al., 2019; Shafawi, Anis Natasha et al., 2021). The adsorption properties of biochar obtained from sewage sludge pyrolysis are based on the surface characteristics of the solid particle. The adsorption ability is greatly influenced not only by the pore size or surface area of the macropores and microporous, but also by their chemical properties. Micropores have a significant role in the physical aspects of adsorption, while the surface groups can affect rather the formation of chemical relationships (Igalavithana, Avanthi Deshani et al., 2020b; Jung et al., 2019). When carbon dioxide is adsorbed, the groups containing nitrogen or oxygen usually form chemical linkage through acid-base (Lewis-acid and Lewis-base) reactions, while the groups containing aromatics form chemical linkage through van der Waals bonds (Igalavithana, Avanthi Deshani et al., 2020b; Jung et al., 2019). As a result of activation and surface

modifications carried out in different ways, the relative ratio of before discussed chemical groups can be changed. This can also change the adsorption ability significantly. However during desorption, the strong chemical linkage is disadvantageous in many cases, because it does not exclude the fully removal of the adsorbed components (Igalavithana, Avanthi Deshani et al., 2020b; Jung et al., 2019; Shafawi, Anis Natasha et al., 2021).

### 3.2.3.3 Chitosan for CO<sub>2</sub> capture

Chitosan is a deacetylated-derivative of chitin (abundantly available biopolymer after cellulose) that has been used in various fields, including cosmetics, food industry, pharmaceuticals, biomedicine, agricultural and wastewater treatment (Pakizeh et al., 2021). Chitin can be extracted from various sources, including crustaceans, mollusks, insect shells, and cell walls of fungi (Said Al Hoqani et al., 2020; Sayari et al., 2016; Soetemans et al., 2020). Similar to biochar, chitosan possesses excellent properties that are suitable for CCT, which are biodegradability, non-toxicity, functionality, biocompatibility, and high adsorption capacity (El Knidri et al., 2016). The quality of chitosan is characterized by molecular weight (Mw) and degree of deacetylation (DD%), where commercial chitosan has a DD% ranging from 70 to 95% and Mw ranging from 50 kDa to 200 kDa (Sun et al., 2009). In general, chitosan with high Mw (>1000 kDa) exhibits better mechanical properties (suitable to use as an adsorbent), while medium (100-1000 kDa) to low (<100 kDa) Mw exhibit better biological properties (suitable for pharmaceutical applications) (Gonçalves et al., 2021; Kou et al., 2021).

Chitosan as an adsorbent/precursor for CO<sub>2</sub> capture has recently caught the attention of researchers owing to the natural basicity of chitosan, where the free amino group in the chitosan structure can provide basic sites for CO<sub>2</sub> adsorption. Other advantages of chitosan as an adsorbent/precursor include high thermal stability, chemically inert, tunable surface functional group, minimal energy for recovery, and it is inexpensive due to the ability of mass production from chitin sources (Kamran and Park, 2020). Previous studies applied chitosan-based adsorbents in CO<sub>2</sub> capture and revealed that CO<sub>2</sub> could be adsorbed on the adsorbent surface and converted into ammonium carbamates at room temperature, then released as CO<sub>2</sub> from the adsorbent upon heating (Ababneh and Hameed, 2021). However, pure chitosan possesses low CO<sub>2</sub> adsorption and therefore, modification of the surface properties of chitosan is required to improve or maximize its adsorption efficiency toward CO<sub>2</sub> (Kumar et al., 2018; Peng, H.L. et al., 2019). The chitosan adsorbent can be prepared via thermochemical technology such as hydrothermal carbonization, or surface functionalization with chemicals or structural modification.

Hydrothermal carbonization (HTC) operated at a temperature ranging from 180 to 260 °C with the presence of water and autogenous pressure, is a promising method for preparing chitosan-based adsorbent. It is a simple, low-cost process without the use of a catalyst or organic solvents. Thus, it has

been introduced as a greener approach for the synthesis of functionalized chitosan and improving its CO<sub>2</sub> adsorption efficiency (Titirici and Antonietti, 2010). Research by Chagas et al. (2020) reported an outstanding performance of HTC chitosan adsorbent where the CO<sub>2</sub> uptake is 4-fold higher than the pure chitosan. The HTC of chitosan has been shown to increase the carbon content, and reduce the oxygen content but does not significantly change the amount of nitrogen in chitosan. Interestingly, the structural characterization of chitosan revealed the production of more aromatic amines at a longer HTC reaction time, hence causing lower basicity of chitosan, but showed a higher CO<sub>2</sub> adsorption capacity, suggesting that aromatic structure in HTC chitosan exposed the N atom for CO<sub>2</sub> adsorption (Chagas et al., 2020). Modification of the chitosan into a spherical structure via HTC was an alternative to improve the CO<sub>2</sub> adsorption efficiency of chitosan due to the carbon sphere providing properties such as a large contact area, adjustable surface chemistry, and open-pore structure for adsorption reactions. For instance, Wu, Q. et al. (2019) have reported that the chitosan sphere (3.28 mmol/g) has a higher BET surface area (462 m<sup>2</sup>/g), with up to 85.5% of micropore structure and ultra-micropore (<0.9 nm) able to enhance CO<sub>2</sub> capture compared to rod-structure (1.36 mmol/g) and 2D sheet structure (2.61 mmol/g) of chitosan. However, chitosan hydrochar still possesses low CO<sub>2</sub> adsorption efficiency and thus HTC combined with a different technique such as chemical impregnation is required to modify the surface chemistry to enhance the CO<sub>2</sub> capture performance.

Physical activation such as steam activation usually requires a long reaction time to achieve a high temperature, which may lead to high energy consumption (Yek et al., 2020). In contrast, chemical activation requires chemical reagents to carbonize and develop the porosity of the chitosan under low-temperature conditions and short reaction time, thus reducing energy consumption (Wang, Jing et al., 2021). In particular, NaOH, KOH, and K<sub>2</sub>CO<sub>3</sub> have been discovered as effective chemical activation agents that can enhance the development of porosity in carbonaceous materials (Liew et al., 2018; Liew et al., 2019). For instance, Wang, Jing et al. (2021) reported on the use of mild KOH as an activation agent to enhance the porosity of chitosan hydrochar, resulting in the production of a high surface area of chitosan hydrochar (up to 2547 m<sup>2</sup>/g). Chitosan hydrochar produced at a temperature of 600 °C exhibited the highest CO<sub>2</sub> capture capacity (4.41 mmol/g) compared to the other carbon produced under different precursors (e.g., walnut shell) and activating agents (e.g., NaNH<sub>2</sub>), which only possessed CO<sub>2</sub> uptake of 3.06 mmol/g (Yang, Z. et al., 2019). This suggests the potential of chitosan hydrochar as a desirable precursor and KOH as an effective activation agent in producing carbon with high porosity as an adsorbent for CO<sub>2</sub> uptake.

Other than alkalis, acids can also be used as an alternative activation agent. Xiao, J. et al. (2022) introduced phytic acid into the carbon network of chitosan gel to fabricate N, P-co-doped porous carbon materials (NPPCs). The surface area of NPPCs (690 – 1010 m<sup>2</sup>/g) was lower than carbon produced using alkali but exhibited a higher CO<sub>2</sub> uptake (5.31 mmol/g) as compared to chitosan hydrochar in the previous study (2547 m<sup>2</sup>/g and 4.41 mmol/g, respectively) (Wang, Jing et al., 2021), thus showing the

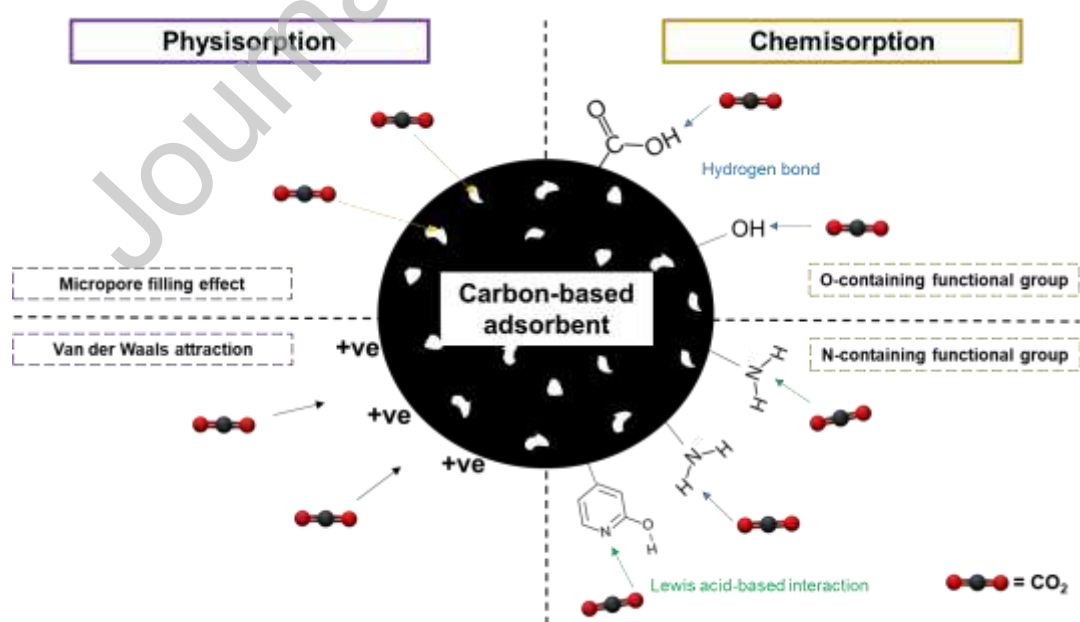
better potential of NPPC to be used as a CO<sub>2</sub> capture. The effects of different chemical activators for chitosan activation were performed by Li, J. et al. (2022) using KOH, potassium acetate (KAc), potassium carbonate (KHCO<sub>3</sub>), and potassium bicarbonate (K<sub>2</sub>CO<sub>3</sub>). The research revealed that activation via KOH produces a chitosan-based adsorbent with a high surface area (1928 m<sup>2</sup>/g) and high CO<sub>2</sub> adsorption capacity (3.91 mmol/g). However, KOH is highly corrosive, and an alternative has been provided by the author by using KAc activation that produced a chitosan-based adsorbent with comparable surface area (1273 m<sup>2</sup>/g) and CO<sub>2</sub> adsorption capacity (3.52 mmol/g).

Physical impregnation has emerged as a new research area for the synthesis of chitosan-based adsorbents for CO<sub>2</sub> adsorption. For instance, Peng, H.-L. et al. (2019) synthesized an amine-impregnated adsorbent by impregnating chitosan-derived adsorbent with a pentaethylenhexamine (PEHA), which was inspired by conventional CO<sub>2</sub> adsorption using liquid amine. Chitosan loaded with PEHA showed higher CO<sub>2</sub> (3.72 mmol/g) uptake compared to pure chitosan-derived adsorbent (0.21 mmol/g) at 100 °C, thus implying the effectiveness of amines-impregnated carbon to capture CO<sub>2</sub>. Besides that, Yang, C. et al. (2022) developed N-doped porous carbon via mixing and ball-milled chitosan and NaNH<sub>2</sub>. The use of NaNH<sub>2</sub> as the source of nitrogen and porogen during carbonization has increased the surface area and pore structures of the N-doped porous carbon. N-doped carbon material showed a high surface area (2398 m<sup>2</sup>/g) and high CO<sub>2</sub> adsorption capacity (6.33 mmol/g), showing better CO<sub>2</sub> adsorption performance compared to carbon-based adsorbent produced using ZnCl<sub>2</sub> (2.62 mmol/g) (Xu, Ying et al., 2020). Although much research has been carried out to modify the physicochemical properties of chitosan to be used in CO<sub>2</sub> adsorption, there are many research gaps to be filled as compared to biochar as CO<sub>2</sub> adsorbents, such as the optimization of carbonization parameters, utilization of suitable activator and the CO<sub>2</sub> adsorption temperature and pressure. It is worth noting that chitosan has a more desirable properties such as high surface N-functional group in nature, low cost, biodegradable and non-toxic as compared to biochar, thus, novel and optimize research for chitosan-based adsorbent for CCT should be performed. Table summarizes the synthesis techniques of chitosan-based adsorbent for CO<sub>2</sub> capture.

The CO<sub>2</sub> adsorption mechanism of biochar and chitosan are similar as both carbon materials have N-containing functional group on the surface, and pore structure that facilitates the adsorption processes. Studies have indicated that CO<sub>2</sub> adsorption to the adsorbent occurs *via* physisorption and chemisorption. Physisorption of CO<sub>2</sub> is dominated by the pore structure and surface area, where micropore sizes of 0.3–0.8 nm are preferable, and < 0.5 nm are optimum for CO<sub>2</sub> adsorption (Igalavithana, Avanthi Deshani et al., 2020c). Physisorption is mainly induced by van der Waals and micropore-filling effects (Shafawi, Anis Natasha et al., 2021). The chemisorption of CO<sub>2</sub> is dominated by Lewis acid-base interaction and hydrogen bond interaction. The hydrogen bond is formed between CO<sub>2</sub> and O-containing functional groups. In general, O-containing functional groups are acidic, which may hinder the adsorption of acidic CO<sub>2</sub>. Interestingly, some studies revealed that hydroxyl (-OH) and carboxyl group (-COOH) enhance

the hydrogen bond interaction. This is attributed to the electronegativity different of H atom (2.1) and O atom (3.5), causing the H atom from -COOH and -OH having high electropositivity to interact with the O atom from CO<sub>2</sub> via hydrogen bond (Liu and Wilcox, 2012). However, this hydrogen bond is weak and the presence of H<sub>2</sub>O molecules would hinder the formation of the hydrogen bond. This is because the presence of H<sub>2</sub>O molecules created a strong dipole moment on the adsorbent surface compared to the weak quadrupole moment of CO<sub>2</sub> (Liu and Wilcox, 2012). Thus, H<sub>2</sub>O molecules are selected for hydrogen bonding instead of CO<sub>2</sub> with the adsorbent.

Lewis acid-based interaction occurs between N-containing functional group on the adsorbent surface and the CO<sub>2</sub> molecule. Generally, the N atom is electron-rich, attributed to the presence of a lone pair of electrons, thus it facilitates the adsorption of CO<sub>2</sub>. Other than lewis acid-based interaction, some N-containing functional groups can form hydrogen bonds with CO<sub>2</sub> molecules owing to their naturally high electropositivity (Lim et al., 2016; Liu, C. et al., 2013). Thus, CO<sub>2</sub> can form hydrogen bonds with the N-containing functional group on the adsorbent. For instance, Fan et al. (2013) reported that a major of pyridone was present in the chitosan-derived CO<sub>2</sub> adsorbent, and contributed mainly to CO<sub>2</sub> adsorption. The presence of -OH adjacent to the N atom resulted in a  $p-\pi$  conjugation effect (from -OH) with the  $\pi$  bond, thus increasing the adsorbent's electron density and improving its Lewis basicity. Figure 3.23 shows the possible reaction that occurs during CO<sub>2</sub> adsorption to biochar/chitosan adsorbent. Although many studies have been carried out to identify the possible reaction mechanism for CO<sub>2</sub> adsorption on the carbon-based adsorbent, the variation of feedstock types can significantly affect the functional groups of the adsorbent, thus affecting the adsorption efficiency of CO<sub>2</sub>.



**Figure 3.23. Possible reaction mechanism of CO<sub>2</sub> adsorption on carbon-based adsorbent.**

Table 3.9 Summary of chitosan as CO<sub>2</sub> adsorbent.

Sample	Biochar porous characteristic					N content (wt%)	CO <sub>2</sub> adsorption capacity (mg/g) (adsorption temperature)	Ref.
	BET area (m <sup>2</sup> /g)	surface	Total volume (cm <sup>3</sup> /g)	pore	Average pore width (nm)			
Chitosan hydrochar	2.6		N/A		N/A	7.5	19.8 (25 °C)	(Chagas et al., 2020)
Carbon sphere	462		0.27		2.04	4.6	142 (25 °C)	(Wu, Q. et al., 2019)
Carbon sphere	384		0.27		N/A	11.6	154 (0 °C)	(Primo et al., 2012)
Chitosan hydrochar	1249		0.67		N/A	7.6	304 (0 °C) 194 (25 °C)	(Wang, Jing et al., 2021)
N,P-co-doped chitosan	895		0.73		6.56	N/A	234 (25 °C)	(Xiao, J. et al., 2022)
KOH activated N-doped chitosan	1928		0.72		N/A	4.1	172 (25 °C)	(Li, J. et al., 2022)
KAc activated N-doped chitosan	1273		0.46		N/A	5.4	156 (25 °C)	(Li, J. et al., 2022)
K <sub>2</sub> CO <sub>3</sub> activated N-doped chitosan	1147		0.42		N/A	5.3	155 (25 °C)	(Li, J. et al., 2022)
KHCO <sub>3</sub> activated N-doped chitosan	1054		0.38		N/A	8.4	146 (25 °C)	(Li, J. et al., 2022)
K <sub>2</sub> CO <sub>3</sub> activated chitosan	1673		0.73		0.60	5.3	169 (25 °C)	(Fan et al., 2013)
NaNH <sub>2</sub> modified chitosan	1740		0.98		N/A	5.1	278 (0 °C)	(Yang, C. et al., 2022)



### 3.2.4 Solid amine-based sorbent

Amine-based adsorbents have the advantages of high adsorption capacity, thermal stability, and good regeneration performance in comparison with granular solid adsorbents (Raganati et al., 2021). By means of the addition of amine functional groups, it could evenly disperse in solid adsorbents, providing alkaline sites for the adsorption of acid gas ( $\text{CO}_2$ ). Porous solid supports, such as porous silica, alumina, porous carbons, zeolites, polymers, and metal organic frameworks (MOFs), always have large pore volumes and specific area.  $\text{CO}_2$  adsorption performances of diverse amino-solids are discussed in the following sections.

#### 3.2.4.1 Reaction mechanism

Solid amine-based sorbents are the functional combination of aqueous amine and porous solid adsorbents. As for existing amines, tethered amines onto solid adsorbents could substantially reduce energy requirements to liberate captured  $\text{CO}_2$  from the relatively dilute amine solutions, and avoid equipment corrosion occurring during the amine scrubbing process. Conceivably, the interaction between amino groups is strengthened within the constrained space of porous solid material. From the perspective of porous solid adsorbents, the incorporated amine will dramatically improve  $\text{CO}_2$  capacity and selectivity via chemical adsorption even at low pressure, but might increase mass transfer resistance of adsorbate to contact amine groups within microporous materials. Therefore, the performance of solid amine-based sorbents reflects a compromise on the advantages and disadvantages between aqueous amine and porous solid adsorbents. To deeply uncover adsorption-desorption mechanism, the structure of amines and their reaction routes with adsorbate, the texture of different solid supports and their physisorption properties, as well as the interaction between amines and solid supports, should be taken complete account. Three aspects i.e. reaction mechanism of  $\text{CO}_2$  with amines, adsorption thermodynamics and kinetics, and the deactivation mechanism, are discussed.

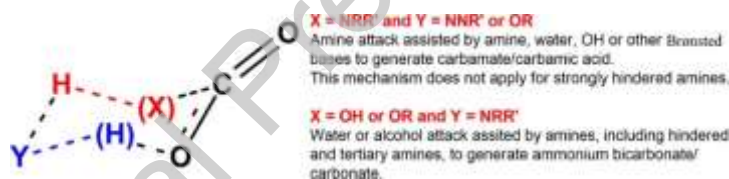
##### 3.2.4.1.1 Adsorption mechanism

$\text{CO}_2$  adsorption mechanism of solid amine-based sorbents is analogous to one that occurs by absorption of amine solutions via acid-base interaction, which is confirmed by numerous in situ spectroscopic studies using solution- and solid-state nuclear magnetic resonance (SSNMR) and infrared (IR) spectroscopy combined with theoretical calculations (Chen et al., 2018; Forse and Milner, 2020). Under dry conditions, the formation of carbamate is achieved by substituting hydrogen of amine with  $\text{CO}_2$ , which means only H-containing amines, i.e. primary and secondary amines are available. According to Reaction 3.3, two amidogens are necessitated to capture one molecule of  $\text{CO}_2$ . Whereas the introduction of moisture, which exists widely in various sources for  $\text{CO}_2$  capture, could improve amine efficiency by one fold via the formation of bicarbonate or carbonate compared with that without moisture. In Reaction 3.4, water attributes a hydroxide to  $\text{CO}_2$  molecule. Therefore, it is suitable for all primary, secondary and tertiary amines. Obviously, amine-based adsorbents could achieve higher  $\text{CO}_2$  adsorption under

humid conditions, while moisture is deleterious on the CO<sub>2</sub> adsorption capacity of porous zeolites and MOFs owing to their hydrophilic nature over exposed metal ions. It should be noted that the amine efficiency is limited to 0.5-1 under humid conditions because of kinetically controlled bicarbonate formation (Serna-Guerrero, 2008).



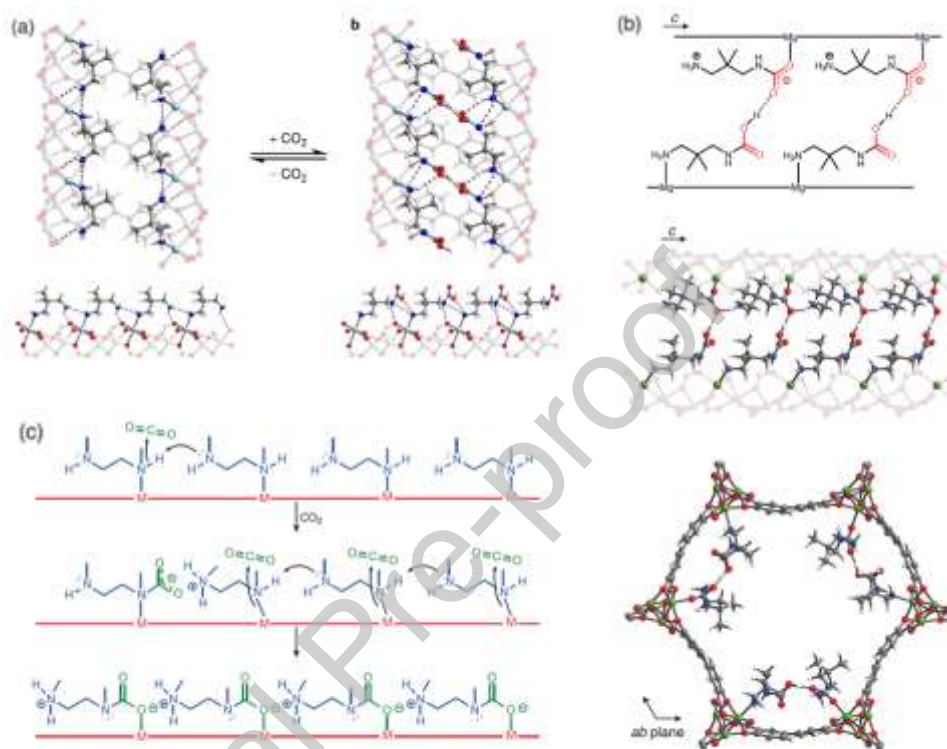
Said et al. (Said et al., 2020) proposed a unified approach to CO<sub>2</sub>-amine reaction mechanism in Figure 3.24. At high amine loading under dry conditions, nucleophilic attack of CO<sub>2</sub> by amines is primarily assisted by a neighbouring amine (X = N, Y = N), which leads to a 1,n-zwitterion (n>3) or to alkylammonium carbamate, and it depends on whether two amines involved are linked or separated. At low amine loading, nucleophilic attack of CO<sub>2</sub> by isolated amines may be assisted by hydroxyl groups (X = N, Y = O), leading to carbamic acid or hydronium carbamate. Under humid conditions, water may assist nucleophilic attack of CO<sub>2</sub> by amines (X = N, Y = O) to form hydronium carbamate or play a role of a nucleophile assisted by amines to form ammonium bicarbonate (X = O, Y = N) at the expense of carbamate. The latter mechanism applies for tertiary and hindered amines, regardless of surface density.



**Figure 3.24.** The unified schematic mechanism for CO<sub>2</sub>-amine-water interactions (Said et al., 2020).

Initially, amine-based silica sorbents are widely investigated. Therefore, classical preparation methods, referring to impregnation and grafting by silane linkage, are derived from amine-silica adsorbents. Meanwhile, the proposed reaction mechanism above is based on amino-silicas. In the last decade, thriving porous materials such as MOFs, covalent organic polymers (COPs), and their amine functionalized adsorbents have drawn more attention. New reaction pathways beyond the traditional formation of ammonium carbamates are then proposed (Forse and Milner, 2020). Long et al. proposed a unique cooperative mechanism of CO<sub>2</sub> adsorption involving the formation of ammonium carbamate chains (Milner et al., 2017; Siegelman et al., 2017), and firstly demonstrated the feasible formation of carbamic acid pair to compete with ammonium carbamate chain during CO<sub>2</sub> adsorption over dmpn-Zn<sub>2</sub>(dobpdc) (dmpn= 2,2-dimethyl-1,3-diaminopropane) (Figure 3.25a) (Milner et al., 2017). Later, they elucidated a new chemisorption mechanism using dmpn-Mg<sub>2</sub>(dobpdc), which involved the formation of a 1:1 mixture of ammonium carbamate and carbamic acid (Figure 3.25b) (Forse et al.,

2018). Also, a cooperative mechanism, the formation oxygen-bound carbamate chains by CO<sub>2</sub> inserting into the metal-N bonds, given rise to unusual step-shaped CO<sub>2</sub> adsorption (Figure 3.25c) (Kim, 2020; McDonald et al., 2015). It was anticipated that coordination forms of amine and porous material with different structure could give rise to a spectacular mechanism in the future.

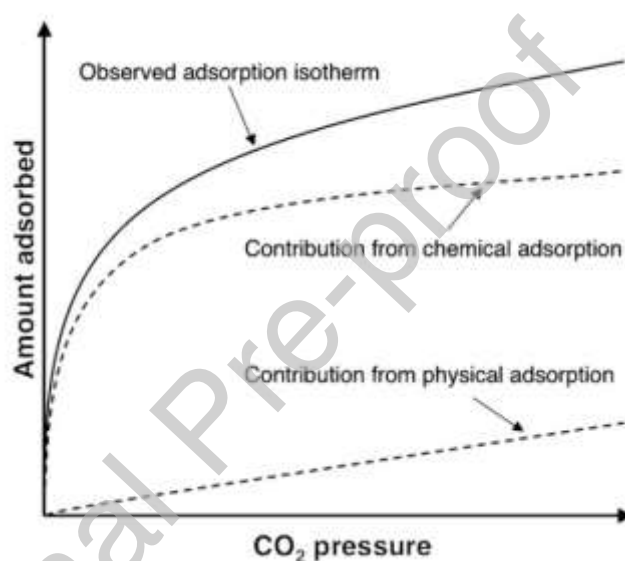


**Figure 3.25.** The cooperative mechanism over amine-functionalized MOFs sorbents (a) The formation of carbamic acid pairs over dmpn-Zn<sub>2</sub>(dobpdc) (Milner et al., 2017); (b) Mixed chemisorption structure with ammonium carbamate and carbamic acid in a 1:1 ratio for dmpn-Mg<sub>2</sub>(dobpdc) (Forse et al., 2018); (c) The formation of carbamic acids and mixed ammonium carbamates/carbamic acids over mmen-M<sub>2</sub>(dobpdc) (mmen=N,N9-dimethylethylene diamine, M=Mg, Mn, Fe, Co, Zn) (McDonald et al., 2015).

#### 3.2.4.1.2 Adsorption thermodynamics & kinetics

Equilibrium adsorption capacity, reaction heat, and kinetics are key parameters for overall evaluation. These parameters could be obtained by adsorption isotherms. The distinction caused by amine functionalization is principally summarised. As for amine-functionalized solid sorbents, CO<sub>2</sub> adsorption is implemented via two independent mechanisms, i.e. chemisorption with amine-functionalized groups and physisorption on surface of solid adsorbent. In Figure 3.26, chemical adsorption contributes to a

high initial CO<sub>2</sub> uptake at the lower partial pressure while physisorption is enhanced with the increasing partial pressure. Langmuir isotherm model and Freundlich isotherm model, suitable for both chemisorption and physisorption processes, are widely adopted for describing the adsorption behaviour of amine functionalized adsorbent. However, Serna-Guerrero et al. (Serna-Guerrero et al., 2010) pointed out that these two isotherm models were acceptable for describing adsorption profiles at low concentrations of CO<sub>2</sub> but less reliable at higher pressures. Therefore, they adapted a semi-empirical two-site Toth isotherm model, including two parts to represent chemisorption and physisorption, respectively. The model was successfully employed on different amine-functionalized materials with various adsorbates (Bollini et al., 2012a; Gebald et al., 2014).

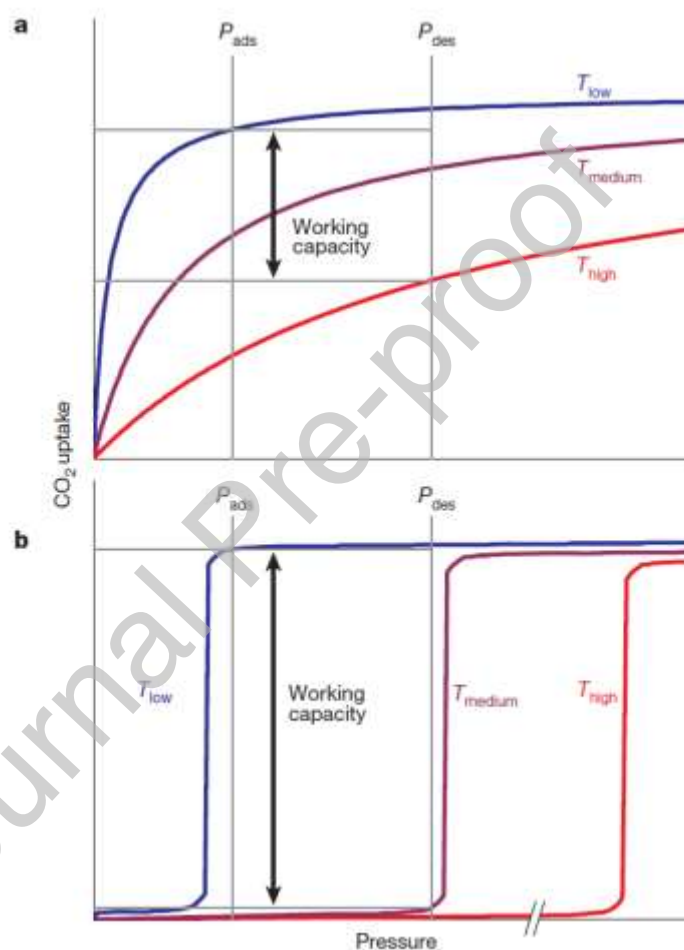


**Figure 3.26.** Schematic representation of CO<sub>2</sub> adsorption on amine-functionalized mesoporous adsorbents (Serna-Guerrero et al., 2010).

Adsorption heat can be calculated from the adsorption isosteric curve by applying Clausius–Clapeyron. Generally, adsorption heat lower than 50 kJ/mol indicates weak physical adsorption, while that higher than 50 kJ/mol indicates the effects of chemical adsorption or reaction (Gelles et al., 2019; Siriwardane, 2005). High adsorption heat demonstrates strong interaction between CO<sub>2</sub> and amine, and further improves CO<sub>2</sub> selectivity, however, will increase the temperature of the process. Higher temperatures can decrease the adsorption capacity of the adsorbents, meanwhile resulting in higher desorption energy demands. To reduce energy consumption, two approaches are listed as follows:

1) Tuning the structure of solid support material and its interaction with suitable amine types through a new reaction mechanism. For instance, the distinct adsorption route of dmpn-Mg<sub>2</sub>(dobpdc) to CO<sub>2</sub>, i.e. the formation of both ammonium carbamates and carbamic acids, results in high entropy penalty (-

74 kJ/mol) coupled with a large entropic penalty (-204 J/mol/K). It can reduce the temperature required to desorb CO<sub>2</sub> in a temperature-swing adsorption process to lower than 100 °C (Milner et al., 2017). Long et al. prepared serials of diamine-appended MOFs, which could behave as ‘phase-change’ adsorbents with unusual step-shaped CO<sub>2</sub> adsorption isotherms (McDonald et al., 2015). As shown in Figure 3.27, adsorption isotherm shifts markedly with temperature, resulting that a large working capacity can be achieved with only a small increase in temperature. Besides, they demonstrated tetraamine-appended MOFs with two-step cooperative CO<sub>2</sub> adsorption that could use low-temperature steam for the desorption process (Kim, 2020).

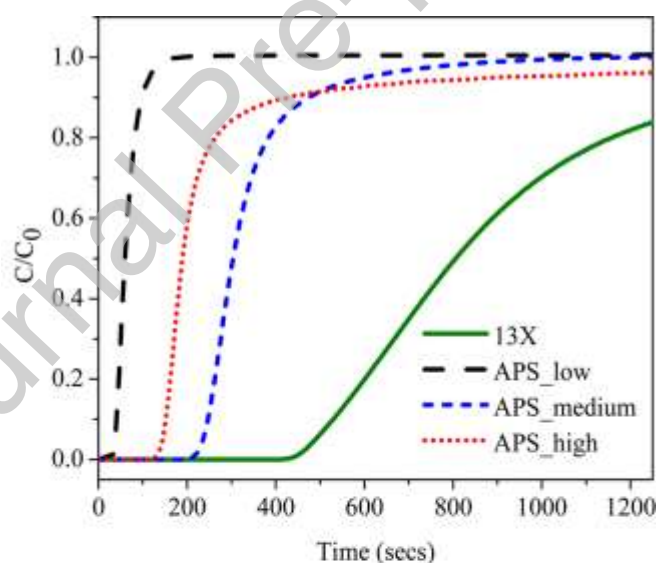


**Figure 3.27.** Variation in the idealized adsorption isotherm behaviour with temperature for a classical microporous adsorbent (a) The usual Langmuir-type isotherm shape, compared with that of a phase-change adsorbent (b) Step-shaped (sometimes referred to as ‘S-shaped’) isotherms (Kim, 2020).

2) System analysis and optimization of the whole reaction process. Zhang et al. (Zhang, W. et al., 2016) systematically evaluated the effect of significant parameters, i.e. adsorbent property, adsorption heat, specific capacity, working capacity, moisture adsorption, swing temperature difference and heat

recovery degree. The calculated regeneration heat for PEI/silica adsorbent was 2.47 GJ/tCO<sub>2</sub>, while this value was 3.9 and 3.3 GJ/tCO<sub>2</sub> for a typical aqueous and an advanced MEA system, respectively.

Similar to porous adsorbents, kinetics for amine-functionalized adsorbents can be modelled by pseudo-first order law, pseudo-second order law, Elovich equation, Avrami model, and film diffusion model, among which pseudo-first order and pseudo-second order models are the simplest to understand the interaction mechanism of gas-solid adsorption (Syeda Saba Fatima, 2021). In Figure 3.28, compared with benchmark adsorbent, the dynamic adsorption breakthrough curve of CO<sub>2</sub> over amine-functionalized adsorbents displayed a relatively sharp trend followed by a long tail. The sharp trend inferred favourable interactions between CO<sub>2</sub> and amine groups, while long tails signified large mass transfer resistance because of diffusion hindrance of amine groups (Bollini et al., 2012a, b). It has been well established that the adsorption behaviour of CO<sub>2</sub> onto benchmark adsorbent was driven by thermodynamic effects, while an opposing trend for amine functionalized adsorbent was controlled by kinetic effects. It is of significance to balance the thermodynamic and kinetic effects of CO<sub>2</sub> adsorption. Besides, adsorption kinetics are largely influenced by the process temperature, amine type, amine loading, and support material, which have been widely discussed in previous literature.



**Figure 3.28.** APS-functionalized silica adsorbents at three different amine loadings compared to the benchmark zeolite 13X at 25 °C (Bollini et al., 2012a, b).

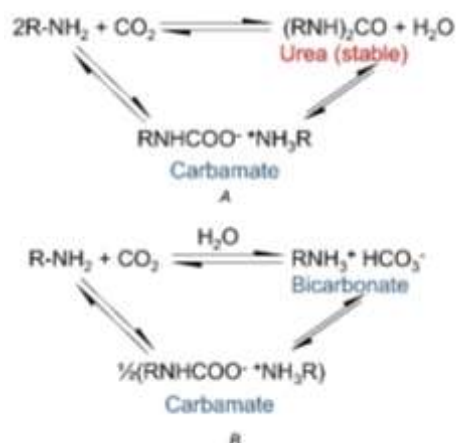
#### 3.2.4.1.3 Deactivation mechanism

Stabilities of amine-functionalized CO<sub>2</sub> adsorbents during multiple adsorption-desorption cycles are the prerequisite for its industrial applications. A robust adsorbent should withstand many adverse effects including physical and chemical properties, feed gas composition and characteristics, and operational

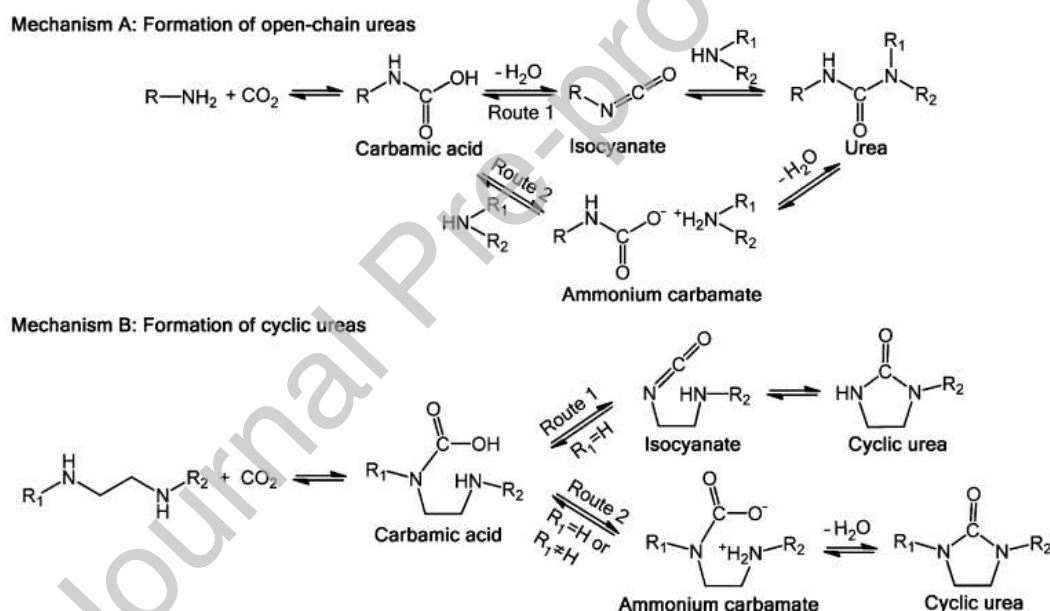
parameters. More detailed reviews have been summarized by Lashaki et al. (Jahandar Lashaki et al., 2019) and Fan et al. (Fan and Jia, 2022). Herein, chemical deactivation associated with the interaction between amines and different gas compositions is focused, such as O<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub> and CO<sub>2</sub>.

Due to the existence of oxygen in the feeding gas, such as 3-15% from power plant flue gas (Siegelman et al., 2021), 21% in the air, oxidative degradation of adsorbents has to be concerned. Akin to gas-liquid absorption systems, amine in adsorbents is prone to be oxidized to imine, imide, amide or nitron groups when exposed to high O<sub>2</sub> concentration, elevated temperature and metal ions (Heydari-Gorji, Aliakbar et al., 2011). Amine structure obviously affects its oxidative degradation, which indicates that single secondary amines and mixed amines readily degrade to oxygen-containing gas mixtures at high temperatures (Bali et al., 2013). Though strategies such as conversing primary amines into secondary/tertiary amines (Choi et al., 2016; Zhang et al., 2012), chelating ppm-level metal impurities of PEI (Min et al., 2018), and using longer linkers between amine groups in amino-polymers (Pang et al., 2018) could mitigate the adverse effect of oxygen, the mechanism of oxidative degradation is still unclear.

CO<sub>2</sub>-induced deactivation refers to the formation of stable urea between amine and CO<sub>2</sub>. In Figure 3.29, urea groups may form readily by direct interaction between amine species and CO<sub>2</sub> at high temperature under dry conditions. When moisture-containing gases are employed, urea formation can be strongly inhibited, even at a relatively low humidity (Belmabkhout, 2010; Li, K. et al., 2016). Sayari et al. (Sayari et al., 2012) investigated the interaction between CO<sub>2</sub> and amines-containing mesoporous silica under dry condition, and proposed different reaction pathways depending on the structure and nature of amine-containing species (Figure 3.30). As for primary amines, CO<sub>2</sub>-induced deactivation undergoes through intermediacy of isocyanate followed by reaction with primary or secondary amine into di- and trisubstituted open-chain urea or N-substituted imidazolidinones. As for materials containing ethylenediamine units with secondary amines, formation of the corresponding N,N'-disubstituted imidazolidinones takes place through the dehydration of ammonium carbamate or carbamic acid. Also, they pointed out that all or some CO<sub>2</sub>-deactivated materials may be regenerated via urea hydrolysis using a humidified inert gas under relatively high temperature (100-200 °C). Furthermore, Jung et al. (Jung et al., 2017) found that the conversion of primary into secondary amines in different oligomers and polymers via functionalization with 1,2-alkylepoxyde, 1,3-butadiene diepoxyde and epichlorohydrin could effectively inhibit the formation of urea linkages.



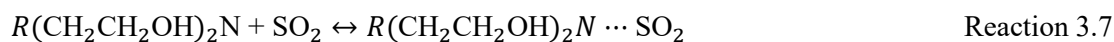
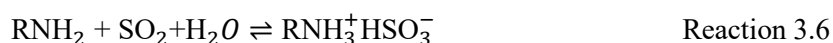
**Figure 3.29** (A) Schematic representation of urea formation under dry adsorption conditions, and (B) Inhibition thereof in the presence of added water vapour (Belmabkhout, 2010).



**Figure 3.30.** Mechanisms of  $CO_2$ -induced degradation of supported amines (Sayari et al., 2012).

Generally,  $SO_x$  and  $NO_x$  in the flue gases potentially cause adsorbent deactivation by competing adsorption with  $CO_2$ , resulting from adsorption reversibility on amines in the order of  $CO_2 > SO_2 > NO_2$  (A. Diaf, 1994). Since  $SO_2$  is a stronger Lewis acid,  $SO_2$  can interact strongly with all amines, including tertiary amines, through Reaction 3.5 under dry conditions and Reaction 3.6 under humid conditions, respectively. Nevertheless, Tailor and Sayari (Heldebrant et al., 2010; Tailor and Sayari, 2016; Yang et al., 2013) found that  $SO_2$  could react with tertiary amines by Reaction 3.7 and Reaction 3.8 to form non-covalent charge transfer complexes, leading to adsorbent deactivation.

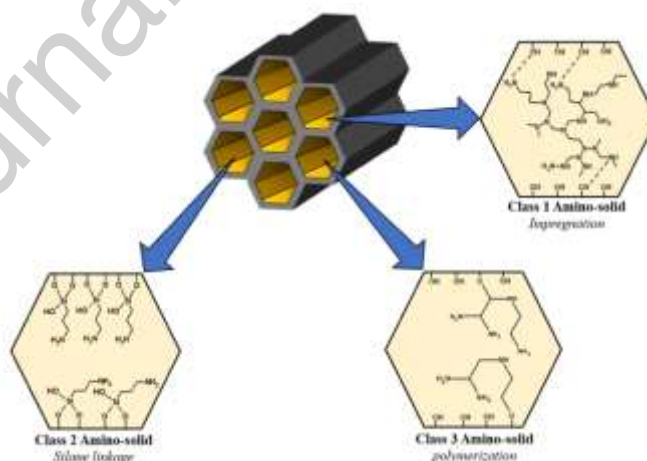




### 3.2.4.2 Modification of different adsorbents

#### 3.2.4.2.1 Description of three subclasses (I, II, III class)

Considering bond structures and preparation methods, amine-based adsorbents could be divided into three subclasses in Figure 3.31. Class I materials are prepared by physical impregnation with monomeric or polymeric within the pore of the supports, bonding through hydrogen bonds and/or dipole interactions. Class II materials are obtained by covalently grafting the targeted amines with relatively low molecule weight onto the surface of the support. As for Class III materials, they are prepared via in-situ polymerization of amine-containing monomers. Also, Class I materials are considered as promising candidates for industrial CO<sub>2</sub> capture because of high CO<sub>2</sub> adsorption capacity under the condition of low CO<sub>2</sub> concentration. However, shorter chained amines are preferable for the formulation of class II or class III adsorbents due to lower activation energies which aid in the facilitation of tethering (Bollini et al., 2011).



**Figure 3.31.** Amino-solids based on preparation methods (Didas et al., 2015).

#### 3.2.4.2.2 Porous Silica Supports (I, II, III)

As one of the important porous materials, porous silica is a chemically and thermally stable material with tunable textural and surface properties, e.g. pore size, pore distribution, surface area, and surface hydroxyl groups (Gawande et al., 2015; K, 1979; Verma et al., 2020). These features make it versatile and used in various technological or industrial applications, e.g. adsorption, medical, energy, catalyst and support materials (Liang et al., 2017). Thus, a variety of porous silica materials functionalized with amine have been synthesized and characterized to chemisorb CO<sub>2</sub> from different gas streams. For three classes of supported amine adsorbents, recent advances in porous silica support are summarized and discussed in this section.

#### *Class I: Amine-impregnated silica*

The first ever literature reported in the field of amines impregnated silica was by Song and others in 2002 (Xu, 2002), and they used a high surface area mesoporous silica MCM-41 as the support material for PEI loading, and the resulting adsorbent was termed as “molecular basket”. With PEI loading amount of 75 wt%, the highest CO<sub>2</sub> adsorption capacity of 3.02 mmol/g was achieved at a pure CO<sub>2</sub> atmosphere and 75 °C. The pore structure of porous silica was an important factor that affected the distribution of PEI. Son et al. (Son et al., 2008) further synthesized mesoporous silica with different pore structures and impregnated it with the same amount of PEI (50 wt%). CO<sub>2</sub> uptake capacity was in the order of KIT-6 (3D) > SBA-15 (1D) ~ SBA-16 (3D) > MCM-48 (3D) > MCM-41 (1D). The highest CO<sub>2</sub> adsorption capacity achieved by KIT-6 was mainly attributed to the large pore size and 3D structure. To further investigate the influence of the pore structure of silica on CO<sub>2</sub> adsorption, Yan et al. (Yan et al., 2011b) investigated PEI impregnated SBA-15 with different pore structures, and found that CO<sub>2</sub> adsorption amount increased proportionally with the total pore volume of SBA-15 support. However, pore size was not the main factor influencing CO<sub>2</sub> adsorption capacity. Besides, roles of micropores in SBA-15 were found not obvious as they have been blocked by amine (Yan, X. et al., 2013). Overall, the ideal silica support would have high pore volume, which can load a high amount of amines and it should leave the voids in the pores for CO<sub>2</sub> diffusion. Thus, extensive research on the amine-impregnated porous silica for CO<sub>2</sub> capture have been reported. Some typically porous silica supports used for amine impregnation are summarized and given in Table 3.10.

Table .10. Amine-porous silica CO<sub>2</sub> adsorbent prepared by physical impregnation method.

Support material	Amine type	Temperature (°C)	CO <sub>2</sub> partial pressure (atm)	Adsorption capacity (mg/g, dry CO <sub>2</sub> )	Ref.
MCM-41	PEI	75	0.15	89	(Xu X., 2005)

<b>Pore expanded MCM-41</b>	PEI	75	1	210	(Heydari-Gorji, A. et al., 2011)
<b>SBA-15</b>	PEI	75	0.15	105	(Yan et al., 2011b)
<b>As-syn SBA-15</b>	Tetraethylenepentamine	75	1	173	(Yue et al., 2006)
<b>HMS</b>	PEI	75	1	184	(Chen et al., 2010)
<b>KIT-6</b>	PEI	75	1	135	(Son et al., 2008)
<b>As-syn KIT-6</b>	PEI	75	1	139	(Kishor and Ghoshal, 2016)
<b>Silica monolith</b>	PEI	75	1	210	(Chen, C. et al., 2009)
<b>Mesocellular silica foam</b>	PEI	75	0.15	152	(Yan et al., 2011a)
<b>MSU-F silica</b>	Tetraethylenepentamine / diethanolamine	50	1	260	(Goepper et al., 2011)
<b>Fumed silica</b>	PEI	25	0.0004	52	(Goepper et al., 2011)
<b>CARiACT G10 silica</b>	PEI	80	1	123	(Ebner et al., 2011)
<b>Mesoporous silica nanotubes</b>	PEI	85	0.6	121	(Niu et al., 2016)
<b>Rice husk derived silica</b>	PEI	75	0.15	159	(Zeng and Bai, 2015)
<b>TUD-1 mesoporous sponge</b>	PEI	75	0.15	116	(Wang, X. et al., 2014)
<b>Hollow silica microspheres</b>	PEI	25	1	149	(Cecilia et al., 2016)

### *Class 2: Amine-containing silane modified silica*

The grafted amines on silica often have better thermal stability up to 200-250 °C when compared with physically impregnated silica (Sayari, 2006). Hydroxyl groups of silica supports played an important role because covalent bonds will be formed between hydroxyl groups and amino-silanes. Thus, available hydroxyl groups determine the content of amines grafted. Similar to the amine physically impregnated silica, the CO<sub>2</sub> adsorption capacity of amine containing silane modified silica was also affected by the pore structure of the silica support. Fayaz et al. (Fayaz and Sayari, 2017) found that P10 silica with a pore size of 21 nm exhibited a high CO<sub>2</sub> adsorption capacity of 86 mg/g after 3-[2-(2-aminoethylamino)ethylamino] propyltrimethoxysilane grafted. Lashaki et al. (Jahandar Lashaki et al., 2017) synthesized SBA-15 with different pore structures, and functionalized them with 3-[2-(2-Aminoethylamino) ethylamino] propyltrimethoxysilane for CO<sub>2</sub> adsorption. Results indicated that

amine-silane grafted SBA-15 with larger pore size exhibited a higher CO<sub>2</sub> adsorption capacity. The CO<sub>2</sub> capture performance of aminesilane-modified silica is included in Table 3.11.

**Table 3.11.** Amine-porous silica CO<sub>2</sub> adsorbent prepared by the amine-silane grafting method.

Support Material	Amine Type	Temperature (°C)	CO <sub>2</sub> partial pressure (atm)	adsorption capacity (mg/g, dry CO <sub>2</sub> )	Ref.
<b>Pore-expanded MCM-41</b>	N-(3-trimethoxysilylpropyl) diethylenetriamine	75	0.2	92	(Loganathan and Ghoshal, 2017)
<b>MCM-48</b>	2-[2-(3-trimethoxysilylpropylamino)ethylamino]ethylamine	25	0.15	70	(Nigar et al., 2016)
<b>SBA-15</b>	3-[2-(2-Aminoethylamino)ethylamino] propyltrimethoxysilane	25	0.05	83	(Jahandar Lashaki et al., 2017)
<b>HMS</b>	Aminopropyltrimethoxysilane	20	0.9	53	(Knowles and Chaffee, 2016)
<b>P10 silica</b>	3-[2-(2-Aminoethylamino)ethylamino] propyltrimethoxysilane	50	0.05	86	(Fayaz and Sayari, 2017)
<b>Amorphous silica</b>	[3-(methylamino)propyl]trimethoxysilane	30	0.17	60	(Park et al., 2016)
<b>SBA-16</b>	N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane	60	0.15	32	(Wei et al., 2008)
<b>SBA-12</b>	3-Aminopropyltrimethoxysilane	25	0.1	46	(Zelenak et al., 2008)
<b>MSU-F silica</b>	3-[2-(2-Aminoethylamino)ethylamino] propyltrimethoxysilane	45	0.3	72	(Lee et al., 2011)
<b>Silica gel</b>	3-Aminopropyltrimethoxysilane	27	1	18	(O. Leal, 1995)
<b>Fumed silica</b>	3-[2-(2-Aminoethylamino)ethylamino]propyltrimethoxysilane	25	1	41	(Czaun et al., 2013)
<b>SiO<sub>2</sub> aerogel</b>	3-Aminopropyltrimethoxysilane	25	0.1	86	(Cui, Sheng et al., 2011)
<b>Double-walled silica nanotube</b>	3-[2-(2-Aminoethylamino)ethylamino] propyl trimethoxysilane	25	1	98	(Ko et al., 2013)

*Class 3: In situ polymerized amine on silica*

Class 3 adsorbents bind amines covalently to hydroxyl groups of the support, which is similar to class 2 sorbents. However, the densities of amine groups are similar to class 1. Thus, Jones et al. defined class 3 as a combination of class 1 and 2 (Sanz-Perez et al., 2016a). Usually, the adsorption capacities of Class 3 sorbents are higher than that of Class 2 adsorbents due to their high amine loading amounts, and they also have good reusability in successive runs. Porous silica support has a large surface area, pore volume and plenty of surface -OH groups, which facilitate the grafting of the amines. Thus, different kinds of silica materials have attracted considerable research interest since 2000s (Acosta et al., 2004; Chaikittisilp, W. et al., 2011; Lunn and Shantz, 2009). A summary of the CO<sub>2</sub> adsorption capacity of grafting amines by in-situ polymerization onto porous silica is given in Table 3.12.

**Table 3.12.** Amine-porous silica CO<sub>2</sub> adsorbent prepared by the in-situ polymerization method.

Support material	Amine type	Temperature (°C)	CO <sub>2</sub> partial pressure (atm)	adsorption capacity (mg/g, dry CO <sub>2</sub> )	Ref.
Pore-expanded - MCM-41	3-[2-(2-aminoethylamino)ethylamino]propyl trimethoxysilane	25	0.05	62	(Sayari, 2006)
SBA-15	3-aminopropyltrimethoxysilane	25	0.1	50	(Chaikittisilp, W. et al., 2011)
Mesoporous Silica	Polyethenimine	75	0.15	124	(Klinthong et al., 2016)
Silica spheres	Trimethoxy [3-(methylamino)propyl]silane	50	0.1	44	(Hahn et al., 2016)
Silsesquioxane aerogel	(3-Aminopropyl)triethoxysilane	50	0.01	134	(Kong et al., 2016)
Precipitated silica	(3-Aminopropyl)triethoxysilane	50	0.14	45	(Quang et al., 2017)
Silica monolith	tetraethylenpentamine	75	1	171	(Wen et al., 2010)
SiO <sub>2</sub> aerogel	3-Aminopropyltriethoxysilane	25	0.1	86	(Cui, Sheng et al., 2011)

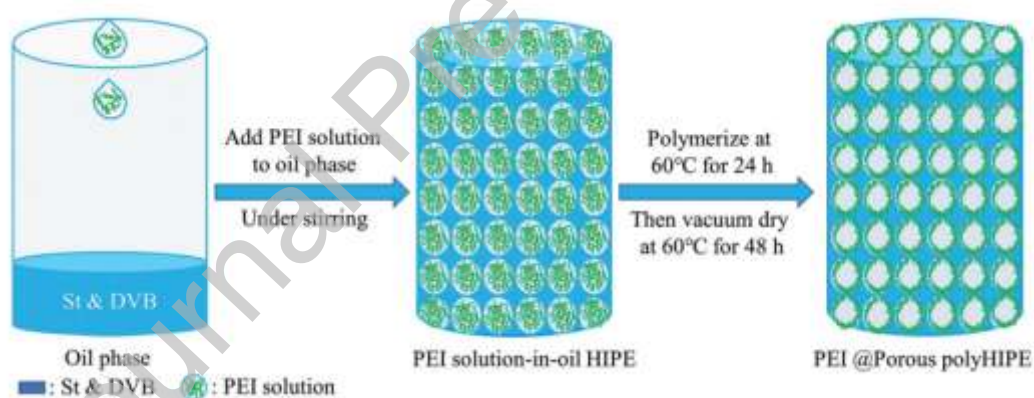
3.2.4.2.3 *Polymer Supports (I, II, III)*

Polymers can refer to inorganic polymers (e.g. geopolymer, clay etc.), organic polymers (i.e. porous organic polymers, POPs) and inorganic-organic coordination polymers (e.g. MOFs). Since geopolymer, MOFs and their amine-tethered adsorbents have been introduced in other sections, amine-tethered POPs adsorbents are especially focused. Amine adsorbent known as HSC+, which was applied by NASA to regeneratively remove CO<sub>2</sub> from space shuttle in 20 years ago, belongs to the amine-tethered polymer adsorbents (Satyapal, 2001). This proprietary material bonds polyethyleneimine (PEI) to solid polymethyl methacrylate polymeric support, with poly(ethylene glycol) (PEG), to enhance CO<sub>2</sub> adsorption and desorption rates. POPs with ultrahigh surface areas, tunable pore structure and adjustable chemical properties can be synthesized diversely from organic molecular building blocks (Cooper, 2009; Dawson et al., 2012), and are ideal supports for amine functionalization because of their chemically inert, high stability, and low production cost (Slater and Cooper, 2015). Amine modification can improve POPs not only for CO<sub>2</sub> adsorption capacity, but also for CO<sub>2</sub> selectivity (Lu et al., 2012). For example, amine e.g. EDA, DETA, TETA, TAEA, AA, PEI and 2,5-dibromoaniline anchored onto PPN-6, CMP-1, polymethylmethacrylate (PMMA) could increase CO<sub>2</sub> uptake when compared with corresponding pristine supports (Gelles et al., 2019; Han et al., 2015; Hu, Xiayi et al., 2020; Jahandar Lashaki et al., 2019; Jiang et al., 2013; Mukhtar et al., 2020). A detailed list of amine-modified POPs and their CO<sub>2</sub> adsorptive properties can be found in a recent review (Zou, L. et al., 2017).

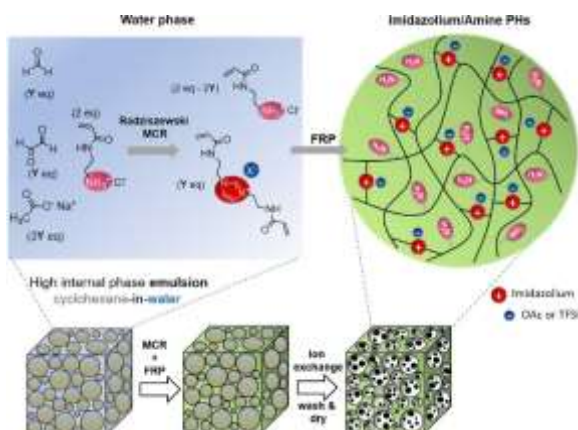
For amine-loaded polymers, researchers have focused on amine selection and polymer preparation. Jafari et al. (Jafari et al., 2017) synthesized mesoporous polydivinylbenzene (PDVB) materials using 2, 2'-Azobis (2-methylpropionitrile) (AIBN) as the initiator through microwave-assisted polymerization and then impregnated the material with the amine-rich co-monomers of vinylimidazole (VI) and vinyl triazole (VT). With more active sites, VT-modified PDVB had a maximum CO<sub>2</sub> adsorption of 2.65 mmol/g at 0 °C under 100 kPa, while the adsorption capacity of VI-modified PDVB was 2.35 mmol/g under the same conditions. Liu et al. (Liu, F. et al., 2017) prepared PDVB through one-pot, timsolvothermal polymerization and impregnated them with PEI. The optimum formulation was 58 wt% PEI (to the adsorbent) impregnated PDVB (0.58PEI@PDVB) with maximum adsorption capacities of 3.76 and 3.00 mmol/g under pure CO<sub>2</sub> and 10% CO<sub>2</sub>, respectively, at 75 °C. The stability under both conditions was maintained after ten adsorption cycles under both dry and wet conditions. Zheng (Zheng et al., 2019) synthesized an N-abundant and mesopores-rich POPs by solvothermal copolymerization of divinylbenzene (DVB) and 1-vinylimidazole (VI) without the use of any templates. It was found that PEHA-impregnated P (DVB-VI) adsorbents displayed CO<sub>2</sub> capacities as high as 4.56 mmol/g at 75 °C and atmospheric pressure, together with excellent CO<sub>2</sub>/N<sub>2</sub> selectivity and good recycling stability.

To reduce the cost of material development, a simplified preparation route and utilization of existing polymers have drawn more attention. Wang et al. (Wang, S. et al., 2022) reported a novel synthesis method by in situ ring-opening grafting copolymerization of aziridine with the polyHIPE (HIPE=high internal phase emulsion). The adsorption capacity of 2.40 and 3.25 mmol/g could be achieved under

dry and humid conditions at 0.1 atm partial pressure of CO<sub>2</sub>, respectively. Further, they fabricated 4.0PEI70k@polyHIPE adsorbent by one-step method (Figure 3.32), which indicated a maximum adsorption capacity of 4.18 mmol/g at 20 °C under humid conditions (Wang, S. et al., 2021). Stiernet et al. (Stiernet et al., 2022) combined Radziszewski's multicomponent reaction and high internal phase emulsion (HIPE) polymerization in a one-pot manner (Figure 3.32). The bifunctional amine/imidazolium foams revealed superior CO<sub>2</sub> capture performances when compared to their monofunctional counterparts, indicating the synergy between functional groups. Yang et al. (Yang, Y. et al., 2019) developed a facile strategy that converted a cost-effective porous organic polymer, which was synthesized by Friedel-Crafts alkylation reaction of dichloro-p-xylene, into outstanding CO<sub>2</sub> adsorbents through one-step post-synthesis functionalization with polyamines. Adsorbents showed good CO<sub>2</sub> uptake capacity, fast adsorption-desorption kinetics and excellent stability toward both water vapor and regeneration cycles under dynamic flow conditions. As for existing polymers, Meng et al. (Meng et al., 2021) found that tethering PEI onto conventional porous supports HP20 could achieve superior adsorption properties with above 4 mmol/g and cyclic stability with around 1% loss after 30 cycles, which were rather than ones synthesized through complex approaches.



**Figure 3.32.** Synthetic procedure for PEI functionalized polyHIPE (Wang, S. et al., 2021).



**Figure 3.33.** Imidazolium/amine polyHIPEs synthesis combining Radziszewski MCR and emulsion templating polymerization (Stiernet et al., 2022).

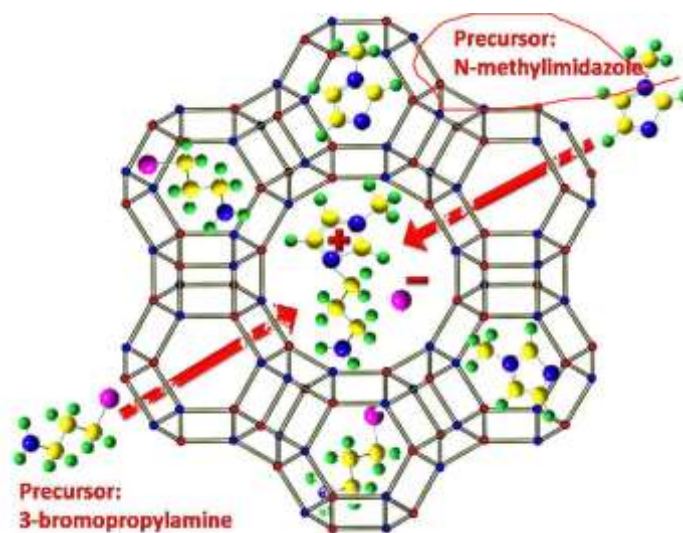
#### 3.2.4.2.4 Zeolite Supports (I, II, III)

Zeolites, possessing the merit of tunable textural properties, variable pore sizes, and interconnecting channels and cavities, have been widely used in CO<sub>2</sub> via their steric effect, kinetic effect, equilibrium effect and trapdoor effect (Bai, R. et al., 2022; Yue et al., 2022). However, hydrophilic nature and physical adsorption behavior incapacitate zeolites for CO<sub>2</sub> separation under the conditions of humidity, high temperature (>30 °C), and low pressure (<2 bar). Amine-functionalized zeolites have been demonstrated to empower CO<sub>2</sub> capture from humid streams and improve selectivity (Chen, C. et al., 2015; Kim, C. et al., 2016; Kolle, J. M. et al., 2021; P. D. Jadhav, 2007; Su et al., 2010). Two kinds of amine-functionalized zeolites, prepared by impregnation and grafting, are discussed as follows respectively.

##### *Class I: Physical impregnation of monomeric and polymeric amines.*

Impregnation is a cost-effective method for the preparation of amine-functionalized zeolites. However, two issues should be addressed. Firstly, microporous zeolite is prone to be blocked by impregnated amines, resulting in the decrease of adsorption capacity. Murge et al. (Murge et al., 2019) found that the adsorption capacity of in-house-synthesized zeolites decreased with increasing TEPA loading. Meanwhile, the decrease in physisorption capacity was several times higher than the expected increase in chemisorption capacity. However, commercial zeolites had an optimal amine loading 2.5%. On the contrary to high amine loading up to 70%, Panda et al. (Panda et al., 2019) synthesized a binder-containing zeolite 4A bodies (IBA-Z4A) modified with 0.3% iso-butylamine, which exhibited excellent CO<sub>2</sub> adsorption performance with adsorption capacity of 2.56 mmol/g and remarkably high CO<sub>2</sub>/N<sub>2</sub> selectivity of 335 at 25 °C and 1 bar. Whereas CO<sub>2</sub>/N<sub>2</sub> selectivity of pristine binder-containing zeolite 4A bodies was only 24. The other issue is that the impregnated amines is liable to evaporate at elevated temperature, especially for small-molecular amines. It remarkably affects adsorption thermal stability. To hinder the amine loss, Yu et al. (Yu, Y. et al., 2014) proposed a ship-in-a-bottle method to prepare NaY zeolites loaded with amine functionalized ionic liquids (Figure 3.34) by employing unique cage structures of microporous zeolites. The trick of this method lay in the in-situ synthesis of large molecular ionic liquid, 1-aminopropyl-3-methylimidazolium bromide ([APMIM]Br) within super cage using the smaller precursors (e. g. N-methylimidazole and 3-bromopropylamine) that can diffuse through zeolite windows. Whereas the formed target guest ([APMIM]Br) is too big to cross the windows. These host-guest systems exhibited superb adsorption capacity up to 4.94 mmol/g and good cyclic ability with 5% decreasing adsorption capacity after 20 working cycles.





**Figure 3.34.** Schematic illustration of ship in a bottle synthesis of [APMIM]Br@NaY (Liu, F. et al., 2017).

Heat consumption and cost should be taken into account for industrial applications. Kalantarifard et al. (Cheng et al., 2021b) synthesized EDA impregnated ZSM-5 for CO<sub>2</sub> adsorption, with the highest CO<sub>2</sub> adsorption capacity of 6.13 mmol/g in the presence of water at 75 °C. Microwave heating was employed for the desorption process, and the fastest desorption time was 9 min for 70% EDA loaded ZSM-5. Recently, Cheng et al. (Cheng et al., 2021a) tethered monoethanolamine (MEA) and hydroxyethyl ethylenediamine (AEEA) onto HZSM-5 zeolites via wet impregnation method, respectively. The result indicated that MEA and AEEA fixed HZSM-5 zeolites had good CO<sub>2</sub> adsorption capacities, with maximum values of 4.27 and 4.44 mmol/g, respectively. Notably, the CO<sub>2</sub> desorption process of AEEA loaded HZSM-5 exhibited a low activation energy of 54.27 kJ/mol. HZSM-5 zeolite provided a large number of free H<sup>+</sup> ions to directly participate in carbamate breakdown, and metal atoms (Al) that attached to N atom of carbamate, thereby stretching the C-N bond and promoting decomposition. To further reduce the cost of adsorbents, Thakkar et al. (Thakkar et al., 2017) prepared ZSM-5, zeolite-Y and SAPO-34 from kaolin clay and modified them with TEPA for capturing CO<sub>2</sub> from the air. The best adsorption capacity was 1.12 mmol/g for the TEPA-loaded ZY at 25 °C using 5000 ppm CO<sub>2</sub> in nitrogen.

#### *Class II: Grafting.*

Similar to the impregnated amine onto zeolites, the grafted amine can reduce adsorption capacity, but improve the selectivity over other gas and amine stability. Kim et al. (Kim, J.-Y. et al., 2013) functionalized SAPO-34 with 3-aminopropyltrimethoxysilane (APMS). It demonstrated that the functionalized mesoporous SAPO-34 (NH<sub>2</sub>-SAPO(M)-34) had a lower CO<sub>2</sub> adsorption capacity than its pristine counterparts. However, it exhibited improved CO<sub>2</sub>/N<sub>2</sub> selectivity. Bezerra et al. (Bezerra et al., 2014) found that increasing amine grafted to zeolite 13X adsorbent tended to reduce micropore

volume of the resulting adsorbents by pore blocking with MEA. Kim et al. (Liu, F. et al., 2017) synthesized an ethylenediamine-grafted Y zeolite with working capacities higher than 1.1 mmol/g over 20 temperature swing adsorption (TSA) cycles, and reported that the strongly co-adsorbed H<sub>2</sub>O within the hydrophilic zeolite micropores suppressed urea formation under desorption conditions according to Le Chatelier's principle. Yang et al. (Yang et al., 2012) concluded that CO<sub>2</sub> adsorption capacity varied in the sequence of MCM-22 (2.09) > NH<sub>2</sub>-ITQ-2 (1.73) > ITQ-2 (1.64) > NH<sub>2</sub>-MCM-22 (1.52) > MCM-36 (1.32) > NH<sub>2</sub>-MCM-36 (1.20) > Fe-MCM-22 (1.20 mmol/g) at 298 K, but NH<sub>2</sub>-ITQ-2 showed exceptionally high CO<sub>2</sub>/N<sub>2</sub> selectivity of 10.8.

To further boost the stability of APTES grafted zeolite β, Liu et al. (Liu, L. et al., 2020) proposed an alkyl-functionalization method for the stoichiometric conversion of primary amines to secondary amines. Alkyl-functionalized-APTES zeolite exhibited the adsorption capacity of 1.44 mmol/g of 15% CO<sub>2</sub> at 90 °C and a very high sorption rate ( $t_{1/2}$ =0.69 min of over 90% of total sorption capacity within 5 min). Also, long-term stability after 20 cycles in a TSA operation with above 0.9 mmol/g at pure CO<sub>2</sub> regeneration was observed.

Recently, another zeolite-like adsorbent, geopolymers, was adopted as efficient amine support. Chen et al. (Chen, H. et al., 2022) grafted APTES onto the geopolymer treated with nitric acid and achieved a high grafting amount of 3.5 mmol N/g due to the large specific surface area of 412 m<sup>2</sup>/g and superior silanol density of 4.25 mmol/g. The as-prepared amine functionalized solid sorbent showed a remarkable adsorption capacity of 1.82 mmol/g with fast adsorption kinetics and low energy requirement for regeneration.

### *Class III*

Liang et al. (Liang et al., 2022) immobilized monoethanolamine (MEA) and ethylenediamine (ED) via ionic bond to the zeolite Y framework to overcome amine degradation. The elemental analysis demonstrated that ED had successfully grafted almost twice as many amino groups as MEA within the same solvent concentration. It indicated that 20% ED@HY had the highest CO<sub>2</sub> adsorption capacity of 1.76 mmol/g at 90 °C with superior performance in cyclic thermal stability in the condition of the adsorption temperature of 90 °C and the desorption temperature of 150 °C. Satriyo et al. (Wahono et al., 2021) deposited a solid-state amine adsorbent on natural mordenite-clinoptilolite zeolite through a simple plasma polymerization. The plasma deposition of amine polymer under certain conditions resulted in a significant increase in surface area-weighted CO<sub>2</sub> adsorption capacity and weakened the strength of the interaction between CO<sub>2</sub> and the adsorbent.

Post-synthetic functionalization by organic molecules has been proposed as an effective strategy to tailor the adsorption properties of zeolites (Nik et al., 2011). Small amine molecules can be chemisorbed onto micropore walls via conjugate acid-base formation between the Brønsted acid sites of the zeolite and the basic N atoms. Kwon et al. (Kwon et al., 2022) adopted this method to covalently attached

various functional groups (-PhNH<sub>2</sub>, -PhCH<sub>2</sub>NH<sub>2</sub>, -PhCOOH, -PhOH, -Ph) onto the micropore walls of beta zeolites to modify their adsorption properties. The results conducted that the benzylamine functionalized  $\beta$  zeolite exhibited higher CO<sub>2</sub> adsorption than its pristine counterpart under flue gas conditions with 10.5% CO<sub>2</sub>, 5% H<sub>2</sub>O and 84.5% N<sub>2</sub>, which might be attributed to the synergistic effect of the hydrophobic benzene and basic amine moieties in the benzylamine group.

Hierarchical microporous and amorphous is another strategy for improving the properties of amine functionalized zeolite (Ge et al., 2021; Jia, Y. et al., 2022). Liu et al. (Liu, X. et al., 2016) fabricated a series of 5A zeolite-based hybrids with a shell of mesoporous silica-supported-amine (5A@MSAs) to dynamically hinder the diffusion of water molecules into the zeolite core. 5A@MSA-30 was demonstrated to be the best candidate for CO<sub>2</sub> capture with the CO<sub>2</sub> uptake as high as 5.05 mmol/g at 298 K and 10 cyclic stable adsorption/desorption operation.

#### 3.2.4.2.5 MOF Supports (I, II, III)

MOFs as porous crystalline materials are composed of metal nodes that are combined with organic linkers. In view of their well-ordered porous structures, such as high specific surface area, pore volume and easily adjustable composition and pore structure, MOFs have been viewed as promising candidates for CO<sub>2</sub> capture technology. Over the last two decades, research on MOFs and MOFs-amine composites has been the study button and widely studied. However, the crystalline or microcrystalline form factor has limited the development of MOFs for commercialization application (Sanz-Perez et al., 2016a). Therefore, the modification of MOFs by amines has been sought in an effort to advance the utility of MOFs.

##### *Class I*

Class I amine-modified MOFs are common in adsorption applications because large pore volume allows the loading of high amine contents, which results in physisorption and chemisorption conducted at the same time. Therefore, Class I amino-MOFs always show high CO<sub>2</sub> adsorption capacity. However, unlike traditional mesoporous amine-based adsorbents, MOFs are microporous materials. The bulky amino polymers have the possibility to block the pores during the impregnation process and even decompose the structure (Gelles et al., 2019). A majority of Class I amino-MOFs select MIL-101 as support in view of its chemical stability, which could prevent pore degradation as a result of unintended side reactions (Gelles et al., 2019). For example, the impregnation of PEI onto MIL-101 was first reported in 2013. The results demonstrated an increase in CO<sub>2</sub> adsorption capacity, reaching 5.1 mmol/g at 25 °C, 1.75 bar when the amine loading is 100% (Lin, Y. et al., 2013). Also, Uio-66 was impregnated with PEI and achieved a CO<sub>2</sub> adsorption capacity of 1.65 mmol/g and 2.41 mmol/g under the condition of a dry and humid environment. After several adsorption and regeneration experiments, the composite

could recover the capture performance completely (Xian et al., 2015a). Typical class I amino-MOFs are summarized in Table 3.13.

**Table 3.13** CO<sub>2</sub> adsorption capacity of class I amine-MOFs CO<sub>2</sub> adsorbent.

Support Material	Amine Type	Temperature (°C)	CO <sub>2</sub> partial pressure (kPa)	Adsorption capacity (mmol/g, dry CO <sub>2</sub> )	Reference
MIL-101	PEI	25	175	5.10	(Lin, Y. et al., 2013)
MIL-101	PEI	25	100	3.30	(Xian et al., 2015a)
MIL-101(Cr)	PEI	25	10	1.30	(Yan, Q. et al., 2013)
MIL-101(Cr)	DETA	23	100	3.56	(Hu, Y. et al., 2014)
MIL-101(Fe)	DETA	25	100	1.82	(Mutyala et al., 2019b)
MIL-101(Cr,Mg)	PEI	25	100	3.04	(Gaikwad et al., 2019)
MIL-101(Cr)	PEI	75	100	3.81	(Mutyala et al., 2019a)
MIL-101	TREN	25	0.04	2.60	(Darunte et al., 2016)
MIL-53	TEPA	45	500	1.40	(Martínez et al., 2016)
Uio-66	PEI	65	100	1.65	(Xian et al., 2015a)
Uio-66	PEI	35	10	0.75	(Xian et al., 2015a)
Cu <sub>3</sub> (BTC) <sub>2</sub>	PEI	25	100	10.0	(Aarti et al., 2016)
HKUST-1	TEPA	45	500	2.3	(Martínez et al., 2016)
ZIF-8	TEPA	45	500	2.0	(Martínez et al., 2016)
ZIF-8	PEI	35	10	1.4	(Yang, F. et al., 2022)
ZIF-8	PEI	65	100	1.61	(Xian et al., 2015b)
Zn/Co ZIF	PEI	25	100	1.82	(Cheng, J. et al., 2019)
MOF-177	DETA	25	100	2.83	(Gaikwad et al., 2021)
MOF-177	TEPA	25	100	3.82	(Gaikwad et al., 2021)
MOF-177	TEPA	55	100	4.6	(Gaikwad et al., 2021)
Mg-MOF-74	TEPA	25	100	5.68	(Su et al., 2017)

### Class II

Class II amine-MOFs CO<sub>2</sub> adsorbents are rarely reported due to the lack of functionalized sites, which are suitable for silane attachment. Pokhrel et al. (Pokhrel et al., 2018) grafted APTES onto ZIF-8, and

the results suggested CO<sub>2</sub> adsorption capacity of 0.8 mmol·g<sup>-1</sup> was achieved under the condition of 1 bar dry CO<sub>2</sub> atmosphere at 25 °C. Also, the capture performance of class II amino-ZIF didn't change (0.8 mmol/g) under 10% RH humid condition and humidified stability was improved. Also, deprotonated MEA was grafted onto UiO-66, which reveals a CO<sub>2</sub> capacity of 0.8 mmol·g<sup>-1</sup> at 0.15 bar CO<sub>2</sub> and 298 K, and it could maintain the adsorption performance even at high relative humidity (82%) (Li, L.-J. et al., 2015). When it comes to adsorption performance, markedly improvement was not observed between class II and class III amino-MOFs. Therefore, considering the inefficient synthesis procedure of preparation of amino-MOFs, class II amino-MOFs prepared by the grafting method are not suitable for scaled applications (Gelles et al., 2019).

### Class III

As for class III amine-MOFs CO<sub>2</sub> adsorbents, less energy is required for amine-tethering in comparison with the energy used for silane attachment of class II amino-MOFs making them attractive candidates for capture application. As for class III materials, ED was first incorporated into ZIF-8, and the experimental results demonstrated the potential for stable CO<sub>2</sub> adsorption. At 1 bar, the composite showed a CO<sub>2</sub> adsorption capacity of 0.68 mmol/g (Pokhrel et al., 2018). Since then, various supports have been selected for amine modification with different amines. For example, MIL-101 was grafted with PEHA and TEPA, and increased CO<sub>2</sub> adsorption capacities were observed, with the highest adsorption capacity up to 3.1 mmol/g at 25 °C, 1 bar (Huang et al., 2016). Similarly, a number of attempts have been conducted for Mg<sub>2</sub>/DOPDC and Mg<sub>2</sub>(dobpdc). And class III amino-MOF adsorbents are listed in Table 3.14 (Gelles et al., 2019).

**Table 3.14** CO<sub>2</sub> adsorption capacity of class III amine-MOFs CO<sub>2</sub> adsorbent.

Support Material	Amine Type	Temperature (°C)	CO <sub>2</sub> partial pressure (kPa)	Adsorption capacity (mmol/g, dry CO <sub>2</sub> )	Reference
ZIF-8	ED	25	100	0.68	(Pokhrel et al., 2018)
ZIF-8	ED	25	2500	10.0	(Zhang, Z. et al., 2013)
ZIF-8	ED	35	1000	4.8	(Thompson et al., 2013)
MIL-101	PEHA	25	100	1.3	(Anbia and Hoseini, 2012)
NH <sub>2</sub> -MIL-101	TEPA	25	100	3.1	(Huang et al., 2016)
MIL-101(Cr)	TEPA	25	100	2.75	(Wang, X. et al., 2012)
Mg <sub>2</sub> /DOPDC	m-2	25-120	100	5.0	(Siegelman et al., 2017)
Mg <sub>2</sub> /DOPDC	mm-2	25-120	100	5.1	(Siegelman et al., 2017)
Mg <sub>2</sub> /DOPDC	mmen	25-120	100	5.0	(Siegelman et al., 2017)

<b>Mg<sub>2</sub>/DOPDC</b>	i-2	25-120	100	4.9	(Siegelman et al., 2017)
<b>Mg<sub>2</sub>/DOPDC</b>	ii-2	25-120	100	5.1	(Siegelman et al., 2017)
<b>Mg<sub>2</sub>/DOPDC</b>	e-2	25-120	100	4.5	(Siegelman et al., 2017)
<b>Mg<sub>2</sub>/DOPDC</b>	ee-2	25-120	100	4.4	(Siegelman et al., 2017)
<b>Mg<sub>2</sub>/DOPDC</b>	e-2-e	25-120	100	4.6	(Siegelman et al., 2017)
<b>Mg<sub>2</sub>(dobpdc)</b>	dmen	40	100	4.34	(Lee, W.R. et al., 2015)
<b>Mg/DOBDC</b>	ED	25	100	4.5	(Lee, W.R. et al., 2014)
<b>Mg/DOBDC</b>	ED	25	0.04	1.6	(Choi, S. et al., 2012)
<b>Mg/DOBDC</b>	mmen	25-75	100	4.0	(McDonald et al., 2015)
<b>Mg<sub>2</sub>(dobpdc)</b>	pn	40	100	4.6	(Milner et al., 2017)
<b>Mg<sub>2</sub>(dobpdc)</b>	mpn	40	100	3.8	(Milner et al., 2017)
<b>Mg<sub>2</sub>(dobpdc)</b>	dmpn	40	100	4.2	(Milner et al., 2017)
<b>Co/DOBDC</b>	mmen	25-75	100	3.9	(McDonald et al., 2015)
<b>Fe/DOBDC</b>	mmen	25-75	100	3.5	(McDonald et al., 2015)
<b>Mn/DOBDC</b>	mmen	25-75	100	3.5	(McDonald et al., 2015)
<b>Ni/DOBDC</b>	mmen	25-75	100	3.9	(McDonald et al., 2015)
<b>Zn/DOBDC</b>	mmen	25-75	100	3.0	(McDonald et al., 2015)

### 3.2.4.2.6 Carbon Supports (I, II, III)

Carbonaceous adsorbents are utilized widely in the field of gas adsorption and separation processes due to high surface area, large pore volume, high stability and relatively low adsorption/desorption temperatures (Lee, M.-S. et al., 2015). Amine-modified carbonaceous materials, such as activated carbon (AC), carbon nanotubes (CNTs) and porous carbon supports, could perform similar CO<sub>2</sub> adsorption performance as amine-modified porous silica because of their stable structural pores. Among various carbonaceous materials, cost-effective ACs are the most common in practical applications. ACs supports always use lignocellulose and coal, e.g. coconut shell, bamboo and coke, as raw materials. After the physical or chemical activation process, pore structures of ACs are improved. The high surface area of ACs allows for subsequent amine modification. After surface amine modification, ACs display higher affinities towards CO<sub>2</sub>, which could then improve CO<sub>2</sub> adsorption capacity. As advanced materials, CNTs have been investigated widely in recent years in light of their high thermal and chemical stability as well as their unique physiochemical properties. Additionally, CNTs exhibit similar CO<sub>2</sub> adsorption performance as functionalized high surface area ACs (Lawson et al., 2018).

*Class I*

Class I materials have been widely investigated due to the simplicity of the physical impregnation method. Gholidoust et al. impregnated DEA onto oil sands coke-based ACs and reported the highest CO<sub>2</sub> adsorption capacity of 5.63 mmol/g at 50 °C. The results suggested a 75% improvement in comparison with commercial zeolite 13X (Gholidoust et al., 2017). Moreover, the effects of different amines, including DEA, MDEA and TEPA were investigated. The results indicated that ACs impregnated with secondary amines (DEA) have a more profound reaction with CO<sub>2</sub> than tertiary amines (MDEA), which agreed with CO<sub>2</sub> and amine reactivity: order primary>secondary>tertiary (Gholidoust et al., 2017). Also, the stimulatory effect of water was proven by MDEA@AC, increasing from 0.58 mmol/g to 1.70 mmol/g at 20% RH. Gibson physically impregnated EDA and TETA onto microporous and mesoporous ACs. The results demonstrated that microporous ACs were not suitable for amine-impregnation because the filling of the external channel led to the blockage of pores and then restrained further diffusion into the inner pores (Gibson et al., 2015). For CNTs, Zhou compared the CO<sub>2</sub> capture capacity of two types PEI-modified CNTs (L-PEI and B-PEI). The results suggested that although lower CO<sub>2</sub> adsorption capacity was achieved by L-PEI-impregnated CNT when compared with CNT modified by B-PEI, it exhibited lower desorption and better stability, which allowed for practical application for a long time (Zhou, Z. et al., 2017). CO<sub>2</sub> adsorption capacity of class I amine-carbon materials are shown in Table 3.15.

**Table 3.15.** CO<sub>2</sub> adsorption capacity of class I amine-carbon materials CO<sub>2</sub> adsorbent.

Support Material	Amine Type	Temperature (°C)	CO <sub>2</sub> partial pressure (kPa)	Adsorption capacity (mmol/g, dry CO <sub>2</sub> )	Ref.
Oil sands coke-based AC	DEA	50	66	5.63	(Gholidoust et al., 2017)
Oil sands coke-based AC	MDEA	50	66	0.58	(Gholidoust et al., 2017)
Oil sands coke-based AC	TEPA	50	66	0.90	(Gholidoust et al., 2017)
AC	MEA	75	10	1.70	(Bezerra et al., 2011)
AC	TEA	75	10	0.27	(Bezerra et al., 2011)
Palm shell-based AC	AMP	25	30	1.50	(Lee, C.S. et al., 2013)
Palm shell-based AC	AMPD	25	30	1.20	(Lee, C.S. et al., 2013)

AC	AMP	26	15	0.77	(Khalil et al., 2012)
AC	MEA	25	15	1.11	(Khalil et al., 2012)
Mesoporous AC	BPEI	25	0.04	2.25	(Wang, J. et al., 2015)
Mesoporous AC	BPEI	25	0.5	3.34	(Wang, J. et al., 2015)
Nanoporous carbon	PEI	75	100	0.26	(Tang et al., 2013)
Nanoporous carbon	PEI	75	100	1.01	(Tang et al., 2013)
Nanoporous carbon	PEI	75	10	0.23	(Tang et al., 2013)

### Class II

Class II amino-carbon materials are always focused on CNTs supports rather than ACs supports because covalent functionalization on the CNTs interface does not compromise the structural integrity of the supports (Gelles et al., 2019). By means of covalently bonding PEI onto functionalized-single wall CNTs (SWCNTs), enhanced CO<sub>2</sub> adsorption capacity could reach 1.77 mmol/g at 75 °C, 1 bar (Eoghan P. Dillon, 2008). Similarly, increased CO<sub>2</sub> uptake was also observed by APTES-modified multi-wall CNTs (MWCNTs), reaching 1.25 mmol/g 60 °C and 0.15 bar with 5 wt% APTES loading. Also, in the presence of water, CO<sub>2</sub> capture capacity increased with the increase of water content. Under the same condition of temperature, pressure and amine loading, CO<sub>2</sub> uptake increased from 1.25 mmol/g to 1.53 mmol/g at 35% RH (Su et al., 2009). What's more, due to the combined adsorption capacities of chemisorption and physisorption for amine-based CNTs, CO<sub>2</sub> adsorption capacity enhanced with the increase of amine loading amounts. The investigation of PEI-modified MWCNTs demonstrated the steam and resultant suitability for CO<sub>2</sub> capture in post-combustion process after eleven working cycles (Zhou et al., 2018). Class II amine-carbon adsorbents are listed in Table 3.16.

**Table 3.16.** CO<sub>2</sub> adsorption capacity of class II amine-carbon materials CO<sub>2</sub> adsorbent.

Support Material	Amine Type	Temperature (°C)	CO <sub>2</sub> partial pressure (kPa)	Adsorption capacity (mmol/g, dry CO <sub>2</sub> )	Reference
SWCNT	PEI	75	100	1.77	(Eoghan P. Dillon, 2008)
MWCNT	APTES	60	15	1.25	(Su et al., 2009)
MWCNT	APTES	50	15	1.95	(Su et al., 2011)
MWCNT	PEI	70	20	0.98	(Zhou et al., 2018)
CNTs	APTS	25	10	0.93	(Chungsyng Lu, 2008)



CNTs	APTS	25	50	2.19	(Chungsyng Lu, 2008)
Granular AC	APTS	25	50	1.81	(Chungsyng Lu, 2008)
CNTs	APTS	20	15	0.98	(Su et al., 2009)

### Class III

CO<sub>2</sub> adsorption capacities of Class III amine-carbon materials have also been investigated widely, especially for ACs. Firstly, after anchoring TETA onto the surface of carbonaceous material, the highest CO<sub>2</sub> adsorption performance was 1.90 mmol/g with 10 wt% TAEA loadings at 70 °C and 1 bar, and CO<sub>2</sub>/N<sub>2</sub> selectivity also increased (Zhao et al., 2010). Zhao et al. modified graphene oxide with ED, DETA and TETA. In particular, ED modified graphene oxide showed the highest CO<sub>2</sub> adsorption capacity in the presence of a longer amine chain and enhanced N content, reaching 1.06 mmol/g with 50 wt% ED loadings (Zhao et al., 2012). Houshand et al. grafted ED and DETA onto AC. The results suggested that the inclusion of toluene in the solvent resulted in increased active sites (Lee, C.S. et al., 2013). The CO<sub>2</sub> adsorption capacity of class III amine-carbon materials is summarized in Table 3.17.

**Table 3.17** CO<sub>2</sub> adsorption capacity of class III amine-carbon materials CO<sub>2</sub> adsorbent.

Support material	Amine type	temperature (°C)	CO <sub>2</sub> partial pressure (kPa)	Adsorption capacity (mmol/g, dry CO <sub>2</sub> )	Ref.
Carbonaceous material	TAEA	70	100	1.90	(Zhao et al., 2010)
Graphene oxide	ED	30	100	1.06	(Zhao et al., 2012)
Palm shell-based AC	MMEA	25	30	1.00	(Lee, C.S. et al., 2013)
Mesoporous carbon	PEI	30	100	3.80	(Wang, J. et al., 2013)

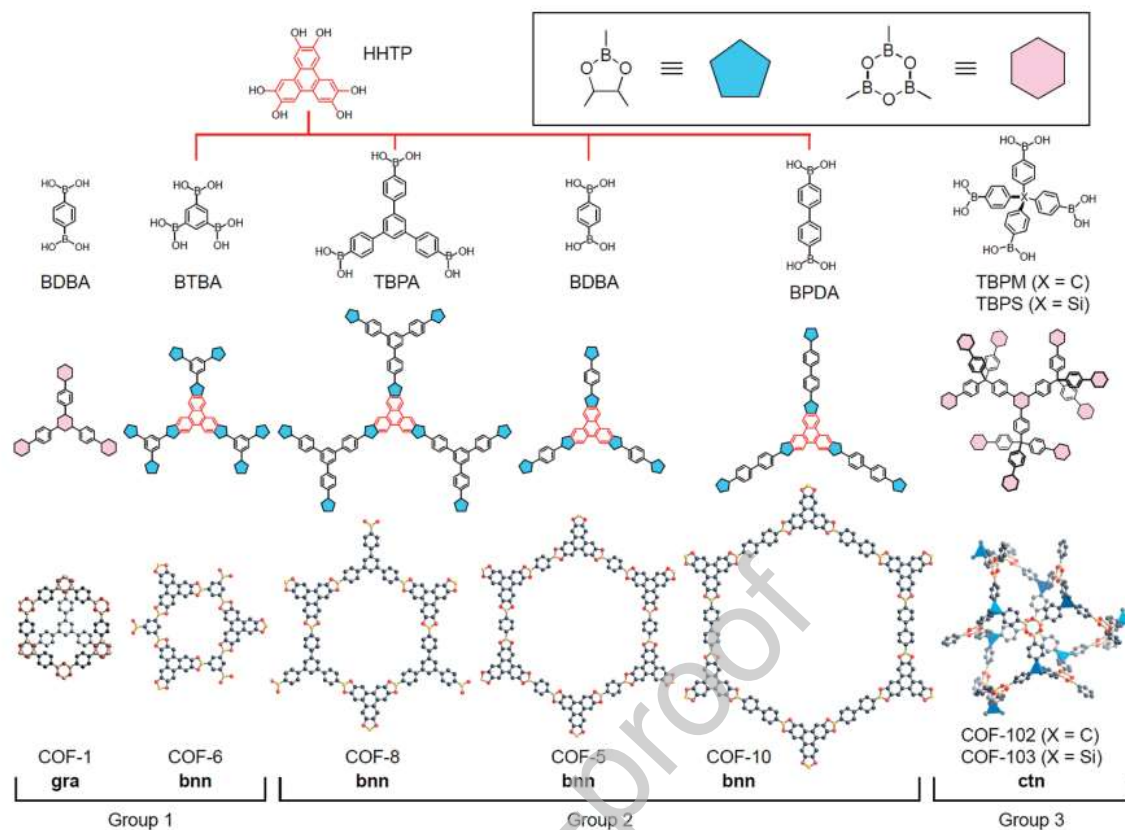
## 3.2.5 Other low-temperature solid adsorbents

### 3.2.5.1 COF-based materials for CO<sub>2</sub> capture

Covalent organic frameworks (COFs), a newly emerging class of porous crystalline materials, have been regarded as a promising alternative for CO<sub>2</sub> capture due to their easy pore surface engineering, ordered pore distribution, structural tenability endow them with excellent CO<sub>2</sub> selectivity, good stability, and low energy requirement for regeneration even under moist conditions (Cote et al., 2005; El-Kaderi et al., 2007; Tilford et al., 2006). COFs are constructed by strong organic covalent bonds in a periodic arrangement entirely from light elements such as C-C, C-N, C-O, B-O, C=N, and C-Si (Biswal et al., 2013; Wan et al., 2008). Since the first pioneering work of CO<sub>2</sub> adsorption of COFs in 2009, great

efforts have been devoted to improving the CO<sub>2</sub> capture performance of COFs, including Boron-based COFs, Triazine-Based COFs, and Imine-Based COFs (Aksu et al., 2022; Van Der Jagt et al., 2021; Zeng et al., 2016).

**Boron-based COFs.** According to the structural dimensionality and corresponding pore size, the boron-based COFs can be classified into three groups: Group 1 consists of 2D structures with 1D small pores (9 Å for each of COF-1 and COF-6), group 2 includes 2D structures with large 1D pores (27, 16, and 32 Å for COF-5, COF-8, and COF-10, respectively), and group 3 is comprised of 3D structures with 3D medium-sized pores (12 Å for each of COF-102 and COF-103) (Figure 3.35) (Furukawa and Yaghi, 2009; Modak and Jana, 2019). As previously reported, Ar adsorption isotherm of COFs follows the sequence of BET surface area, COF-102 (3620-3530 m<sup>2</sup> g<sup>-1</sup>) > COF-10 (1760 m<sup>2</sup> g<sup>-1</sup>) > COF-5 (1670 m<sup>2</sup> g<sup>-1</sup>) > COF-8 (1350 m<sup>2</sup> g<sup>-1</sup>) > COF-1 and COF-6 (750 m<sup>2</sup> g<sup>-1</sup>). However, CO<sub>2</sub> uptake capacity at 273 K and 1 bar decreased in the order of COF-6 > COF-1 > COF-103 > COF-102 > COF-8 > COF-5 > COF-10, that is, group 1 > group 3 > group 2 COFs. COF-6 with a 9 Å pore diameter can adsorb CO<sub>2</sub> as high as 85 cm<sup>3</sup> g<sup>-1</sup> at 273 K and 1 bar, outperforming the other six COFs despite its lowest BET surface area of (750 m<sup>2</sup> g<sup>-1</sup>), indicating that the low-pressure CO<sub>2</sub> uptake mainly depends on the pore width of COFs rather than the BET surface area and pore volume. The adsorbed amount of CO<sub>2</sub> at 298 K and 55 bar follows the order of COF-102 (611 cm<sup>3</sup> g<sup>-1</sup>) > COF-103 (606 cm<sup>3</sup> g<sup>-1</sup>) > COF-10 (514 cm<sup>3</sup> g<sup>-1</sup>) > COF-5 (443 cm<sup>3</sup> g<sup>-1</sup>) > COF-8 (321 cm<sup>3</sup> g<sup>-1</sup>) > COF-6 (158 cm<sup>3</sup> g<sup>-1</sup>) > COF-1 (117 cm<sup>3</sup> g<sup>-1</sup>), that is group 3 > group 2 > group 1 COFs, revealing that the high-pressure CO<sub>2</sub> uptake capacities are dominantly determined by pore volumes and BET surface area of COFs (Olajire, 2017).



**Figure 3.35.** Condensation reactions of boronic acids and HHTP are used to produce COFs (top) and resulting fragments of COFs (middle). Atomic connectivity and structures of crystalline 2D and 3D COFs (bottom). The topology and the group classification number are indicated for each COF. Inset: the  $C_2O_2B$  (blue) and the  $B_3O_3$  (pink) rings are formed by condensation reactions (Furukawa and Yaghi, 2009).

**Triazine-based COFs.** Compared to boron-based COFs, triazine-based COFs exhibit excellent thermal and chemical stability, high  $CO_2$  capacity, and selectivity even in water vapor, making them ideal candidates for  $CO_2$  capture (Bhunja et al., 2013; Katekomol et al., 2013). The first triazine-based COF (CTF-1), possessing a hexagonal structure with 1D pore channels and a BET surface area of  $1000 \text{ m}^2 \text{ g}^{-1}$ , was synthesized by Thomas and co-workers via the ionothermal synthesis method (Kuhn et al., 2008). They constructed CTF-1 by cyclotrimerization of 1,4-dicyanobenzene in the presence of  $ZnCl_2$  at  $400 \text{ }^\circ\text{C}$ . As previously reported, perfluorinated alkanes not only exhibit more hydrophobic and lipophobic characteristics than their corresponding hydrocarbons but also show an extraordinary affinity to  $CO_2$  molecules. Han et al. designed and synthesized a perfluorinated triazine-based COF (FCTF-1) for selective  $CO_2$  capture (Zhao et al., 2013). It was found that the  $CO_2$  capture capacity of FCTF-1 was as high as  $1.76 \text{ mmol g}^{-1}$  at  $273 \text{ K}$  and  $0.1 \text{ bar}$  due to the enhanced  $CO_2$  electrostatic interaction caused by the high electronegativity of F. In addition, FCTF-1 exhibited an exceptional  $CO_2$ -

$N_2$  selectivity of 77 under kinetic flow conditions in mixed-gas breakthrough experiments because the incorporation of F groups produced a significant amount of ultra-micropores ( $<0.5$  nm). Moreover, FCTF-1 proved to be tolerant to water and its  $CO_2$  capture performance remained excellent when there was moisture in the gas mixture, due to the hydrophobic nature of the C–F bonds. Because only a few triazine-based COFs exhibit crystallinity to some extent and their performance greatly depends on the synthetic conditions, the abovementioned drawbacks are inevitable issues during their further development (Ren et al., 2012).

**Imine-based COFs.** Another class of COFs is the imine-based COFs, first developed by Yaghi and co-workers using the strategy of dynamic covalent chemistry (Uribe-Romo et al., 2009). Compared with the CTFs, the imine-based COFs have much better crystallinity and structural regularity, which are beneficial to tuning the order of pore size (Kandambeth et al., 2013; Kandambeth et al., 2015). Imine-based COFs are divided into two types based on the covalent formation of distinct  $-C=N-$  bonds. One is the “Schiff base” type formed by the co-condensation of aldehydes and amines, and the other is the “hydrazine” type built by the co-condensation of aldehydes and hydrazides (Uribe-Romo et al., 2011). The first application of imine-based COFs in  $CO_2$  adsorption was reported by Banerjee et al. in 2012 (Kandambeth et al., 2012). They reported two chemically stable (acid and base) 2D COFs (TpPa-1 and TpPa-2) through reversible and irreversible routes, which were constructed from 1,3,5-triformylphloroglucinol (Tp) with p-phenylenediamine (Pa-1) and 2,5-dimethylp-phenylenediamine (Pa-2), respectively. The  $CO_2$  uptake of TpPa-1 and TpPa-2 was measured to be 78 and 64  $cm^3 g^{-1}$  at 273 K and 1 bar, respectively. More COFs were prepared using similar building blocks with different functional groups (Chandra et al., 2013). The order of  $CO_2$  capacity at 273 K and 1 bar is TpPa-1  $>$  TpPa- $NO_2$  (73  $cm^3 g^{-1}$ )  $>$  TpPa-2 (64  $cm^3 g^{-1}$ )  $>$  TpBD- $(NO_2)_2$  (52  $cm^3 g^{-1}$ )  $>$  TpBD (40  $cm^3 g^{-1}$ )  $>$  TpBDMe $_2$  (37  $cm^3 g^{-1}$ )  $>$  TpPa-F $_4$  (35  $cm^3 g^{-1}$ )  $>$  TpBD-(OMe) $_2$  (27  $cm^3 g^{-1}$ ). Interestingly, these water and chemically stable COFs can be delaminated using the mechanical grinding route to transform into covalent organic nanosheets that were characterized via transmission electron microscopy and atomic force microscopy. The stability of COFs is a central issue before any applications, and the stability of imine-based COFs in most organic solvents and water, when compared with boron-based COFs, has motivated researchers to incorporate several polar groups in the pore walls of imine-based COFs for enhanced  $CO_2$  capture. More importantly, the good water and chemical stabilities of some imine-based COFs also favor their regeneration without loss of their  $CO_2$  uptake performance. All these merits of imine-based COFs coupled with high  $CO_2$  selectivity, large  $CO_2$  capacity, and moderate heat of adsorption will provide a powerful platform for designing functional materials for  $CO_2$  capture.

#### **Surface chemistry of COF based $CO_2$ capture**

EL-Mahdy et al. (El-Mahdy et al., 2018) in 2018 conducted an experiment to synthesize and adsorb  $CO_2$  on triphenylamine COFs (TPA-3NH $_2$ ) and (triphenyltriazine COFs) (TPT-3NH $_2$ ). Various triacrylaldehydes were used in the synthesis of COFs. These varied in planarity, nitrogen concentrations,

and symmetry. Through monitoring the monomer symmetry and planarity, specific crystalline COFs can be prepared targeting particular applications.

Symmetrical monomers were also used in many studies (Gao, Q. et al., 2018; Haase et al., 2017; Zhai et al., 2017), but none showed good gas storage properties. El-Mahdy et al. (El-Mahdy et al., 2018) thought to control the fluctuation in the crystallinity of COFs and study its effect on CO<sub>2</sub> adsorption. The XRD confirmed the crystallinity of the material, which increased with increasing monomers. The surface area of TPT-COF-6 synthesized from most planar and symmetrical linkers came out to be 1535 m<sup>2</sup>g<sup>-1</sup> (calculated with BET). Although, another material (TPT-COF-5) reported a surface area of 1747 m<sup>2</sup>g<sup>-1</sup>, the highest CO<sub>2</sub> uptake capacity was still shown by TPT-COF-6. The study concluded that planarity and symmetry were the two most important factors to vary the total surface area of COFs.

Very few numbers of research have been seen about synthetic routes which can affect the structural variations of COFs. Gao et al. (Gao, Q. et al., 2018) discovered that the combination of tetraphenylethane (Ascherl et al., 2016; Pang et al., 2016) will give [4+4] TPE-COF-I and [2+4] TPE-COF-I upon heating in o-dichlorobenzene and n-butanol solvents, respectively. Keeping it as a basis, the new TPE-COF-II was prepared. It showed surprisingly high CO<sub>2</sub> uptake of 23.2 wt% at 1 bar and 273 K, whereas TPE-COF-I showed only 13.4 wt% CO<sub>2</sub> adsorption. TPE-COF-I and TPE-COF-II displayed a BET surface area of 1535 m<sup>2</sup>g<sup>-1</sup> and 2168 m<sup>2</sup>g<sup>-2</sup>, respectively.

#### ***Effect of water on CO<sub>2</sub> adsorption using COF***

While many COFs have shown good future for CO<sub>2</sub> capture, the industrial implementation of COFs is affected by their intolerance towards harsh conditions like water (Li, H. et al., 2018; Uribe-Romo et al., 2011; Zhang, B. et al., 2018). The crystal structure of COFs depends on the reversible reactions in synthesis process. In the reactions, the amorphous products first dominate the structure, but slowly the formation of low energy products take place, making COF crystals as major products (Zhu and Zhang, 2017). The reactions with which may COFs are synthesized are generally reversible and thus the crystals suffer degradation in mild aqueous surroundings (Spitler et al., 2011). Due to all these complications of reversible reactions, it is emphasized to prepare MOFs from non-reversible reactions. It is a very challenging task, but effective if possible. For the first time, Kandambeth et al. (Kandambeth et al., 2012) prepared COF (TpPa-1 and TpPa-2) from an irreversible reaction. The developed technique was a two-step method; first is reversible Schiff base reactions, and the second is an irreversible keto-enol tautomerization. The CO<sub>2</sub> adsorption capacity of TpPa-1 at 273K was 153 mg.g<sup>-1</sup>. This capacity is in relation to COF-6 (Furukawa and Yaghi, 2009), but with high stability. To further test the material, COFs were immersed in water for 7 days and various analysis were carried. There was no change in the pXRD peaks, and no new peaks were noticed in FTIR testing. Furthermore, the TpPa-2 did not show any change in surface area, FTIR, and XRD analysis even after soaking in NaOH for 7 days. This exceptional stability is due to the irreversible keto-enol tautomerization reaction.

Abdelnaby et al. (Abdelnaby et al., 2018) prepared amine-functionalized crosslinked porous polymer (KFUPM-1) using 1,4-benzenediamine, formaldehyde, and pyrrole with HCl as the catalyst. High concentration of primary and secondary amines in the framework offered very high selectivity for CO<sub>2</sub> over N<sub>2</sub> (i.e. 14 at 298 K) with CO<sub>2</sub> uptake of 15.1 cm<sup>3</sup>g<sup>-1</sup> in wet conditions. The material also exhibited stable activity for 45 cycles with similar selectivity. Later, Abdelnaby et al. (Abdelnaby et al., 2019) prepared another novel crosslinked microporous organic polymer (KFUPM-2) via Friedel-Crafts alkylation between pyrrole and phenothiazine, crosslinked by paraformaldehyde. The material processed 39.1 cm<sup>3</sup>g<sup>-1</sup> CO<sub>2</sub> uptake at 273 K with CO<sub>2</sub>/N<sub>2</sub> selectivity value of 51. Another polymer KFUPM-4 developed from different monomer exhibited superior CO<sub>2</sub> uptake in wet conditions. The presence of aniline and pyrrole monomers dispenses CO<sub>2</sub>-philic properties to the material. It also offers high CO<sub>2</sub>/N<sub>2</sub> selectivity of 79 and CO<sub>2</sub>/CH<sub>4</sub> selectivity of 16. It was also reported that the existence of water vapours in feed improves the CO<sub>2</sub> uptake capacity, which is due to the strong solubility of CO<sub>2</sub> in the presence of water (Alloush et al., 2020).

### 3.2.5.2 Conjugated microporous polymers (CMPs) for CO<sub>2</sub> capture

CMPs (Conjugated Microporous Polymers), represent another class of amorphous covalent organic polymers with a considerable conjugated skeletal structure. These polymers are constructed using  $\pi$ - $\pi$  conjugated rigid structural units, resulting in a rigid framework that can achieve complete conjugation system through tautomerism involving single, double, and triple bonds. The covalent bonds connecting the structural elements ensure the stability of CMPs even at elevated temperatures, making them highly suitable for CO<sub>2</sub> adsorption applications. CMPs have attracted great attention as a versatile platform for CO<sub>2</sub> adsorption, primarily owing to their remarkably high specific surface area (BET), total volume ( $V_{\text{total}}$ ), and exceptional thermal stability. Through manipulating the structural design and synthetic approach, CMPs are then allowed for tuning their CO<sub>2</sub> adsorption capacity and selectivity.

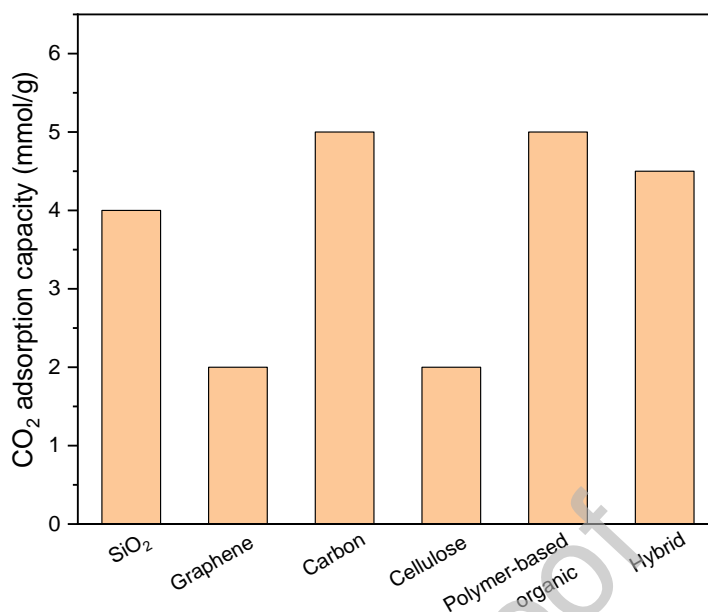
For example, Su et al. (Xu, Yanhong et al., 2019) synthesized two distinct porphyrin-contained CMPs, namely Porp-TPE-CMP and Porp-Py-CMP, using a FeCl<sub>3</sub>-catalyzed coupling reaction. The specific surface area of Porp-TPE-CMP measured at 547 m<sup>2</sup> g<sup>-1</sup> exceeded that of Porp-Py-CMP registered at 31 m<sup>2</sup> g<sup>-1</sup>. This considerable higher BET values of Porp-TPE-CMP is indicative of the substantially higher CO<sub>2</sub> adsorption capacity (88.75 mg g<sup>-1</sup>) when compared to Porp-Py-CMP (54.41 mg g<sup>-1</sup>) under conditions of 273 K and 0.1 MPa. Furthermore, the selectivity ratios for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> between Porp-TPE-CMP and Porp-Py-CMP were evaluated and found to be 55.3 and 40.8, as well as 4.1 and 5.1, respectively.

CMPs are typically prepared through various reactions and by employing different monomers, leading to the fabrication of polymers with diverse CO<sub>2</sub> adsorption properties attributed to variations in porosity and functional groups. Hu and his group (Zhou, H. et al., 2019) synthesized three distinct CMPs using cationic cyclization polymerization, employing monomers with multiple enediyne moieties. The

specific surface area measurements for CMP1, CMP2, and CMP3 were found to be 767, 624, and 780  $\text{m}^2 \text{g}^{-1}$ , respectively. Moreover, the values for specific microporous surface area ( $S_{\text{micro}}$ ) and micropore volume ( $V_{\text{micro}}$ ) for CMP1 were notably higher, at 481  $\text{m}^2 \text{g}^{-1}$  and 0.19  $\text{cm}^3 \text{g}^{-1}$ , than those of CMP2 (302  $\text{m}^2 \text{g}^{-1}$  and 0.12  $\text{cm}^3 \text{g}^{-1}$ ) and CMP3 (134  $\text{m}^2 \text{g}^{-1}$  and 0.02  $\text{cm}^3 \text{g}^{-1}$ ). This enhanced  $S_{\text{micro}}$  and  $V_{\text{micro}}$  of CMP1 contribute to its excellent  $\text{CO}_2$  adsorption performance, registering at 129.60  $\text{mg g}^{-1}$  under conditions of 273 K and 0.1 MPa. Porphyrin-based polymers are widely recognized for their structural stability and inherent porosity. When doped with metal ions, these polymers exhibit increased activity at active sites, thereby improving their performance in gas adsorption applications.

### 3.2.5.3 Aerogels for $\text{CO}_2$ capture

Aerogel have received extensive attention due to well-developed pore structure. There is a wide variety of aerogel materials and numerous synthetic procedures for obtaining aerogel materials. The most common method of synthesizing aerogel is the sol-gel followed by drying. The drying procedures determine the final state of the aerogel. An ambient drying will destroy the structure due to capillary forces. Freeze drying eliminates the capillary forces during the solvent evaporation process. However, during the freezing process, the structure may be slightly damaged. Through supercritical drying, the structure can be preserved completely. After drying, a great number of mesopores and macropores can be obtained, which can provide abundant active sites for gas adsorption (Vinayakumar et al., 2022a; Wu et al., 2022). Competitive adsorption of coexisting gas components often has an adverse effect on the adsorption of target gases. Therefore, most of the research work in recent years has focused on modifying aerogels to improve their adsorption capacity or selectivity for target gases (Ho and Leo, 2021; Keshavarz, L. et al., 2021; Maleki, 2016; Vinayakumar et al., 2022a). In terms of  $\text{CO}_2$  adsorption and capture, for  $\text{SiO}_2$  aerogels (Cui, S. et al., 2011; Cui et al., 2017; Lin, Y.F. et al., 2013; Zhou et al., 2021),  $\text{SiC}$  aerogels (Cui et al., 2017; Guo, Y.F. et al., 2018; Han, S. J. et al., 2014), graphene aerogels (Pruna et al., 2021) and other new aerogels (Wang, W.J. et al., 2019b). At present, basic active centers are mainly introduced by amino functionalization, nitrogen doping, etc. (Jeon et al., 2015; Li, Y.W. et al., 2020; Tian, L. et al., 2021; Wormeyer et al., 2012; Wormeyer and Smirnova, 2013; Xu, J. et al., 2021). Chemisorption can also improve the adsorption capacity and selectivity of  $\text{CO}_2$  by aerogels. For aerogels, the specific surface area and micropores can be further increased by activation, which also plays a key role in  $\text{CO}_2$  adsorption at the same time. The  $\text{CO}_2$  adsorption capacity of a few common aerogels is shown in Figure 3.36.



**Figure 3.36.** The approximate adsorption capacity of CO<sub>2</sub> (Keshavarz, Leila et al., 2021; Kong et al., 2017; Lee and Park, 2020; Shao et al., 2018; Vinayakumar et al., 2022b; Wang, Y.L. et al., 2020; Wu et al., 2022; Yay and Gizli, 2019; Zhang, T.M. et al., 2020; Zhu, W.K. et al., 2020).

*SiO<sub>2</sub> aerogel.* As an adsorption material, SiO<sub>2</sub> aerogel has the advantages of high adsorption efficiency, convenient desorption, and stable performance. It is the most studied and mature aerogel material, and was first applied to the field of gas adsorption and purification. The current research work focuses on amino functionalization or hydrophobic modification of SiO<sub>2</sub> aerogel to further improve its adsorption performance for CO<sub>2</sub>. There are two main modification methods: one is grafting, and impregnation after the formation of wet gel or after supercritical drying (Fang, Q.X. et al., 2020; Linneen et al., 2014). The other method is to functionalize the surface of SiO<sub>2</sub> aerogel, which is to introduce functionalized precursors in the sol-gel reaction process, and use a mixed silicon source to endow SiO<sub>2</sub> aerogel with specific properties through in-situ polymerization (Liu, Z.Y. et al., 2021; Xu, Y. et al., 2018). Amino functionalization of SiO<sub>2</sub> aerogels is currently the main method to improve its selectivity to CO<sub>2</sub>, increase the saturated adsorption capacity and accelerate the CO<sub>2</sub> adsorption rate. The presence of an appropriate amount of water vapor in the mixed gas can significantly improve the adsorption capacity of CO<sub>2</sub> by aerogels.

*Carbon aerogel.* Activation is a common method to control the pore structure of porous carbon materials. During the activation, the microporous structure can be introduced into the mesoporous pores of carbon aerogels, increasing the specific surface area further. Therefore, it is beneficial to the application of carbon aerogels as CO<sub>2</sub> adsorption materials. Similar to SiO<sub>2</sub> aerogels, the adsorption performance of



carbon aerogels for CO<sub>2</sub> can also be improved by means of amino functionalization, nitrogen doping, and the introduction of active metals (Geng et al., 2020; Li, H.M. et al., 2019; Marques et al., 2013; Robertson and Mokaya, 2013; Xie et al., 2017; Zhuo et al., 2016).

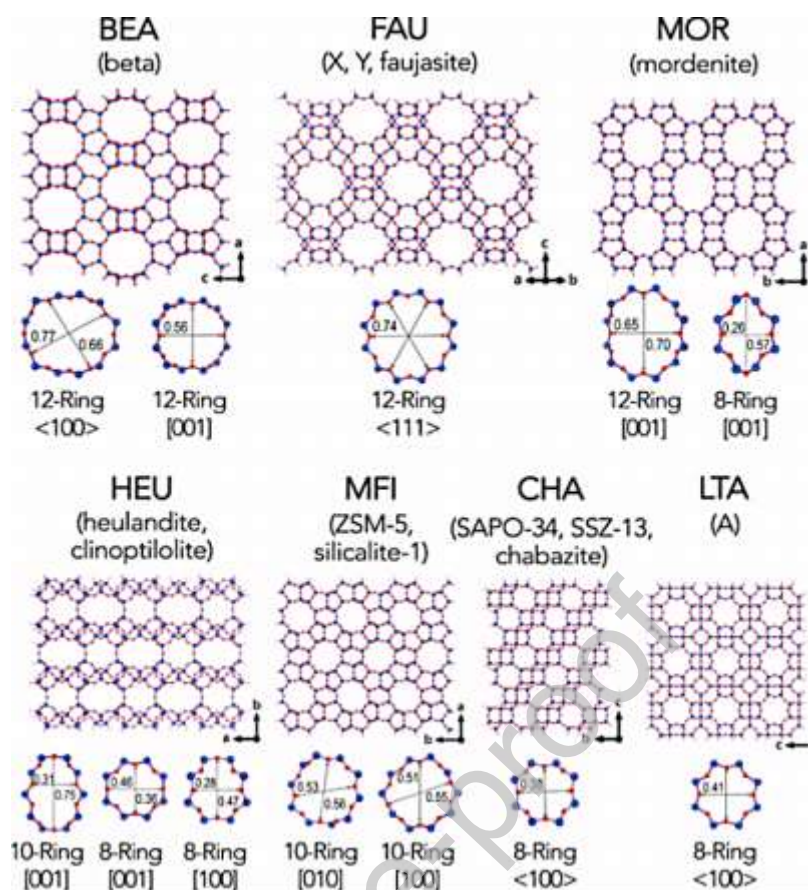
*Graphene aerogel.* Graphene sheet layers stacked on top of each other can form graphene aerogels with three-dimensional porous network structures, which have not only the characteristics of fast graphene electron transport rate, but also rich surface oxygen groups, large aerogel specific surface area, high porosity, and easy for further modification (Pruna et al., 2021; Ren et al., 2020).

*Metal oxides aerogel.* Metal oxide aerogel is a type of inorganic aerogel. Whether it is the preparation of one-component or multi-component metal oxide aerogels, the metal salts are first dissolved in organic solvents or water, and the reaction reagents can be added after adjusting the concentration and pH value of the solution to form a gel. Metal oxide aerogels are rich in surface active sites such as metal centers, active hydroxyl groups, etc., which have high chemical adsorption capacity and selectivity. (Li, Z. et al., 2019)

*Polymer-based organic aerogels.* Polymer-based organic aerogels are polymer molecules passed with glue, and the body particles are formed by combining hydrogen bonds or van der Waals forces organic compounds with porous network structures. Compared to conventional inorganic aerogels, the performance of organic aerogels depends mainly on the type of polymer. Therefore, the polymer based organic aerogels offer flexible design and performance adjustability. Assemble synth-based organic aerogels mainly include polyurethane (PU), polyurea (PUA), polyimide (PI), etc (Kong et al., 2015; Li, H.M. et al., 2019).

#### 3.2.5.4 Zeolites materials for CO<sub>2</sub> capture

Zeolites have been widely used as CO<sub>2</sub> adsorbents due to the large surface area, high stability, and tunable physicochemical properties. Zeolites are porous aluminosilicates with three-dimensional rigid frameworks consisting of corner-sharing SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra through shared oxygen atoms. The framework of zeolites contains the periodic arrangement of cages and channels with molecular dimensions (3-15 Å in diameter). According to the number of oxygen atoms forming the largest pore aperture, zeolites can be divided into small-pore zeolites (8-membered ring), medium-pore zeolites (10-membered ring), large-pore zeolites (12-membered ring) and extra-large-pore zeolites (≥14-membered ring). The frameworks of pure silica zeolite are electrically neutral. The isomorphous replacement of Si<sup>4+</sup> by Al<sup>3+</sup> in the lattice will induce negative charges on the framework, which require extra-framework cations for charge balance. The physicochemical properties of zeolites can be tuned by incorporating extra-framework cations via ion exchange or impregnation methods. Zeolites with desired properties can be achieved for target applications by tuning the topology of zeolites (Figure 3.37), and the type and density of extra-framework cations.



**Figure 3.37.** Selected widely applied zeolite frameworks. The three-letter code relates to the type of framework, assigned by the International Zeolite Association (IZA) (in bold). The size of the pore window and the ball-stick atomic model are given. Blue and red spheres represent T atoms and oxygen atoms, respectively (Li, Y. et al., 2017).

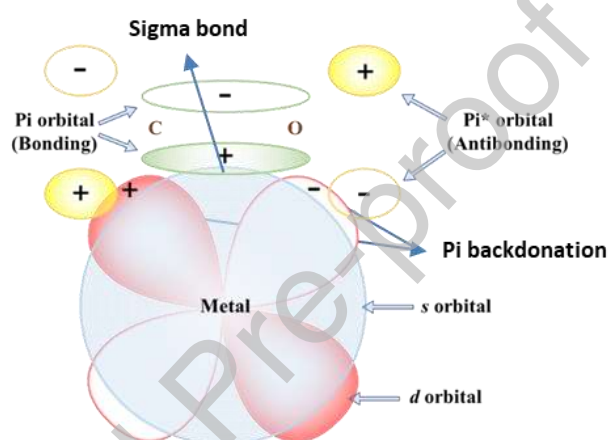
Zeolites show outstanding  $\text{CO}_2$  adsorption performance in terms of high  $\text{CO}_2$  capacity and selectivity, and excellent regenerability, which highly rely on the properties of zeolites. Generally, materials with large surface areas show high adsorption capacities. However, the high surface area with non-specific nature benefits the adsorption of both target and unwanted adsorbates, which is not enough when the selectivity is considered. The selectivity on the other hand is governed by the distinct adsorbent/adsorbate interaction, which relates to the type of the adsorption sites (e.g., extra-framework cations, functional groups etc.). In the case of  $\text{CO}_2$  separation, a higher affinity of zeolite towards  $\text{CO}_2$  over other accompanying species is desired, such as  $\text{N}_2$  and  $\text{CH}_4$  in flue gas and biogas/natural gas, respectively. However, an overly strong gas-host interaction requires a high energy consumption during the regeneration process.  $\text{CO}_2$  adsorption on various zeolites is reviewed aiming to provide references for its utilization in industrial processes.

Separating molecules with similar sizes (e.g., CO<sub>2</sub>, 3.3 Å; N<sub>2</sub>, 3.6 Å; CH<sub>4</sub>, 3.8 Å) is challenging through the sieving effect due to the difficulty in precisely adjusting the pore size locating just in between the sizes of molecules. (Shang et al., 2012; Shang et al., 2013) Small-pore zeolites are effective and highly selective adsorbents for CO<sub>2</sub> capture due to the similar sizes of the window aperture (3~5 Å) and the kinetic diameters of adsorbates (CO<sub>2</sub>, 3.3 Å; N<sub>2</sub>, 3.6 Å; CH<sub>4</sub>, 3.8 Å), which enables the separation through size sieving and “molecular trapdoor” mechanism. (Shang et al., 2012) In addition, the high thermal and mechanical stability make small-pore zeolites attractive in industrial processes. Shang *et al.* have studied the CO<sub>2</sub> and N<sub>2</sub> adsorption on alkali metal ion-exchanged chabazite (CHA) zeolites (Si/Al of 1~50). (Shang et al., 2012; Shang et al., 2013) They achieved ultra-high selectivity for CO<sub>2</sub>/N<sub>2</sub> (325, 20 kPa, 273 K) and CO<sub>2</sub>/CH<sub>4</sub> (98, 100 kPa, 233 K) by Cs<sup>+</sup>CHA (Si/Al=2.2) and K<sup>+</sup>CHA (Si/Al=2.2), respectively. The high selectivity was attributed to the temperature-dependent “molecular trapdoor” mechanism (Figure 3.38), which describes the different capability of gas molecules to deviate the cation from the center of the 8-ring windows to enter the pores of zeolites. Molecules such as CO<sub>2</sub> with high polarizability can interact with the “door-keeping” cation (e.g., Cs<sup>+</sup> and K<sup>+</sup>) strongly and need to pay lower energy toll than the “weak molecules” (e.g., CH<sub>4</sub> and N<sub>2</sub>). In terms of the zeolites, the key factors for realizing this mechanism are the cations with proper size, and the proper Al distribution on the pore aperture providing enough electronegativity for cations to coordinate to large extent for the effective blockage. The kinetics on the other hand is an important parameter to evaluate the CO<sub>2</sub> capture performance, especially during the industrial processes, which is determined by the energy barrier for cation deviation. The cation with smaller size or a weaker cation-window interaction strength requires lower energy for deviation, which can help in improving the kinetics. Further tunings among the zeolites topology, the Si/Al ratio and the type of cations are required for developing CO<sub>2</sub> adsorbents with both high selectivity and promising kinetics.



**Figure 3.38.** Illustration of the “molecular trapdoor” mechanism in discriminative gas separation: Cs<sup>+</sup> locating in the middle of 8MR acts as a doorkeeping cation, which can only be deviated by strong gas molecules (e.g., CO<sub>2</sub>), but not by weak molecules (e.g., CH<sub>4</sub>) at certain temperature. (Shang et al., 2012)

Typically, high selectivity and high regenerability cannot be attained simultaneously. Highly selective materials tend to consume lots of energy for the completed regeneration, and conventional physisorption-driven adsorbents with easy regeneration always feature low selectivity. To address this contradiction, Sun *et al.* prepared transition metal (Co, Ni, Zn, Fe, Cu, Ag, La, and Ce) ion-exchanged SSZ-13 zeolites (CHA type, Si/Al=12) for flue gas (CO<sub>2</sub>/N<sub>2</sub>:15/85) separation.(Sun, M. et al., 2019) The selectivity of Co<sup>2+</sup>SSZ-13 and Ni<sup>2+</sup>SSZ-13 reached above 50 at 273 K, which was higher than the alkali metal ion-exchanged SSZ-13 zeolites (23-36).(Bower et al., 2018) The improvement was attributed to the Pi-complexation interaction (Figure 3.39) formed between CO<sub>2</sub> and the transition metal ions, which is with moderate interaction strength between those of physisorption and chemisorption. The isosteric heat of adsorption of CO<sub>2</sub> is 30~60 kJ/mol, much lower than that of chemisorption (> 80 kJ/mol), which enables regeneration under mild conditions.



**Figure 3.39.** Pi-complexation interaction formed between Pi-structured molecules and transition metal ion (Sun, M. et al., 2019).

Considering the higher polarizability and quadrupole moment of CO<sub>2</sub> than the unwanted gases (N<sub>2</sub> or CH<sub>4</sub>) in the mixture, cations with strong polarizing power are highly desired, which can improve the affinity of adsorbents towards CO<sub>2</sub>. Researchers have studied the CO<sub>2</sub> adsorption behavior on alkali metal (Li, Na, K, Rb, Cs) ion-exchanged FAU (X and Y) and MFI (ZSM-5) zeolites.(Dunne et al., 1996; Katoh et al., 2000; Walton et al., 2006; Wirawan and Creaser, 2006a, b; Yamazaki et al., 1993) Generally, the CO<sub>2</sub> capacity is reduced in the order of LiZ > NaZ > KZ > RbZ > CsZ (Z representing zeolite), which is coincident with the order of increasing ionic radius. For the ions with the same valance state, those with smaller ionic radius feature higher polarizing power: Cs<sup>+</sup> (3.3 Å) < Rb<sup>+</sup> (2.9 Å) < K<sup>+</sup> (2.7 Å) < Na<sup>+</sup> (1.9 Å) < Li<sup>+</sup> (1.4 Å). The result indicates the interaction of CO<sub>2</sub> with alkali metal is electrostatic interaction dominated. The consistent results were also demonstrated on alkali metal ion-exchanged X zeolite through density functional theory calculations.(Plant et al., 2006) The CO<sub>2</sub> adsorption enthalpies at low coverages vary from 33.20 to 17.17 kJ/mol, decreasing with the increase of the ionic radius. The

smaller cations are with higher affinity towards CO<sub>2</sub>, which was also evidenced by the shorter distance between the oxygen of carbon dioxide and the cations with smaller sizes.

The presence of moisture is unavoidable in the gas separation process, which is another challenge when adopting zeolites as adsorbents due to the extremely hydrophilic nature. Featuring high polarizability, H<sub>2</sub>O is indeed a main inhibitor for CO<sub>2</sub> adsorption even when the water is at a low concentration, by forming a favorable interaction with the adsorption sites, especially the extra-framework cations in the cationic forms of zeolites, which can dramatically reduce the CO<sub>2</sub> capacity. (Brandani and Ruthven, 2004) Grafting amine functional groups in zeolites was found as a powerful approach for CO<sub>2</sub> capture under wet conditions. (Kim, C. et al., 2016) Kim *et al.* prepared ethylenediamine (ED)-modified Y zeolite prepared via the gas-phase titration method and tested the CO<sub>2</sub> capture performance in wet flue gas (Kim, C. et al., 2016). CO<sub>2</sub> was effectively captured through interacting with the amine groups, and H<sub>2</sub>O was co-adsorbed in the micropores of zeolites without forming urea. The CO<sub>2</sub> working capacity was maintained at a stable level (> 1.1 mmol/g) during 20 temperature swing adsorption (TSA) cycles. The ED-modified Y zeolite features a high H<sub>2</sub>O tolerance and remarkable resistance against the urea formation simultaneously.

In the industrial separation process, the energy lost due to the undesirable pressure drop in the fixed bed needs additional blower power to maintain the constant flow. Fabricating zeolite powder into monoliths with desired channel sizes, wall thicknesses, and high mechanical properties by 3D printing is a promising strategy to tackle this issue. Wang *et al.* prepared mechanically robust binder-free 3D printing zeolite monoliths (ZM-BF) as a superior configuration for CO<sub>2</sub> capture (Wang, S. et al., 2019). Halloysite nanotubes (HNTs) with high strength were used as printing ink additives, which benefited the formation of robust interfacial “HNTs-bridges” for individual zeolite crystals. ZM-BF showed a promising equilibrium CO<sub>2</sub> capacity of 5.58 mmol/g (298 K, 1 bar), which is higher than other reported 3D-printed CO<sub>2</sub> adsorbents. Compared with the commercial benchmark NaX zeolites, ZM-BF showed superiority in dynamic adsorption breakthrough tests in terms of dynamic, CO<sub>2</sub> capture capacity and selectivity. In addition, the binder-free ZM-BF shows outstanding mechanical properties (with a robust compressive strength of up to 5.24 MPa), higher than most of the reported monoliths with binders. The “3D printing and zeolite soldering” strategy developed in this study afforded a promising approach for precisely fabricating monoliths with desirable configurations, which may provide references for other related applications, such as catalysis and sensing.

The zeolite topology and the type/density of adsorption sites in zeolites are the essential factors for CO<sub>2</sub> adsorption on zeolite materials. The CO<sub>2</sub> capacity can be affected by the type/density of adsorption sites and the surface area of zeolites, as well as the presence of high-affinity components (e.g., H<sub>2</sub>O) in the gas mixture. The high selectivity can be attained by introducing the adsorption sites with high CO<sub>2</sub> affinity, as well as through the “molecular trapdoor” mechanism. However, it still requires efforts to

achieve easy regeneration and fast kinetics simultaneously. Thus, tuning the physiochemical properties of zeolites together with optimizing the experimental conditions are required for approaching effective CO<sub>2</sub> capture in industries.

### 3.3 Photo-responsive adsorbents for low-energy CO<sub>2</sub> capture and release

For post combustion CO<sub>2</sub> capture techniques to achieve widespread feasibility, energy cost must be substantially reduced. Traditional CO<sub>2</sub> liberation technologies highly relied on pressure (pressure swing adsorption, PSA), temperature (temperature swing adsorption, TSA), vacuum (vacuum swing adsorption, VSA), or any combination of them (Li, H. and Hill, M. R., 2017). Both VSA and PSA are in demand of large amounts of electrical energy to alter the pressure for driving the CO<sub>2</sub> to be liberated from adsorbents (Mason et al., 2011). Although waste heat can be exploited in the TSA method, some adsorbents are so thermally insulating that these methods cannot be applied on a large scale unless the heating transformation distance can be designed into the gas adsorbent contactor (Labreche et al., 2015). Apart from that, the long cycle time and the demand for high vapor to heat the column also resist the development of the TSA method (Qiao et al., 2022). Considering that the traditional triggers for the liberation of adsorbed CO<sub>2</sub>, such as high temperature and vacuum, are so energy consuming (Lyndon et al., 2013), it's necessary to establish new stimuli that are more naturally abundant and renewable resources such as solar light. In this case, the adsorbents with maximum CO<sub>2</sub> uptake capacity and further reduced energy will obtain a more prospective and wide application (Huang et al., 2022).

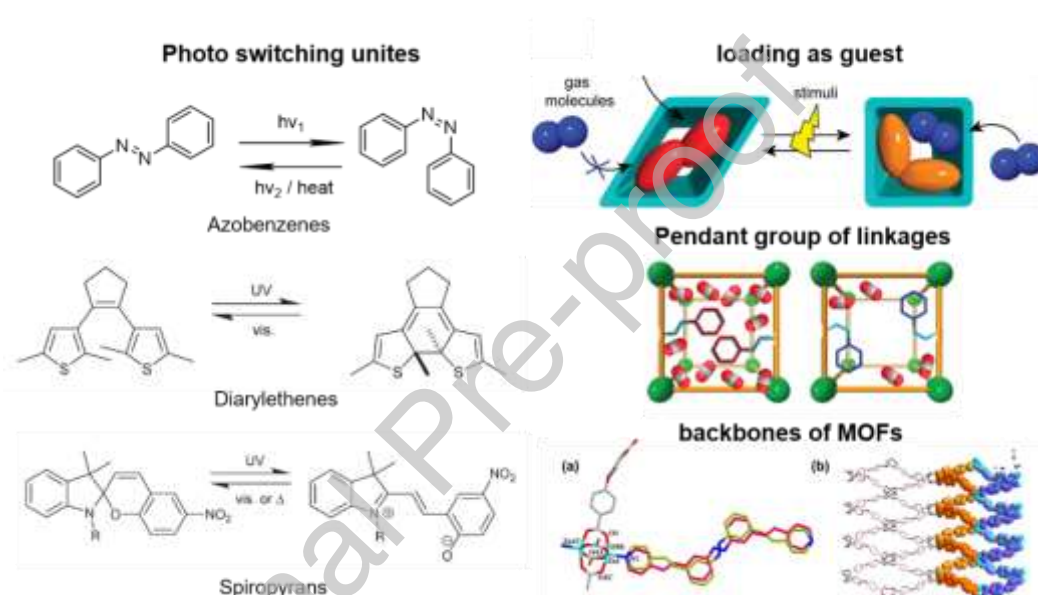
Light, particularly concentrated solar light, as a naturally abundant, renewable resource, is an extremely appealing trigger for regenerating the adsorbents. Compared to traditional technologies, light can be regarded as the most energy-efficient method (Li, Haiqing and Hill, Matthew R, 2017). When the adsorbents show strong light absorption, combined with the large amounts of CO<sub>2</sub> desorption, much energy cost could be saved (Jiang et al., 2019). Therefore, through the different directions of adsorbents functionalization, light triggered different applications can be developed.

#### 3.3.1. Photo responsive porous polymer adsorbents for CO<sub>2</sub> switching capture

Recently, porous materials have been reported as attractive light responsive candidates for low energy CO<sub>2</sub> capture (Heinke and Wöll, 2019). Because of their large surface area, structural variety and easy functionalization ability, high CO<sub>2</sub> adsorption performance and the potential for integration with light responsive photochromic units in the pore channels can be realized. Such light triggered CO<sub>2</sub> release performance of porous materials can be achieved by the functionalization of photochromic units into the structural molecules of porous materials (Huang and Wu, 2022). Such photochromic organic molecules can undergo a reversible photoisomerization process, and then change the electronic state and molecular structures under light irradiation. Up until now, azobenzene (AB), diarylethene (DET)



and spiropyran (SP) are the most reported photochromic units that were successfully reported to be incorporated into porous materials (Figure 3.40) (Jones et al., 2016). Among them, azobenzene can transition between the trans/cis state through different wavelength number of light irradiation, and DET can undergo a structural transition through ring-open/close reaction while SP molecules can switch between the zwitterionic merocyanine counterpart upon light exposure (Bigdeli et al., 2020). These photo switchable compounds can be either integrated into the backbones or side chain of porous materials or directly loaded as the guest to pore channels (Halder et al., 2019). Therefore, the light triggered photoisomerization transition of these materials can finally contribute to a remote light controlled CO<sub>2</sub> capture and release recycle.



**Figure 3.40.** A schematic representation of different strategy to integrate photoswitchable components into a metal–organic framework (MOF) (Jones et al., 2016).

### 3.3.1.1 Photo responsive MOFs for CO<sub>2</sub> switching

Photo switching MOFs are the most widely reported porous materials for low energy CO<sub>2</sub> capture owing to their high uptake capacity, crystallinity and adjustable structures (Mukhopadhyay et al., 2014). For photoswitching MOFs, azobenzene functionalized photo switching MOFs were widely reported because of the easy functionalization method. For example, azobenzene based PCN-123 can switch the conformation upon UV light irradiation and lateral thermal heating (Park et al., 2012). Such material was fabricated by the introduction of azobenzene pendants to the organic linkage. After UV light irradiation, a release of 54%, from 22.9 cm<sup>3</sup>/g to 10.5 cm<sup>3</sup>/g, in CO<sub>2</sub> uptake capacity could be realized. In addition, the CO<sub>2</sub> uptake ability could also be recovered by thermal heating. Apart from

functionalization as linkage pendants, azobenzene groups could also be incorporated as backbones of MOF materials. Matthew et al. (Lyndon et al., 2013) reported an azobenzene based  $Zn(AzDC)(4,4'-BPE)_{0.5}$  by directly incorporating the azobenzene units into the backbone of the framework. The switching of  $CO_2$  uptake capacity was found to be tremendously strong, with up to 64% changes under dynamic light switch on/off conditions. In addition, azobenzene molecules were also reported to be directly loaded as a guest in MOF materials. Matthew et al. (Lyndon et al., 2015b) also reported Mg-MOF-74 materials. Through methyl red loading, such MOF exhibited 84% tailored  $CO_2$  uptake changes after visible light irradiation.

DET and SP based MOFs are also other promising alternatives for low energy  $CO_2$  capture. For example, a photochromic diarylethene linkage was utilized to fabricate a photo responsive DMOF material (Luo, F. et al., 2014). The local photoisomerization reactions induced by UV and lateral visible light irradiation in DMOF frameworks contributed to a 76% desorption of  $CO_2$  capacity. Apart from that, Deanna et al. (Healey et al., 2016) also reported a photoactive spiropyran based MOF-808-SP adsorbent through a post-synthetic modification strategy. Such MOF material suggested both photo responsive BET surface area and light triggered tailorable  $CO_2$  capture performance, which provides a promising, remote light controlled, low energy cost gas separation and storage method.

### 3.3.1.2 Other photo responsive porous polymer adsorbents for $CO_2$ switching

Considering the structural tunability, some other porous materials are also promising candidates for fabricating the light responsive adsorbents for tailorable carbon capture. For instance, porous organic polymers are one of the most developed adsorbents for carbon capture, which possess many similar inherent properties as MOFs, such as high porosity and gas uptake capacity. Bradley et al. (Lyndon et al., 2015a) fabricated a diarylethene based porous aromatic framework-1 materials. Such DArE@PAF-1 material exhibited an up to 26 wt.% desorption capacity of  $CO_2$  at the 50 wt.% DArE guest molecules loading. The photo responsive ability could also be modulated by different guest loading content, which provided greatly controlling for carbon capture and release for industrial applications.

Zhang et al. (Zhu and Zhang, 2014) also reported the first example of azobenzene based porous organic polymer. Under UV light irradiation and, consequently thermal heating, both the pore size distribution and the  $CO_2$  uptake ability could be reversibly changed. In contrast to most reported azobenzene based MOFs, the trans to cis isomerization in this material suggested increasing adsorption of  $CO_2$  because of the enhanced dipole-quadrupole interactions between  $CO_2$  molecules and cis isomer pendants. In detail, the UCBA-1 showed a dramatic increase in  $CO_2$  adsorption capacity, up to 29%, which could complement the most reported photo responsive MOF materials so far.



### 3.3.1.3 Photo responsive chemicals for CO<sub>2</sub> switching

Fabian et al. (Wilm et al., 2022) first fabricated photo responsive superbases containing the photochromic DET units. The reported N-heterocyclic imines can undergo a reversible electronic isomerization under UV light exposure and lateral visible light irradiation, with multiple cycles. The transition between ring opening and ring closing states was accompanied by a remarkable pK<sub>a</sub> shift (up to 8.7 units). The ring closing isomers of these imines are effectively basic to act as CO<sub>2</sub> capture sites via the production of zwitterionic bases, which enable the light triggered CO<sub>2</sub> capture and release cycles. Such light stimulated basicity alterations provided guidance for developing new photo switching transformations in a variety of fields of research.

### 3.2.2 Photothermal conversion applied in low light-triggered temperature of CO<sub>2</sub> adsorbents regeneration

Endowing the adsorbents with photothermal conversion capability is also another alternative way to utilize the sunlight for CO<sub>2</sub> adsorbent regeneration. Through combining photothermal conversion ability, thermos sensitivity with the high density of amino sites with CO<sub>2</sub> affinity, an energy saved light triggered high capacity of CO<sub>2</sub> capture and release process can be achieved. He et al. (Lu et al., 2022) synthesized solar energy triggered cellulose nanofiber based thermos responsive fiber adsorbents. The contained poly (N-isopropylacrylamide), graphene oxide and polyethyleneimine served as thermos responsive switchers, photothermal conversion switchers and CO<sub>2</sub> uptake sites. Therefore, the prepared CNF-TBFA fiber adsorbents exhibited a high CO<sub>2</sub> uptake capacity of up to 6.52 mmol/g, and low regeneration temperature (60 °C) at the same time. These provide a great promising strategy for energy saved CO<sub>2</sub> adsorbents regeneration method.

Since noble metal crystals such as Ag and Au can effectively absorb sunlight photons and convert them to thermal energy, Paolo et al. (Li, Haiqing et al., 2016) utilized Ag nanocrystals as “nanoheaters” to form silver incorporated Ag/UiO-66 composites. Considering the low-cost and high CO<sub>2</sub> adsorption performance of UiO-66 MOF, such composites are an ideal adsorbent for remote light triggered CO<sub>2</sub> low energy CO<sub>2</sub> capture and release. Under visible light irradiation, 90.5% captured CO<sub>2</sub> in Ag/UiO-66 composites can be released out, which demonstrates a promising energy saved method for remotely regenerating the MOF adsorbents under the natural abundant light resources.

### 3.4. Medium temperature solid sorbents

#### 3.4.1 MgO-based materials for CO<sub>2</sub> capture

Depending on the origin of the CO<sub>2</sub>-containing gas stream, e.g. a combustion process, it may be more efficient thermodynamically to operate the CO<sub>2</sub> process at elevated temperature, instead of cooling the gas stream to near-ambient temperatures prior to CO<sub>2</sub> removal. Sections 3.4 – 3.5 review recent developments of CO<sub>2</sub> capture processes with solid sorbents at medium (> 250 °C) and high (> 500 °C) temperatures, respectively. To this end, mostly alkali or alkaline earth metal oxides have been used as sorbents, often mixed with other metal oxides that themselves are not active for CO<sub>2</sub> sorption. Such “inactive” metal oxides function as support materials, or structural stabilizers, for binary oxides to mitigate the cyclic decay in CO<sub>2</sub> sorption activity that all alkali or alkaline earth metal oxides have in common due to the rather low melting temperatures of the carbonates formed (Dunstan et al., 2021); they also can play an important role in the carbonation mechanism of ternary oxide sorbents. The formation of carbonate phases, rather than adsorbed carbonate species upon exposure to CO<sub>2</sub>, is one of the most significant differences of medium- to high temperature solids sorbents when compared to low temperature solid sorbents, and influences the overall process design appreciably. Table 3.18 provides an overview of binary alkali metal oxide/carbonate pairs that have been investigated frequently for CO<sub>2</sub> capture.

**Table 3.18:** Overview of properties of binary alkali metal oxide/carbonate pairs for CO<sub>2</sub> capture applications. \* Below the equilibrium temperature CO<sub>2</sub> sorption and the formation of MeCO<sub>3</sub> are favored thermodynamically, whereas above the equilibrium temperature CO<sub>2</sub> release and the formation of MeO are favored for a given partial pressure of CO<sub>2</sub>,  $p_{\text{CO}_2}$ , in the gas environment.

Alkali metal oxide /carbonate pair (MeO/MeCO <sub>3</sub> )	Reaction enthalpy in kJ/mol <sub>MeO</sub> (at 298 K)	Melting temperature in °C of MeO/MeCO <sub>3</sub>	CO <sub>2</sub> uptake capacity in g <sub>CO2</sub> /g <sub>MeO</sub> (mmol <sub>CO2</sub> /g <sub>MeO</sub> )	Equilibrium temperature in °C for $p_{\text{CO}_2} = 1 \text{ bar}$ *	Potential applications
MgO/MgCO <sub>3</sub>	±101	2825/990	1.094 (24.86)	395	Pre-combustion CO <sub>2</sub> capture, Sorption enhanced conversion reactions
CaO/CaCO <sub>3</sub>	±178	2900/1330	0.786 (17.86)	885	Pre-combustion CO <sub>2</sub> capture, Post-combustion CO <sub>2</sub> capture, Sorption enhanced conversion reactions, Thermochemical energy storage
SrO/SrCO <sub>3</sub>	±241	2530/1495	0.426 (9.68)	1225	Thermochemical energy storage

BaO/BaCO <sub>3</sub>	±272	1973/1555	0.288 (6.54)	1560	Thermochemical energy storage
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### 3.4.1.1 Introduction of MgO-based sorbents

Thermodynamically, MgO-based sorbents are suitable materials for CO<sub>2</sub> capture ( $\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3$ ,  $\Delta H_{298\text{K}} = -100.9 \text{ kJ}\cdot\text{mol}^{-1}$ ) at intermediate temperatures, with CO<sub>2</sub> sorption being feasible up to  $\sim 400 \text{ }^\circ\text{C}$  when the partial pressure of CO<sub>2</sub> is 1 bar. MgO-based materials have a lower energy penalty associated with the decomposition of the carbonate phase (i.e. the regeneration of the metal oxide phase) than other alkali metal oxide/carbonate pairs (e.g. CaO/CaCO<sub>3</sub>, Table 3.18) due to their lower reaction enthalpy and the lower regeneration temperatures ( $< 500 \text{ }^\circ\text{C}$ ). Further, they possess a high theoretical CO<sub>2</sub> sorption capacity ( $1.09 \text{ g}_{\text{CO}_2}/\text{g}_{\text{MgO}}$  – the highest among the alkali earth metals) (Chi et al., 2014). Mg-containing minerals are abundant (the earth crust contains ca. 2 mol.% of Mg)(Goff and Lackner, 1998), environmentally benign and are less extensively used in other industries, e.g. building and construction, than limestone, such that there is less competition for raw materials with these industries compared to CaO/CaCO<sub>3</sub>.

### 3.4.1.2 CO<sub>2</sub> capture capacity and kinetics of MgO-based sorbents

Despite the promising theoretical characteristics, there has been only little interest in using MgO-based sorbents for CO<sub>2</sub> capture applications due to their slow CO<sub>2</sub> sorption (i.e. carbonation) kinetics, resulting in low actual CO<sub>2</sub> uptakes (typically less than  $0.02 \text{ g}_{\text{CO}_2}/\text{g}_{\text{MgO}}$  when using commercial MgO). Two reasons for the poor carbonation performance are (i) the formation of a CO<sub>2</sub>-impermeable mono-dentate surface carbonate layer (Harada and Hatton, 2015; Harada et al., 2015), and (ii) the high lattice enthalpy of crystalline MgO (Glasser and Jenkins, 2000; Zhang, K. et al., 2014). Several ways have been suggested to improve the carbonation performance of MgO, including (i) the synthesis of high surface area MgO (in particular for low temperature CO<sub>2</sub> adsorption) (Bhagiyalakshmi et al., 2010; Ruminski et al., 2011), (ii) the synthesis of MgO supported by e.g. ZrO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or C to improve also its structural stability (Han, Seung Ju et al., 2014; Hiremath et al., 2019; Jeon et al., 2012; Li, P. et al., 2017; Liu et al., 2008; Liu, W.-J. et al., 2013), or (iii) the promotion of MgO with molten alkali metal salts (AMS, predominantly nitrates) (Dunstan et al., 2021; Hu, Y.C. et al., 2019). The first two approaches have led only to limited improvement of the CO<sub>2</sub> uptake, typically up to  $0.1 - 0.3 \text{ g}_{\text{CO}_2}/\text{g}_{\text{MgO}}$  both at low and medium temperatures (Hu, Y.C. et al., 2019). The maximum CO<sub>2</sub> uptake of these sorbents scales with their surface area and is reached within several minutes of exposure to CO<sub>2</sub> when the surface is saturated with carbonates. No crystalline MgCO<sub>3</sub> is formed upon exposure of unpromoted MgO to CO<sub>2</sub> (Wang, J.Y. et al., 2014). Modification of MgO with molten AMS, however, enables the rapid formation of crystalline MgCO<sub>3</sub> and leads to a significant improvement in the carbonation performance. With AMS promotion, the conversion of MgO into MgCO<sub>3</sub> proceeds through a nucleation and growth

mechanism (Bork et al., 2021), with the type of the AMS influencing the number of nucleation sites (Jo et al., 2017) and the solubility of CO<sub>2</sub> and MgO in the salt (Dal Pozzo et al., 2019).

### 3.4.1.3 Chemical composition of MgO-based sorbents

The discovery that the addition of AMS to MgO enhances its CO<sub>2</sub> sorption rate (Zhang, K.L. et al., 2013) appreciably has led to the research community focusing on two broad aspects: The optimization of the sorbent's CO<sub>2</sub> capture performance (largely by trial and error) (Harada and Hatton, 2015; Harada et al., 2015; Hu, Y.C. et al., 2019), and the understanding of the promotion mechanism by the AMS (Bork et al., 2021; Gao, W. et al., 2021; Gao, Wanlin et al., 2021; Harada et al., 2015; Jo et al., 2017; Landuyt, 2022; Zhang, K. et al., 2014).

The former includes the optimization of the carbonation conditions (Harada and Hatton, 2015), the amount of the AMS promoter(s) (Dal Pozzo et al., 2019; Harada and Hatton, 2015; Harada et al., 2015), the selection of various synthesis routes for MgO production (Zhao, X. et al., 2018) and, most predominantly, the variation and optimization of the promoter's composition (Dal Pozzo et al., 2019; Huang, L. et al., 2017; Qiao et al., 2017). The promoters investigated range from the single nitrates (LiNO<sub>3</sub>, NaNO<sub>3</sub> or KNO<sub>3</sub>) to their binary and ternary mixtures with lower melting points. Furthermore, the addition of alkali nitrites, such as NaNO<sub>2</sub>, was shown to improve the carbonation performance of sorbents. Some reports, however, have shown that NaNO<sub>2</sub> itself is not stable and transforms into NaNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> upon cyclic operation (Gao, W. et al., 2021; Gao, Wanlin et al., 2021; Gao, W. et al., 2018).

The beneficial effect of the addition of carbonate(s) (e.g. Na<sub>2</sub>CO<sub>3</sub> or CaCO<sub>3</sub>) on the carbonation performance of alkali nitrate-promoted MgO has been demonstrated relatively early on (Zhang et al., 2015). Furthermore, it was shown that the presence of residual amounts of MgCO<sub>3</sub> (obtained by partial regeneration of the sorbent) also has led to an improved carbonation performance in the following reaction cycle (Prashar et al., 2016). Some carbonate additives readily form double carbonates with magnesium, e.g. Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub>, K<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> (Wang, L. et al., 2017) and CaMg(CO<sub>3</sub>)<sub>2</sub> (Cui et al., 2020; Cui et al., 2018; Dong et al., 2022; Hu, Y.W. et al., 2019; Papalas et al., 2021), whereas others do not, e.g. SrCO<sub>3</sub> (Jo et al., 2017). It was suggested that the addition of carbonates enhances the CO<sub>2</sub> sorption performance of alkali nitrate-promoted MgO further by (i) acting as stabilizers (or spacers), preventing the sintering of MgO (Cui et al., 2020), (ii) being dissolved in the molten alkali nitrate promoter increasing the concentration of carbonate ions (Wang, L. et al., 2017) that act as "CO<sub>2</sub> carrier" (Vu et al., 2016), or (iii) acting as nucleation seeds for the MgCO<sub>3</sub> nucleation (Jo et al., 2017).

### 3.4.1.4 Regeneration and cyclic stability of MgO-based sorbents

The major factors governing the long-term stability of other solid sorbents (e.g. CaO) and their CO<sub>2</sub> uptake rate are the available surface area, the sorbent's porosity and the average crystallite size (Alvarez,

D. and Abanades, J. C., 2005; Sun et al., 2007). The formation of  $\text{MgCO}_3$  in AMS-promoted MgO proceeds via a nucleation and growth mechanism (Bork et al., 2021; Harada and Hatton, 2015; Jo et al., 2017); therefore, the stability of the sorbent is influenced by a larger number of parameters, including the properties of MgO, of the promoter(s) and the interaction between them. Importantly, after promotion with AMS, the available surface area of MgO has a much lesser influence on the overall  $\text{CO}_2$  uptake capacity than without AMS (Dal Pozzo et al., 2019; Rekhtina et al., 2020; Zhao, X. et al., 2018). Still, other surface properties of MgO (e.g. surface defects and secondary phases acting as nucleation points) area play an important role in the cyclic stability of the sorbent since  $\text{MgCO}_3$  is formed via a nucleation mechanism. An in-depth understanding of how these surface parameters evolve upon cycling between carbonation and calcination, and how they correlate with the carbonation performance is yet to be obtained. The cyclic evolution of AMS is another important and, thus far, largely under-investigated factor influencing the cyclic performance of sorbent. It has been proposed that the segregation of the molten salt from the MgO surface can lead to a decrease in the cyclic  $\text{CO}_2$  uptake performance of sorbent (Dal Pozzo et al., 2019; Jo et al., 2017). Yet, these conclusions were drawn based on ex-situ contact angle measurements between the salt and the MgO surface, and do not represent the distribution of the molten promoter in the sorbent under operation conditions. Furthermore, the thermal stability of the molten promoter and its effect on the overall performance must be considered in greater detail (Chen, J. et al., 2021; Gao, W. et al., 2021), since the thermal decomposition temperatures of many nitrates, e.g.  $\text{LiNO}_3$  or  $\text{NaNO}_3$ , are below or equal to the typical sorbent regeneration temperature of  $450\text{ }^\circ\text{C}$  (Hoshino et al., 1981; Qiao et al., 2017).

#### 3.4.1.5 Effect of the gas composition

Flue gas contains, besides  $\text{CO}_2$ , a variety of compounds in different concentrations depending on the preceding process, and they all can potentially affect the  $\text{CO}_2$  sorption performance of alkali metal oxide-based sorbents (Aaron and Tsouris, 2005). The presence of water vapor in the  $\text{CO}_2$ -containing gas stream was observed to improve the carbonation performance of both pristine (Fagerlund et al., 2012) and promoted MgO-based sorbents (Jin et al., 2017; Vu et al., 2016; Yang, Xinfang et al., 2016; Zarghami et al., 2015). It was suggested that the MgO is hydrated partially, forming reaction intermediates (e.g.  $\text{Mg}(\text{OH})_2$ ) that have an intrinsically higher reactivity with  $\text{CO}_2$ , and also that the presence of steam alters the morphology of the sorbent such that the surface area is increased (Béarat et al., 2002; Zarghami et al., 2015). Furthermore, it has been shown that the addition of liquid water to a used MgO- $\text{NaNO}_3$  sorbent, followed by calcination, is effective in regenerating its activity, because the water helps to distribute the  $\text{NaNO}_3$  promoter on the surface of MgO and to decrease the average crystallite size of MgO (Dal Pozzo et al., 2019).

MgO can theoretically react with  $\text{SO}_2$  and  $\text{O}_2$  to form  $\text{MgSO}_4$ , which is thermodynamically stable at typical regeneration temperatures of sorbents ( $< 600\text{ }^\circ\text{C}$ ) (Scheidema and Taskinen, 2011). The

accumulation of  $\text{MgSO}_4$  in the sorbent with time would lead to a loss of  $\text{MgO}$  for  $\text{CO}_2$  capture, and hence to a gradual reduction of the  $\text{CO}_2$  uptake capacity. However, the formation of  $\text{MgSO}_4$  does not occur on pristine  $\text{MgO}$  at a fast rate at typical carbonation temperatures such that the presence of  $\text{SO}_2$  may practically not impair the  $\text{CO}_2$  sorption performance of  $\text{MgO}$  (Bakhshi Ani et al., 2021). Thus far, it remains unclear whether molten salts promote the formation of  $\text{MgSO}_4$  at lower temperatures, similar to their promoting effect on the formation of  $\text{MgCO}_3$ .

#### 3.4.1.6 $\text{CO}_2$ capture applications

$\text{MgO}$ -based sorbents, even when promoted with AMS, require high  $\text{CO}_2$  partial pressures ( $\gg 1$  bar) for fast  $\text{CO}_2$  sorption rates and high theoretical  $\text{CO}_2$  capture efficiencies (i.e. the thermodynamic limit of the fraction of  $\text{CO}_2$  that can be removed from a gas stream) (Donat and Müller, 2022). Therefore, they are much more suitable for pre-combustion  $\text{CO}_2$  capture than post-combustion  $\text{CO}_2$  capture in which  $\text{CO}_2$  partial pressures are rather low (usually between 3 and 10 vol.% in a flue gas stream). Experimental studies using  $\text{MgO}$ -based sorbents in packed bed reactors have demonstrated the efficient removal of  $\text{CO}_2$  from high-pressure coal gas (Abbasi et al., 2014; Zarghami et al., 2015) or water-gas shift processes (Hu, Y.W. et al., 2019; Sikarwar et al., 2022) (sorption enhanced water-gas shift reaction, SEWGS).

#### 3.4.2 Hydrotalcites for $\text{CO}_2$ adsorption

Hydrotalcite (HTL) compounds have attracted much attention in the context of  $\text{CO}_2$  capture due to their potential application for the  $\text{CO}_2$  capture from flue gas (Ding and Alpay, 2001; Ram Reddy et al., 2006) and in particular sorption enhanced reactions (SER) for  $\text{H}_2$  production (Bassani et al., 2019; Fang et al., 2019; Gil et al., 2018; Halabi et al., 2012; Qi et al., 2018; Reijers et al., 2006; Yong and Rodrigues, 2002). They exhibit beneficial features including low cost, a wide range of preparation variables, high specific surface area, good regenerability, and high selectivity towards adsorption of  $\text{CO}_2$  over gases like  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{N}_2$  and steam at medium temperature, i.e. 200-500 °C (Baskaran et al., 2015; Cavani et al., 1991; Hufton et al., 1999; Lee et al., 2007; Vaccari, 1998).

Hydrotalcites, which belong to the class of layered double hydroxides (LDH, also known as anionic clays), are naturally occurring minerals (Vaccari, 1998). Since their natural occurrence is limited, the HTLs in use today are prepared by chemical companies (e.g. BASF, Sigma-Aldrich, SASOL, Clariant, Kisuma, Chemicals, or Sakei Chemicals) that sell tons of synthetic hydrotalcite-like compounds yearly (Forano et al., 2013). Synthetic hydrotalcites can be prepared via co-precipitation, urea hydrolysis, hydrothermal, sol-gel, microwave irradiation, steam activation, or solvothermal routes, as detailed in recent reviews (Forano et al., 2013; Othman et al., 2009). Furthermore, Mg-Al hydrotalcites can be prepared even from waste products, for example, using coal fly ash from coal-fired power

plants (Muriithi et al., 2017; Yong and Rodrigues, 2002), and hazardous aluminum waste from the aluminum industry (Bui et al., 2018; Galindo et al., 2015; Gil et al., 2018).

HTLs are described by the general formula  $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_{x/n} \cdot mH_2O]$  or  $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_{(2x-1)/n} \cdot mH_2O]$ , where the metal cations  $M^+ = Li$ ,  $M^{2+} = Mg, Ni, CO, Zn$ , and  $M^{3+} = Al, Cr, Fe$ , and usually,  $x$  has a value between 0.25 and 0.33 for the most widely used HTLs with  $M^{2+}$  and  $M^{3+}$  (Vaccari, 1998). The metal cations together with the hydroxide form a di-metal hydroxide layer, and  $A^{n-}$  denotes anions which, together with the molecules of water, constitute the anionic layer. The hydrotalcite structure can accommodate a plethora of anions including inorganic (e.g.  $CO_3^{2-}$ ,  $NO_3^{2-}$ ), organic (e.g. oxalate, citrate, tartrate), and complex anions (e.g. Fe-, Cr-, porphyrin complexes). A comprehensive list of anions used in the hydrotalcite-like compounds can be found in the review by Baskaran et al. (Baskaran et al., 2015). The structural flexibility of hydrotalcite-like compounds to accommodate a high variety of metals and anions is reflected by their use in a wide range of applications (Corma et al., 1992; Kagunya et al., 1996; Kung and Ko, 1996; Laycock et al., 1991; Orthman et al., 2003; Reichle, 1985; Salam et al., 2020; Takuo et al., 1979).

#### 3.4.2.1 CO<sub>2</sub> adsorption capacity and kinetics of Mg-Al hydrotalcite compounds

Among the considered HTLs, the Mg-Al hydrotalcite, where  $M^{2+}$  is magnesium and  $M^{3+}$  is aluminum, has received the most attention for CO<sub>2</sub> sorption at medium temperature due to the highest CO<sub>2</sub> capture performance (Ding and Alpay, 2000; Lee et al., 2010; Oliveira et al., 2008; Yong et al., 2001; Yong and Rodrigues, 2002). HTLs can adsorb CO<sub>2</sub> at higher temperature (200 – 500 °C), compared to other adsorbents that capture CO<sub>2</sub> below 200 °C such as zeolites, supported amines, or metal organic frameworks (Dunstan et al., 2021). The adsorption capacity is typically < 1 mmol per g sorbent, which is low in comparison with alkali metal oxide solid sorbents (Table 3.18) and is a major challenge for their practical applications (Choi et al., 2009; Ding and Alpay, 2000). For example, Ding et al. (Ding and Alpay, 2000) observed equilibrium adsorption capacities of 0.65 and 0.58 mmol g<sup>-1</sup> during isothermal measurements at 400 and 480 °C, respectively. Generally, the saturation capacity increases with an increase in pressure. Interestingly, Reddy et al. (Ram Reddy et al., 2008) found that diluting the concentration of CO<sub>2</sub> (from 14 % at atmospheric pressure) in the gas feed by almost seven times did not affect the CO<sub>2</sub> sorption capacity. Most of the tested HTLs are powder samples with particle sizes ranging from nanometer to micrometer. Recently, Veerabhadrapa et al. (Veerabhadrapa et al., 2021) produced pelletized (2 mm) exfoliated LDH-based nanosheets to investigate whether they can be used in industrial-scale applications. The best sample displayed a high surface area (264 m<sup>2</sup>/g) and a CO<sub>2</sub> sorption capacity of 1.4 mmol/g at 200 °C and 86 % CO<sub>2</sub> at 1 bar.

The use of alkali metal impregnation has been used widely to increase the HTL's basicity and thereby improve its CO<sub>2</sub> sorption capacity. When Mg-Al hydrotalcites are impregnated with K<sub>2</sub>CO<sub>3</sub> (commonly referred to as K-promoted HTL), an optimum of 20 wt.% offers the maximum adsorption capacity (Choi

et al., 2009; Hutson and Attwood, 2008; Yang and Kim, 2006; Yong and Rodrigues, 2002). Also, it has been found that the CO<sub>2</sub> sorption capacity depends more strongly on the basicity of the surface of the modified HTL than the associated changes in the surface area (Hutson and Attwood, 2008).

There is some debate in the literature about how to best describe and accurately model the kinetics of CO<sub>2</sub> uptake by HTLs (Ebner et al., 2006, 2007; Lee et al., 2007; Singh et al., 2009). Considering K-promoted HTL, the reaction has been described as a diffusion limited reaction similar to a physical adsorption process (Ding and Alpay, 2000, 2001). Comparing the values of the fitted mass-transfer coefficients, as determined by a diffusion limited reaction model, show large differences suggesting that the adsorption mechanism is more complex, as pointed out by Ebner et al. (Ebner et al., 2007). For example, mass transfer coefficients for adsorption have been determined as low as 0.0058 s<sup>-1</sup> for K<sub>2</sub>CO<sub>3</sub> promoted Mg-Al hydrotalcites (Ding and Alpay, 2000). In contrast, other works have shown steep break-through curves for the same type of HTL, suggesting fast kinetics and a high mass transfer coefficient with a fitted value of 0.0151 s<sup>-1</sup> (Soares et al., 2005). Ebner et al. (Ebner et al., 2006, 2007) observed that the CO<sub>2</sub> uptake reached equilibrium saturation only after a very long adsorption time (700 min). To describe this behavior, the authors developed a non-equilibrium model consisting of three reversible reactions and four phases which had a better fit throughout the slow adsorption process. However, the discrepancies in interpretation and modelling can to a large extent, be related to preparation of the HTL, variations in composition, impregnation degree and coverage, pressure range, and temperature range (Halabi et al., 2012). Recent kinetic studies were able to accurately model the CO<sub>2</sub> adsorption kinetics between 300 and 500 °C in dry and wet conditions, where there is competitive adsorption of H<sub>2</sub>O and CO<sub>2</sub> (Coenen et al., 2019).

#### 3.4.2.2 Chemical composition of hydrotalcites

There have been several efforts towards modifying the chemistry of HTLs to improve their CO<sub>2</sub> adsorption capacity and kinetics (Aschenbrenner et al., 2011; Oliveira et al., 2008; Yang and Kim, 2006; Yong et al., 2001). Yong et al. considered different combinations of di- and trivalent cations, including Ni-Al, Co-Al, Cu-Al, Zn-Al, and Mg-Al, and found that the latter showed the best performance (Yong and Rodrigues, 2002). Further optimizing the ratio of Mg and Al affects the number of basic sites and capacity. A high content of Al increases the charge density, providing a higher number of basic sites, but at the same time decreases the interlayer spacing and void space, thereby accommodating less CO<sub>2</sub> molecules (Baskaran et al., 2015; Choi et al., 2009). Increasing the Mg content provides more basic sites, which suggests that there exists an optimal ratio of Mg and Al for highest CO<sub>2</sub> adsorption capacity (Yang and Kim, 2006; Yong et al., 2001). For K-promoted Mg-Al HTL, with 20 wt.% of K<sub>2</sub>CO<sub>3</sub> impregnation, an optimum ratio of Mg/Al = 2 provided the highest CO<sub>2</sub> adsorption capacity (0.77 mmol/g) at 450 °C and 1 bar (Yang and Kim, 2006). While an optimum ratio of Mg/Al = 2 was found specifically for K-promoted HTL under those conditions, a large variation in the optimum ratios of



Mg/Al between 1 and 3 has been reported depending on the type of interlayer anion, whether other metal cations were used, the synthesis procedure, and which conditions they have been tested under (Baskaran et al., 2015; Choi et al., 2009).

The HTL composition changes with temperature and gas atmosphere, exhibiting hydroxylation, decomposition of carbonate and formation of oxides (mixed metal oxide, MMO). The decomposition occurs in four steps: (i) The desorption of interlayer water molecules at 100 to 200 °C, (ii) the loss of OH<sup>-</sup> groups bonded to Al<sup>3+</sup> at 200 to 300 °C, (iii) the loss of OH<sup>-</sup> groups bonded to Mg<sup>2+</sup> at 250 to 450 °C, and (iv) the loss of carbonates at 400 to 600 °C (León et al., 2010; Othman et al., 2009). The calcination temperature to achieve the highest CO<sub>2</sub> adsorption capacity has generally been reported as 400 °C, providing an optimum balance between surface area and basic sites (Ram Reddy et al., 2006). Under reaction conditions for sorption enhanced water gas shift (SEWGS), 400 °C and 5 bar, the layered clay structure decomposes and the material can be described as a mixed magnesium aluminum oxide with basic adsorption properties, and the basicity is further enhanced by the addition of potassium carbonate (van Dijk et al., 2011).

#### 3.4.2.3 Regeneration of hydrotalcites

Hydrotalcites possess good capabilities for regeneration as measured by a small loss in the successive adsorption/desorption CO<sub>2</sub> capacity. For example, Halabi et al. (Halabi et al., 2012) assessed the regenerability of K-promoted HTL over 30 cycles at 400 °C and 1.5 bar. The sorbent displayed an uptake of 0.96 mmol g<sup>-1</sup> in the first cycle, which decreased to 0.89 mmol g<sup>-1</sup> in the second cycle and remained stable afterwards. The synthesis route also affects the ability to regenerate the HTLs. Leon et al. (León et al., 2010) studied the adsorption/desorption mechanism and regenerability of hydrotalcites prepared by different methods. They observed that co-precipitation led to 86 % regenerability (with a low CO<sub>2</sub> adsorption capacity of 0.72 mmol g<sup>-1</sup> at 100 °C and 1 bar) opposed to only 67 % for sonication (with a higher initial CO<sub>2</sub> adsorption capacity of 0.84 mmol g<sup>-1</sup> at 100 °C and 1 bar). The reason for the differences was attributed to the bonding strength of the basic sites. The HTL prepared by sonication conditions had the strongest basic sites due to the formation of unidentate CO<sub>2</sub>-adsorbent species causing irreversibility. On the other hand, co-precipitation produced materials with weaker basic sites with the formation of bidentate and surface bicarbonates causing highly reversible adsorption (León et al., 2010).

#### 3.4.2.4 Effect of the gas composition

The impact of gas composition including H<sub>2</sub>O and impurities such as H<sub>2</sub>S, SO<sub>2</sub> have been investigated with respect to the CO<sub>2</sub> adsorption capacity. Generally, steam enhances both the CO<sub>2</sub> adsorption capacity and the cyclic stability of hydrotalcites (Ding and Alpay, 2000, 2001; J. Hufton, 1999; León et al., 2010; Ram Reddy et al., 2008). Ding et al. measured a 10 % increase in the CO<sub>2</sub> adsorption capacity

under humid conditions compared to dry conditions at 480 °C (Ding and Alpay, 2000). They also found no further increase in the CO<sub>2</sub> adsorption capacity when the partial pressure of steam was increased from 0.03 to 2.45 bar, similar to what has been observed for CaO/CaCO<sub>3</sub> where only low partial pressures of steam have a positive impact on the CO<sub>2</sub> sorption capacity (Donat et al., 2012). The reason for the CO<sub>2</sub> sorption enhancement of Mg-Al HTLs, measured in the range of 300 to 480 °C, has been attributed to the formation of magnesium and aluminum hydroxides, a higher hydroxyl concentration of the surface, and/or avoiding coke deposition (Choi et al., 2009; Ding and Alpay, 2000). Due to the independence of the water concentration in the CO<sub>2</sub> sorption step, it has also been suggested that new adsorption sites are created through the surface coverage of water (Ram Reddy et al., 2008). Furthermore, performing the regeneration of the HTL with steam has proven to be more effective in maintaining a high regenerability than with N<sub>2</sub>, demonstrated by 30-40 % higher CO<sub>2</sub> recovery in the presence of steam at 300 °C and 1 bar (Ding and Alpay, 2001).

Hydrotalcites promoted with K<sub>2</sub>CO<sub>3</sub> are able to reversibly capture both H<sub>2</sub>S and CO<sub>2</sub> with high selectivity. With up to 2000 ppm of H<sub>2</sub>S, the CO<sub>2</sub> sorption capacity is not affected compared to the sulphur-free conditions (van Dijk et al., 2011). The high selectivity and reversibility suggest that SEWGS can eliminate CO<sub>2</sub> and H<sub>2</sub>S simultaneously from the syngas, and an almost CO<sub>2</sub> and H<sub>2</sub>S-free H<sub>2</sub> stream and a separate CO<sub>2</sub> and H<sub>2</sub>S stream can be produced (Bassani et al., 2019; van Dijk et al., 2011). On the other hand, SO<sub>x</sub> has a severe negative impact on the CO<sub>2</sub> adsorption capacity of HTLs, as the adsorbents deactivate rapidly due to irreversible SO<sub>x</sub> adsorption. Also, the adsorption of SO<sub>x</sub> is favored over CO<sub>2</sub> due to strong acid-base interactions, such that a desulfurization unit upstream of CO<sub>2</sub> capture unit is necessary on a process scale (Ram Reddy et al., 2008).

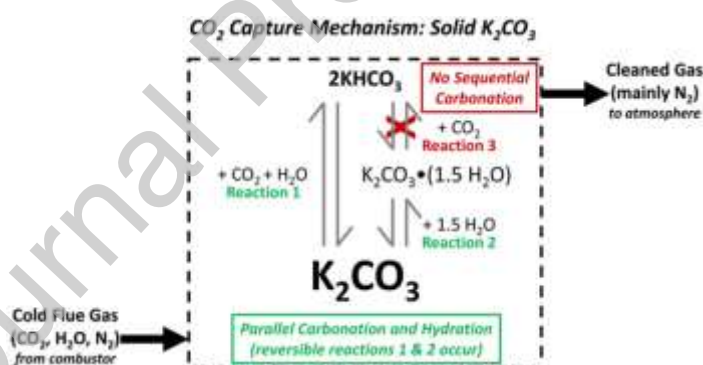
#### **3.4.2.5 CO<sub>2</sub> capture applications**

Similar to MgO-based sorbents, at medium temperatures HTLs are most suitable for pre-combustion CO<sub>2</sub> capture when CO<sub>2</sub> partial pressures are high. Recent European Horizon 2020 projects (e.g. STEPWISE or FReSMe) have demonstrated the large potential of SEWGS using HTLs to reduce CO<sub>2</sub> emissions from the iron and steel industry (Cobden et al., 2018; Gazzani et al., 2015; Manzolini et al., 2020; Sebastiani et al., 2021). Here, the sorbent is operated through a pressure swing adsorption approach (CO<sub>2</sub> sorption at > 20 bar, and CO<sub>2</sub> removal from the sorbent at ~ 1 bar) (Gentile et al., 2022).

#### **3.4.3. Alkali-metal-based carbonates**

Among the various solid sorbents, dry alkali-metal-based solid sorbents are considered promising candidates for post combustion CO<sub>2</sub> capture, which are expected to be cost-effective and energy-efficient (Dong et al., 2015; Rodríguez-Mosqueda et al., 2018). Alkali-metal carbonates, such as K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>, can react with CO<sub>2</sub> to form alkali hydrogen carbonates in the presence of H<sub>2</sub>O at low

temperatures (60-80 °C) as displayed in Reaction 3.9, which can be easily regenerated at 120-200 °C via the reverse reaction of Reaction 3.9 (Qin et al., 2014). By comparison,  $K_2CO_3$  has been revealed to give better performance than  $Na_2CO_3$  in terms of both  $CO_2$  adsorption capacity and kinetics, and thus most attention has been diverted to the former (Jaiboon et al., 2013). Nevertheless, the employment of pure  $K_2CO_3$  is mainly restricted by their low conversion and poor reaction kinetics, which has been proven to be limited by the adsorption, instead of chemical reaction. Furthermore, pure  $K_2CO_3$  is a deliquescent substance with a compact structure and a relatively low surface area, leading to its inferior  $CO_2$  adsorption capacity (Bararpour et al., 2019; Zeng et al., 2022). It has been reported that the hydration of  $K_2CO_3$  (Reaction 3.10) generally occurs as a competing reversible reaction in parallel with Reaction 3.9 during the carbonation process in the presence of a high amount of moisture in the inlet gas, which converts the active adsorption sites to hydrated byproducts with poor  $CO_2$  capture capacity (Figure 3.41) (Bararpour et al., 2020; Gomez et al., 2016). Therefore, the modification of  $K_2CO_3$  sorbents is required to enhance their  $CO_2$  capture capacity and durability before use for cyclic carbonization and regeneration operations.

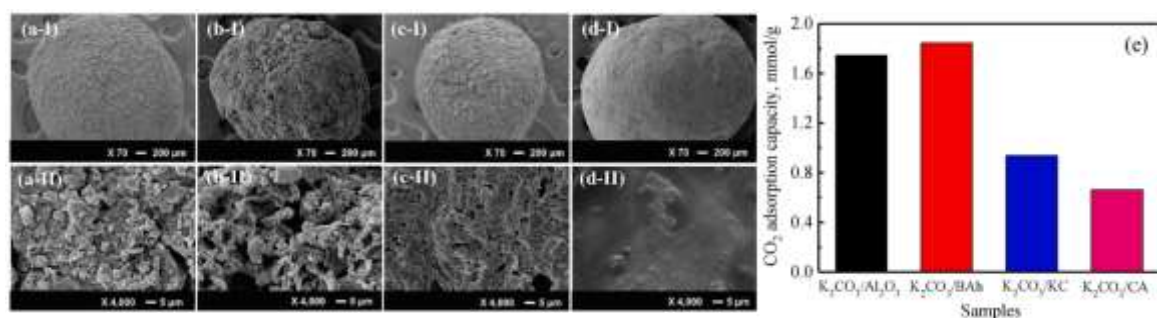


**Figure 3.41.** Reaction mechanism of solid  $K_2CO_3$  for  $CO_2$  capture (Gomez et al., 2016).

The most extensively studied method is to support  $K_2CO_3$  by a stable and porous material, which contributes to better contact between the sorbent and  $CO_2$  and hence increases the overall carbonation rate. The commonly used supports include activated carbon (AC),  $TiO_2$ ,  $CaO$ ,  $MgO$ ,  $ZrO_2$ , silica gel, zeolites and  $Al_2O_3$  (Li et al., 2011).  $Al_2O_3$  and  $MgO$  are the most widely employed supports because of their excellent  $CO_2$  capture capacity. However, the main drawback of  $Al_2O_3$  and  $MgO$  supported  $K_2CO_3$  sorbents is their easy deactivation because of the generation of undesirable byproducts, such as  $KAl(CO_3)_2(OH)_2$ ,  $K_2Mg(CO_3)_2$ , and  $K_2Mg(CO_3)_2 \cdot 4(H_2O)$ , which could not be completely regenerated to the original  $K_2CO_3$  phase (Lee et al., 2008; Qin et al., 2018). For example, Lee et al. (Lee, S.C. et al.,

2014; Lee, S.C. et al., 2013) investigated the phase of  $\text{Al}_2\text{O}_3$  on the  $\text{CO}_2$  capture performance of supported  $\text{K}_2\text{CO}_3$  sorbents by calcining  $\text{Al}_2\text{O}_3$  at various temperatures of 300, 600 ( $\gamma\text{-Al}_2\text{O}_3$ ), 950 ( $\delta\text{-Al}_2\text{O}_3$ ) and 1200 °C ( $\alpha\text{-Al}_2\text{O}_3$ ). They demonstrated that the regeneration capacity of the sorbents increased with elevating the calcination temperature due to the production of less inactive  $\text{KAl}(\text{CO}_3)_2(\text{OH})_2$  byproducts, in spite of the decreased surface area of the sorbents at higher calcination temperature. In this case, the regeneration capacity of the sorbents was more dependent on the structure properties of alumina, rather than the texture properties. In comparison, AC and  $\text{TiO}_2$  supported  $\text{K}_2\text{CO}_3$  sorbents are more promising in retaining the  $\text{CO}_2$  capture capacity with the formation of mainly  $\text{KHCO}_3$  in the carbonation process (Lee et al., 2008; Qin et al., 2018).

It has been proven that the nature and physiochemical properties of the support, such as the surface area, pore structure, and surface property, play a significant role in determining the  $\text{CO}_2$  capture capacity of supported  $\text{K}_2\text{CO}_3$  sorbents. For instance, Qin et al. (Qin et al., 2014) discovered that for  $\text{K}_2\text{CO}_3$  sorbents supported by various materials (fly ash, Portland cement, clay,  $\text{Al}_2\text{O}_3$ , and calcium aluminate cement),  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  displayed the highest  $\text{CO}_2$  capture capacity of 71 mg  $\text{CO}_2/\text{g}$  sorbent, which was stable in 10 cycles. The reason could be explained by the developed mesoporous structure and high surface area of  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  sorbents. Similar results have been reported by Wang et al. that among various  $\text{Al}_2\text{O}_3$ -based supports (i.e., activated alumina ( $\text{Al}_2\text{O}_3$ ), Bayer aluminum hydroxide (Bah), kaolinite clay (KC) and calcium aluminate cement (CA)), Bah supported  $\text{K}_2\text{CO}_3$  displayed the highest  $\text{CO}_2$  sorption capacity of 1.85 mmol  $\text{CO}_2/\text{g}$ , which might be ascribed to its loose surface and well-developed pore structure, as well as its highest surface area and pore volume (Figure 3.42) (Wang, P. et al., 2019). In addition, Masoud et al. (Masoud et al., 2021) studied the role of surface oxygen groups on the carbon supports (i.e. polarities of the support) in  $\text{CO}_2$  capture by  $\text{K}_2\text{CO}_3$  sorbents. The result showed that the apolar carbon support was more favourable to  $\text{CO}_2$  capture, since an apolar support accelerated the adsorption of apolar  $\text{CO}_2$  molecules while decreasing the local concentration of polar  $\text{H}_2\text{O}$  on the sorbent, contributing to a higher carbonation degree. On the contrary, a polar support was expected to promote the hydrate formation by attracting more polar  $\text{H}_2\text{O}$  molecules on the  $\text{K}_2\text{CO}_3$  sorbent, which thereby limited the carbonation reaction.

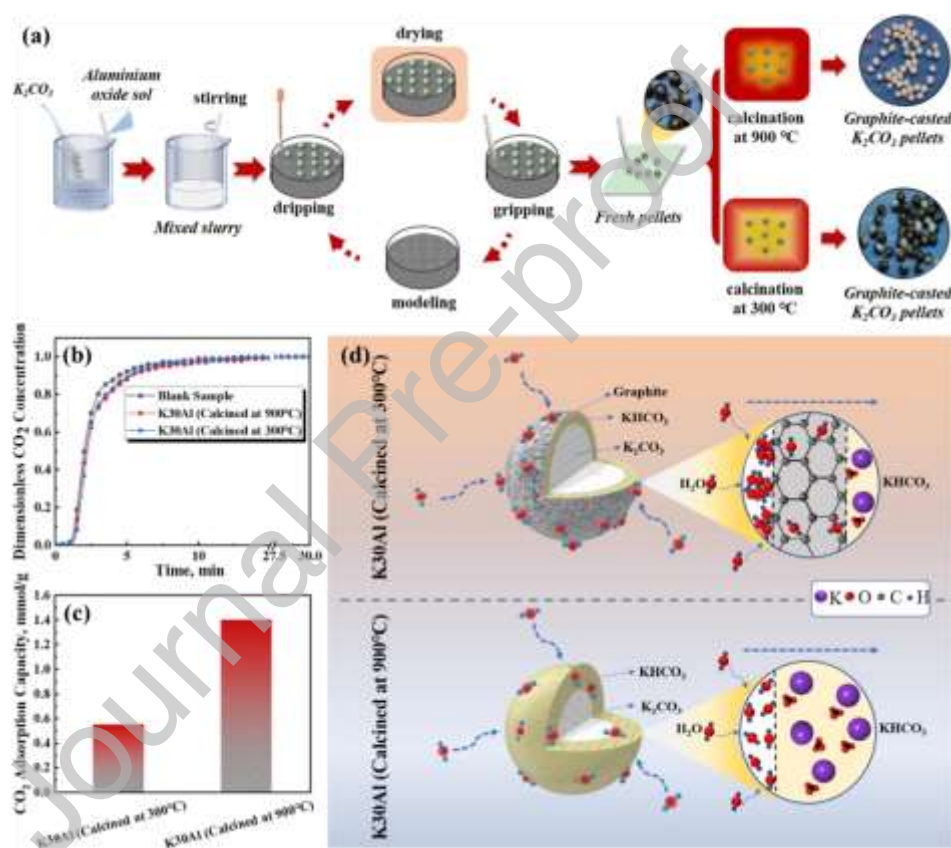


**Figure 3.42.** SEM images of  $K_2CO_3$ -based sorbents supported by (a)  $Al_2O_3$ ; (b) BAh; (c) KC and (d) CA, and (e)  $CO_2$  adsorption capacities of  $K_2CO_3$ -based sorbents with different supports (Wang, P. et al., 2019).

In addition to the support properties, the loading amount of  $K_2CO_3$  on the support is another important parameter affecting the  $CO_2$  capture performance of the composite sorbents. It has been proven that a proper  $K_2CO_3$  loading favours the achievement of well-developed pore structures and surface morphology with active components uniformly distributed on the support, contributing to the enhancement of  $CO_2$  capture performance. On the contrary, excessive  $K_2CO_3$  loading will result in the agglomeration of  $K_2CO_3$  crystallites and hence the coverage and blocking of the surface and pores of the sorbents, which could be responsible for the deteriorated  $CO_2$  capture capacity (Wang, P. et al., 2019). Guo et al. (Guo, Y. et al., 2018) evaluated the  $CO_2$  sorption capacity of silica aerogel supported  $K_2CO_3$  sorbents with various  $K_2CO_3$  loadings of 0-30 wt%. The maximum  $CO_2$  capture capacity of 1.32 mmol  $CO_2/g$  was achieved at a  $K_2CO_3$  loading of 20 wt%, which should be attributed to its best particle morphology with a uniform dispersion of  $K_2CO_3$  and small pores. Zeng et al. (Zeng et al., 2022) also varied the content of  $K_2CO_3$  on  $Al_2O_3$  support from 20 to 60 wt% and discovered a decrease of the surface area and pore volume with increasing the  $K_2CO_3$  content. In spite of the relatively inferior texture properties of K30Al to that of K20Al, K30Al achieved the highest  $CO_2$  capture capacity because of its higher amount of active  $K_2CO_3$ . With the further increase of  $K_2CO_3$  content to 40-60 wt%, the  $CO_2$  capture capacity decreased sharply due to the blockage of the pores, leading to the increase of the internal diffusion resistance of  $CO_2$ .

The synthesis method is another crucial factor influencing the physiochemical properties of the sorbents. In recent years, various methods have been developed for the preparation of  $K_2CO_3$ -based sorbent, in order to enhance its  $CO_2$  capture performance. For example, Sengupta et al. (Sengupta et al., 2015) compared the performance of  $K_2CO_3/Al_2O_3$  sorbents synthesized by single- and multi-step impregnation (SI and MI) methods. They found that the sorbent synthesized by the MI method was more promising than that synthesized by the SI method in terms of  $CO_2$  adsorption capacity and regeneration efficiency. The reason could be the more uniform dispersion of  $K_2CO_3$  in the broad macropores without the blockage of narrower mesopores of  $Al_2O_3$  in the sorbent synthesized by the MI method, which enabled a higher loading of accessible  $K_2CO_3$  for  $CO_2$  adsorption. On the contrary, the blockage of narrower mesopores by large  $K_2CO_3$  aggregates could be obviously observed in the sorbent synthesized by the SI method, which limited the accessibility of  $CO_2$  towards active  $K_2CO_3$  species. In order to eliminate the adverse effect of  $H_2O$  on the  $CO_2$  capture performance of supported  $K_2CO_3$  sorbent, Bararpour et al. (Bararpour et al., 2020) synthesized a core-shell structured support with  $\gamma$ -alumina as the core and  $TiO_2$  as the shell. The result showed that the  $CO_2$  capture performance of

$K_2CO_3/\gamma$ -alumina was significantly enhanced after shelling the support with  $TiO_2$ , due to the low hydrophilicity of the sorbent, which restricted the occurrence of reaction (2). The effect of calcination temperature on the  $CO_2$  adsorption performance of  $Al_2O_3$ -supported  $K_2CO_3$  pellets synthesized by graphite-casting method (Figure 3.43 (a)) has also been investigated in a previous study (Zeng et al., 2022). Although it is widely accepted that a high calcination temperature will lead to a less developed microstructure and hence an inferior  $CO_2$  adsorption capacity because of the aggregation of active components at higher temperatures, the  $K_2CO_3$ -based pellets calcinated at  $900\text{ }^\circ\text{C}$  displayed a 2.5 times higher  $CO_2$  adsorption capacity than that of the sorbent calcinated at  $300\text{ }^\circ\text{C}$  (Figure 3.43 (b) and (c)). The reason could be explained by that the residual graphite coating on the sorbent surface calcinated at  $300\text{ }^\circ\text{C}$  suppressed the diffusion of  $H_2O$  to  $K_2CO_3$  because of the hydrophobicity of graphite.



**Figure 3.43.** (a) Scheme for the preparation of graphite-casted  $K_2CO_3$  pellets, (b) breakthrough curves of  $CO_2$  adsorption, (c)  $CO_2$  adsorption capacity of K30Al calcined at  $300$  and  $900\text{ }^\circ\text{C}$ , and (d) mechanism of the adverse effect of residual graphite coating on  $CO_2$  adsorption (Zeng et al., 2022).

On account of the relatively poorer  $CO_2$  adsorption rate of  $Na_2CO_3$  than that of  $K_2CO_3$ , the studies on  $CO_2$  capture using  $Na_2CO_3$ -based sorbents are limited. However, the primary advantages of using  $Na_2CO_3$  over  $K_2CO_3$  are its easier accessibility, lower regeneration temperature, and lower  $CO_2$  capture

costs (Wu, Y. et al., 2020). If the reaction kinetics of CO<sub>2</sub> capture could be dramatically improved via proper modifications of Na<sub>2</sub>CO<sub>3</sub>-based sorbents, their applications in large-scale CO<sub>2</sub> capture could be significantly broadened. Therefore, the understanding of the rate-limiting steps of CO<sub>2</sub> capture by Na<sub>2</sub>CO<sub>3</sub> is critical to systematically improving the kinetics. Cai et al. (Cai et al., 2019) employed first-principles density functional theory (DFT) to study the structural, mechanistic, and energetic properties of CO<sub>2</sub> adsorption on the low-index (001) and high-index ( $\bar{4}02$ ) surfaces of unmodified Na<sub>2</sub>CO<sub>3</sub> sorbent, in order to clarify the actual reason of the slow kinetics. They discovered that the reaction barriers for bicarbonate formation on the above two facets were comparable with that on K<sub>2</sub>CO<sub>3</sub> surfaces. However, on account of the much lower overall kinetics of CO<sub>2</sub> capture by Na<sub>2</sub>CO<sub>3</sub> observed by experiments, they assumed that the kinetics of CO<sub>2</sub> captured on Na<sub>2</sub>CO<sub>3</sub> was controlled by surface diffusion, rather than by surface carbonation reaction as that observed for K<sub>2</sub>CO<sub>3</sub>.

In order to enhance the reaction kinetics of CO<sub>2</sub> capture on Na<sub>2</sub>CO<sub>3</sub>, the dispersion of Na<sub>2</sub>CO<sub>3</sub> on various supports is considered as the most dominant strategy, where the support effect and Na<sub>2</sub>CO<sub>3</sub> loading are important factors in developing efficient Na<sub>2</sub>CO<sub>3</sub>-based sorbents (Cai et al., 2020; Luo and Kanoh, 2017). It is well accepted that the textural properties of the support play a crucial role in determining the CO<sub>2</sub> capture performance of the sorbent. Kazemi et al. (Kazemi et al., 2020) tried to improve the specific surface area and pore volume of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported Na<sub>2</sub>CO<sub>3</sub> sorbent using a modified sol-gel process with the addition of polyethylene glycol (PEG). They demonstrated that the surface area and pore volume of the modified sorbent were around 38 % and 340 % higher than that of the sorbent synthesized without the addition PEG. As a result, the CO<sub>2</sub> capture capacity of the sorbent increased by 34 %. In addition to the texture properties such as surface area and pore structure, the morphology and distribution of Na<sub>2</sub>CO<sub>3</sub> have also been confirmed to affect the CO<sub>2</sub> capture performance. As observed by Cai et al. (Cai et al., 2020), the morphology of Na<sub>2</sub>CO<sub>3</sub>/ $\gamma$ -AlOOH sorbent could be changed by varying the loading amount of Na<sub>2</sub>CO<sub>3</sub>, which thereby influences the CO<sub>2</sub> capture capacity significantly. At lower Na<sub>2</sub>CO<sub>3</sub> loadings of <17 wt%, Na<sub>2</sub>CO<sub>3</sub> was uniformly dispersed on  $\gamma$ -AlOOH surface sites as a monolayer amorphous form. With the increase of Na<sub>2</sub>CO<sub>3</sub> loading up to 23-29 wt%, the Na<sub>2</sub>CO<sub>3</sub> crystallites grew uniformly to form nanoparticles on the inner surface of  $\gamma$ -AlOOH, contributing to the exposure of more high-index facets of Na<sub>2</sub>CO<sub>3</sub> (such as (1 1 2) and ( $\bar{4}$  0 2) facets) and hence the enhancement of the CO<sub>2</sub> capture capacity.

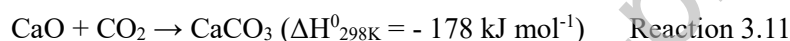
In summary, alkali-metal-based carbonates of K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> are proven as promising candidates for CO<sub>2</sub> capture, while the practical applications of pure carbonates were restricted by their poor capacities and kinetics. As a result, the proper design of efficient K<sub>2</sub>CO<sub>3</sub>- and Na<sub>2</sub>CO<sub>3</sub>-based sorbents is of significant importance in broadening their application prospects. The most potential method for modification of K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> is to load them on a porous support, where the optimization of the support materials, K<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> loading amounts, and preparation methods are expected to improve the texture properties and surface morphology, enhance the dispersion of active K<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub>, and

hence accelerate the CO<sub>2</sub> adsorption. In spite of the extensive studies on this topic, the influence of the abundant impurities in flue gases, such as sulphur- and chlorine-containing species, on the CO<sub>2</sub> capture performance of alkali-metal-based sorbents was rarely studied systematically, which is critical in evaluating their durability and regeneration efficiency in practical applications.

### 3.5. High-temperature solid sorbents

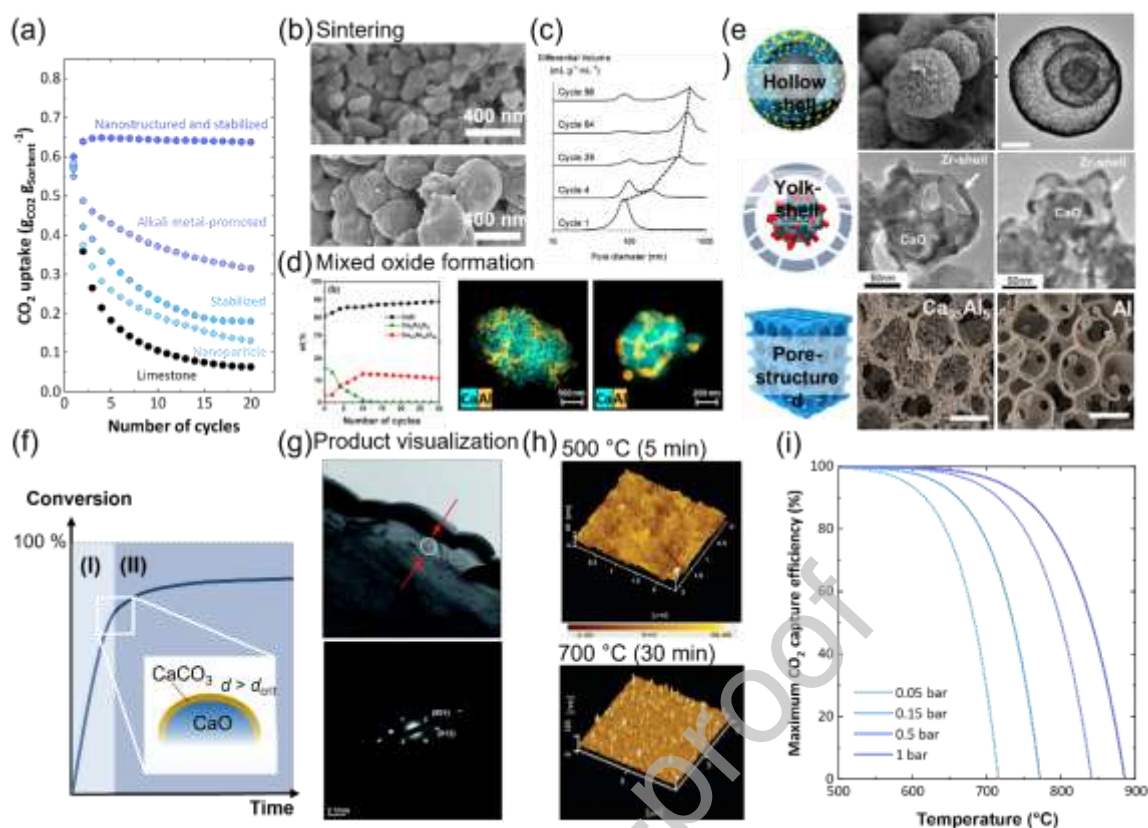
#### 3.5.1 CaO for CO<sub>2</sub> capture

Among the alkali earth metal oxides CaO, SrO, and BaO, CaO has been studied most thoroughly for CO<sub>2</sub> sorption applications at high temperatures (Kierzkowska et al., 2013; Krödel et al., 2020; Omodolor et al., 2020; Yu et al., 2012). Many of the early studies in the 1990s and 2000s benefitted from experience with CaO-based sorbents in the context of flue gas desulfurization, when SO<sub>2</sub> was considered more problematic than CO<sub>2</sub> (Dunstan et al., 2021). The CO<sub>2</sub> capture process using CaO-based sorbents, also referred to as calcium looping (CaL), utilizes the reversible reaction between CaO and CO<sub>2</sub> at elevated temperatures, viz Reaction 3.11:



The operational windows for the carbonation and the calcination reactions are defined by the reaction equilibrium, i.e. the equilibrium partial pressure of CO<sub>2</sub> at a given temperature (Samanta et al., 2012). In sorbent research, calcination is commonly conducted at 800 – 950 °C in air, N<sub>2</sub> or pure CO<sub>2</sub>; at the process level, the calcination reaction would have to be carried out in (almost) pure CO<sub>2</sub> to process the CO<sub>2</sub> released from the sorbent further (e.g. compression and storage) and avoiding additional downstream gas purification. Typically investigated carbonation conditions range between 550 °C and 700 °C as well as 10 – 15 vol.% CO<sub>2</sub> in air or N<sub>2</sub> to reflect CO<sub>2</sub> concentrations in off-gases from (coal) combustion processes. During the carbonation reaction, two reaction regimes are observed: (Bhatia and Perlmutter, 1983; Cai et al., 2017). A fast, kinetically-controlled regime and a slow, diffusion-controlled regime, see Figure 3.44f. The CO<sub>2</sub> uptake in the kinetically-controlled regime correlates directly with the initially available surface area of the CaO-based sorbent, which is usually supplied by pores with diameters smaller than 100 nm (Alvarez, Diego and Abanades, J Carlos, 2005; Alvarez, D. and Abanades, J. C., 2005; Bhatia and Perlmutter, 1983). The shift between the two reaction regimes is often explained with the CaCO<sub>3</sub> product layer reaching a critical thickness, estimated at 30 – 50 nm at which the reaction becomes limited by CO<sub>2</sub> diffusion through CaCO<sub>3</sub> (Figure 3.44g and h).





**Figure 3.44** (a) Typical cyclic CO<sub>2</sub> uptake of selected CaO-based sorbents over 20 carbonation-regeneration cycles, illustrating the performance improvement compared to bare limestone via stabilization, promotion or nanostructuring of the sorbent. (b) SEM micrographs of limestone after the 1<sup>st</sup> calcination (top) and after 10 cycles (bottom)(Naeem et al., 2018). (c) Evolution of the pore volume of La Blanca limestone measured via Hg intrusion porosimetry over 98 carbonation-calcination cycles(Alvarez, D. and Abanades, J. C., 2005). (d) Changes in the phase composition of a Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>-stabilized CaO-based sorbent over carbonation-regeneration cycling derived from in situ XRD using Rietveld analysis(Kim, S.M. et al., 2018). (e) Electron micrographs of a nanostructured hollow multishell CaO-based sorbent reported by Naeem et al.(Naeem et al., 2018), a yolk-shell-type CaO-based sorbent reported by Krödel et al.(Krödel et al., 2022), and pore-structured (via a sacrificial template) CaO-based sorbent reported by Kim et al.(Kim, S.M. et al., 2019) (f) Conversion over time curve for CaO-based sorbents exhibiting the two typically observed regimes: (I) a kinetically-controlled regime and (II) a diffusion-controlled regime. (g) Visualization of the CaCO<sub>3</sub> product on CaO via TEM and SAED(Sun, H. et al., 2019). (h) AFM plots of the CaCO<sub>3</sub> product formation on a CaO single crystal at two different carbonation temperatures and after varying carbonation times(Li, Z.-s. et al., 2012). (i) Maximum CO<sub>2</sub> capture efficiency for CaO-based sorbents as a function of temperature and the partial pressure of CO<sub>2</sub> in the gas stream.

For practical CO<sub>2</sub> capture applications at high temperature, CaO-based sorbents need to be repeatedly cycled between their oxide and carbonate states, making the cyclic CO<sub>2</sub> uptake an important metric for

the CO<sub>2</sub> capture costs (Hanak et al., 2015a). Generally, the cyclic CO<sub>2</sub> uptake should be as close as possible to the theoretical maximum CO<sub>2</sub> uptake capacity of 0.78 g<sub>CO2</sub>/g<sub>CaO</sub> and stable over ideally thousands of cycles. In reality, the cyclic CO<sub>2</sub> uptake of sorbents derived from natural limestones decreases rapidly with cycling, as shown exemplarily in Figure 3.44a. The deactivation of the sorbent is a result of material sintering (Figure 3.44b and c), which (i) reduces the surface area of the regenerated CaO available for the reaction with CO<sub>2</sub>, and (ii) increases the diffusional resistance of CO<sub>2</sub> into the bulk sorbent, such that both the rate and the extent of CO<sub>2</sub> uptake during the carbonation step are reduced (Barker, 2007; Li et al., 2006; Wang, C. et al., 2014). To mitigate the sintering-induced deactivation, research efforts have focused on either reactivating the sorbents, e.g. using a steam treatment at high temperatures, or stabilizing and promoting the sorbent using non-alkali metal oxides and alkali metal salts, respectively (Salaudeen et al., 2018).

### 3.5.1.1 Synthetic stabilized and promoted sorbents

The cyclic CO<sub>2</sub> uptake performance of CaO-based sorbents can be stabilized using metal oxides with high Tammann temperatures such as Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> or MgO (Kierzkowska et al., 2013; Krödel et al., 2020; Naeem et al., 2017; Radfarnia and Iliuta, 2013; Salaudeen et al., 2018). These stabilizers are mixed into the CaO matrix in contents of typically 5 - 20 wt.%, e.g. through ball-milling, co-precipitation, sol-gel or more advanced techniques like atomic layer deposition, and they are assumed to act as physical barriers against the sintering of CaO particles (Kim, S.M. et al., 2018; Kurlov et al., 2020a; Kurlov et al., 2016; Liu, W. et al., 2010). Stabilizers effectively reduce the cyclic decrease of the surface area and pore volume of the sorbents, thereby improving their cyclic CO<sub>2</sub> uptake. For example, Kim et al. reported a Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>-stabilized CaO-based sorbent showing a CO<sub>2</sub> uptake of 0.38 g<sub>CO2</sub>/g<sub>Sorbent</sub> after 30 cycles, an increase of 300 % compared to the benchmark limestone (Kim, S.M. et al., 2018). Other materials utilizing ZrO<sub>2</sub>, MgO or SiO<sub>2</sub> showed similar CO<sub>2</sub> uptakes of up to 0.37, 0.31 or 0.39 g<sub>CO2</sub>/g<sub>Sorbent</sub> after 10 cycles, respectively (Kurlov et al., 2016; Sanchez-Jimenez et al., 2014; Zhao et al., 2014). Despite these improvements, even stabilized materials deactivate with cycling via mixed phase formation with CaO, viz. a loss of the reactive phase for CO<sub>2</sub> sorption, or the agglomeration of the stabilizing phase as surface-segregated particles, reducing the effectiveness of the stabilizer as a physical barrier against sintering of CaO grains/particles (Figure 3.44d) (Kim, S.M. et al., 2018; Kurlov et al., 2016). Hence, optimizing both the distribution and the mobility of the stabilizer phase in the material are crucial aspects for the design of stabilized, long-lasting CaO-based sorbents. Works by Naeem et al. (Naeem et al., 2018) and Armutlulu et al. (Armutlulu et al., 2017) have employed means of stabilization as well as morphological design techniques to derive sorbents with even more stable cyclic CO<sub>2</sub> uptakes (Figure 3.44e). For example, one of the best performing sorbents to date consists of a double shell structure of a CaO-MgO nanocrystalline matrix. This material exhibited a CO<sub>2</sub> uptake of

0.65 g<sub>CO<sub>2</sub></sub>/g<sub>Sorbent</sub> after 10 cycles, which equals 93 % of the theoretical maximum CO<sub>2</sub> uptake of a sorbent containing 10 wt.% MgO.

The promotion of CaO-based sorbents using alkali metal salts (AMS), e.g. Na<sub>2</sub>CO<sub>3</sub>, NaCl, K<sub>2</sub>CO<sub>3</sub> or KCl, is another approach to improve their cyclic CO<sub>2</sub> uptake (González et al., 2011; Kurlov et al., 2020b; Lee et al., 2018; Xu, Yongqing et al., 2018). Added in relatively large amounts (> 5 wt.%), these low Tammann-temperature promoters increase the sintering of the sorbents, thereby reducing the cyclic CO<sub>2</sub> uptake performance significantly compared to benchmark materials without AMS (Krödel et al., 2020). In addition, some alkali metals form low-melting mixed phases with CaO that tend to form either large surface-segregated particles or a layer around the bulk CaO particles (Kurlov et al., 2020b). For example, Kurlov et al. reported the formation of Na<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub> coatings around Na<sub>2</sub>CO<sub>3</sub>-modified CaO particles due to the melting of the mixed phase under calcination conditions (900 °C, 100 vol.% CO<sub>2</sub>), negatively affecting the accessibility of CaO for reaction with CO<sub>2</sub>. On the other hand, low AMS contents of < 1 wt.% have been reported to have a positive effect on both the carbonation and calcination reaction, therefore increasing the cyclic CO<sub>2</sub> uptake (Xu et al., 2023; Xu et al., 2017; Yang et al., 2018). The best reported sorbents to achieve CO<sub>2</sub> uptakes of up to 0.5 g<sub>CO<sub>2</sub></sub>/g<sub>Sorbent</sub> after 10 cycles with < 1 wt.% of promoter added. In nature, various alkali metals are found in the structure of CaCO<sub>3</sub>, which may explain the large differences in the cyclic CO<sub>2</sub> uptake of limestone-derived sorbents of different origin/geographical location (Fennell et al., 2007; Grasa and Abanades, 2006; Valverde et al., 2015; Yoshimura et al., 2017). Similarly, researchers have proposed that alkali metal promoters may be incorporated into the structure of the CaCO<sub>3</sub> product forming during carbonation (Leukel et al., 2018). This could positively affect the rate of carbonation, e.g. by enhancing CO<sub>2</sub> diffusion through CaCO<sub>3</sub>, but evidence for this mechanism is still lacking. It has been reported that AMS affects the transition temperature between CaO and CaCO<sub>3</sub>, leading to the onset of the decomposition of CaCO<sub>3</sub> at lower temperatures which may be interesting from a process perspective. For the CaL process to be implemented at industrially relevant scales, also the mechanical stability of sorbent particles is important, and maintaining a high stability with cycling is currently an active area of sorbent research (Pi et al., 2019; Sun, J. et al., 2019; Sun et al., 2015).

### 3.5.1.2 Effect of the gas composition

Unburnt fuel gases (e.g. CO, H<sub>2</sub>, CH<sub>4</sub>) hardly affect the rate of the carbonation or calcination reaction of CaO-based sorbents (Dunstan et al., 2021); under conditions that favor the reverse water-gas shift reaction, H<sub>2</sub> was observed to react with CO<sub>2</sub> released from the CaCO<sub>3</sub>, thereby accelerating its decomposition. The presence of SO<sub>2</sub> and steam is more influential, and affects the sorbent behavior during both the carbonation and calcination reaction.

SO<sub>2</sub> forms CaSO<sub>4</sub> with CaO in the presence of oxygen, a reaction that has been utilized for high-temperature flue gas desulfurization (He et al., 2021). As the decomposition of CaSO<sub>4</sub> does not proceed

rapidly below  $\sim 1200$  °C (viz. at temperatures much higher than typical decomposition temperatures of  $\text{CaCO}_3$ ) (Tian et al., 2008), the presence of  $\text{SO}_2$  in a flue gas stream is problematic and with time reduces the amount of  $\text{CaO}$  that is available for  $\text{CO}_2$  to form  $\text{CaCO}_3$  (Grasa et al., 2008). The carbonation reaction is faster at typical carbonation conditions (15 vol.%  $\text{CO}_2$ , 550 – 700 °C) than the sulfation reaction, but sulfation rates increase with rising temperatures. The  $\text{CaSO}_4$  product also has an approximately 25 % higher molar volume than  $\text{CaCO}_3$ , increasing the diffusional resistance for  $\text{CO}_2$  further, which shifts the transition between the kinetically-controlled regime and the diffusion-controlled regime to lower  $\text{CO}_2$  uptakes, and also negatively affects the  $\text{CO}_2$  uptake in the diffusion-controlled regime (Borgwardt et al., 1987).

Contrarily, the presence of steam usually enhances both the rate and extent of  $\text{CO}_2$  uptake, mainly in the diffusion-controlled regime (Arias et al., 2012; Dong et al., 2020; Li, Z.-H. et al., 2016). It has been shown both experimentally and computationally that steam concentrations  $< 1$  vol.% are sufficient to achieve this effect. From a morphological point of view, the presence of steam has a positive effect on the surface area and pore volume for pores with diameters  $< 100$  nm, enhancing the rate of carbonation (Dong et al., 2020; Wang, C. et al., 2014). It has also been reported that the presence of steam lowers the driving forces ( $p_{\text{CO}_2} - p_{\text{CO}_2, \text{eq}}$ ) for the carbonation reaction to commence at a fast rate (Blamey et al., 2015). Structurally, it has been proposed that the presence of steam may lead to the formation of  $\text{Ca}(\text{OH})_2$  as an intermediate product. However, bulk  $\text{Ca}(\text{OH})_2$  is not thermodynamically stable under typical carbonation conditions (600 - 700 °C).

### 3.5.1.3 $\text{CO}_2$ capture applications using $\text{CaO}$ -based sorbents

$\text{CaO}$ -based sorbents can be used for a range of applications involving  $\text{CO}_2$  capture, and thus far, post-combustion  $\text{CO}_2$  capture has most frequently been investigated. Different from  $\text{MgO}$ -based sorbents, relatively high  $\text{CO}_2$  capture efficiencies can be realized with  $\text{CaO}$ -based sorbents even at low  $\text{CO}_2$  partial pressures as in flue gases from combustion processes. Several pilot-scale reactor units, typically operated as interconnected fluidized bed reactors involving the transfer of  $\text{CaO}$ -based sorbents between them, have shown  $\text{CO}_2$  capture efficiencies of 90 % or higher with steam present, close to the thermodynamic limit (Figure 3.44i) (Dieter et al., 2013; Duelli et al., 2015; Hanak et al., 2015a). Large demonstration plants at the MW scale have demonstrated the feasibility of the  $\text{CaL}$  process for post-combustion  $\text{CO}_2$  capture (Chang et al., 2014; Diego and Arias, 2020; Hilz et al., 2017; Ströhle et al., 2020), yet there are currently no industrial units in operation.

Closer to the industrial application may be  $\text{CaO}$ -based  $\text{CO}_2$  capture processes that offer, besides the removal or the elimination of  $\text{CO}_2$  emissions, additional economic value, e.g. hydrogen through sorption-enhanced reforming or water-gas shift reactions (Chirone et al., 2022; Di Giuliano and Gallucci, 2018; Harrison, 2008; Ma, X. et al., 2021; Masoudi Soltani et al., 2021; Zhang, C. et al., 2022; Zhu,

Xing et al., 2020) or thermal energy (Arcenegui-Troya et al., 2020; Medina-Carrasco and Valverde, 2022; Perejón et al., 2016).

### 3.5.2 Challenges and Emerging Technologies: A Life Cycle Thinking

Compared with other alternative technologies, calcium looping is expected to substitute amine looping in dealing with fuel gas with low CO<sub>2</sub> concentration ranging from 5-15%. But successful installation and operation of calcium looping should be relied on techno-economically competitiveness. High CO<sub>2</sub> concentration is obviously the main advantage for calcium looping. In addition, This CO<sub>2</sub> from post-combustion unit then only needs to be conditioned and dehydrated prior to compression, transport and commercial purposes. However, despite of the simple chemistry and efficient recycling involved in calcium looping, the following challenges are believed to hinder wider applications of such technology for CO<sub>2</sub> capture.

- 1) The net efficiency of tail-end configuration is reduced by integrating cryogenic air separation unit.(Plaza et al., 2020; Yang, Y. et al., 2021)
- 2) The combustion temperature must be controlled to avoid hot spots in the combustion zone that would enhance NO<sub>x</sub> production in the boiler.(Chen, J. et al., 2020; Hu, Y.C. et al., 2020)
- 3) Fast catalyst deactivation and poor reaction engineering technologies for optimum operations.

Those challenges could be addressed by applying advanced reaction technologies. However, those solutions should be proposed based on techno-economic thinking.(Colelli et al., 2022; Galusnyak et al., 2022; Kong et al., 2022; Moore et al., 2022) From a perspective of process development, the overall techno-economic advantages or disadvantages should be quantitatively assessed to evaluate the feasibility prior to practical implementation. The following aspects have been the main R&D focus in the past five years.

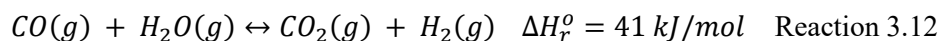
#### *Emerging technologies from a life cycle assessment*

##### (1) Combinatory processes with H<sub>2</sub> generation technologies

The combinatory technologies involving CO<sub>2</sub> capture and in-situ transformation could be a most promising solution to enhance environmental sustainability and technological viable.(Han, R. et al., 2022; Hashemi et al., 2022; Li, B. et al., 2022) Researchers have been proposing a variety of combinatory processes to integrate calcium looping with advanced H<sub>2</sub> generation techniques.

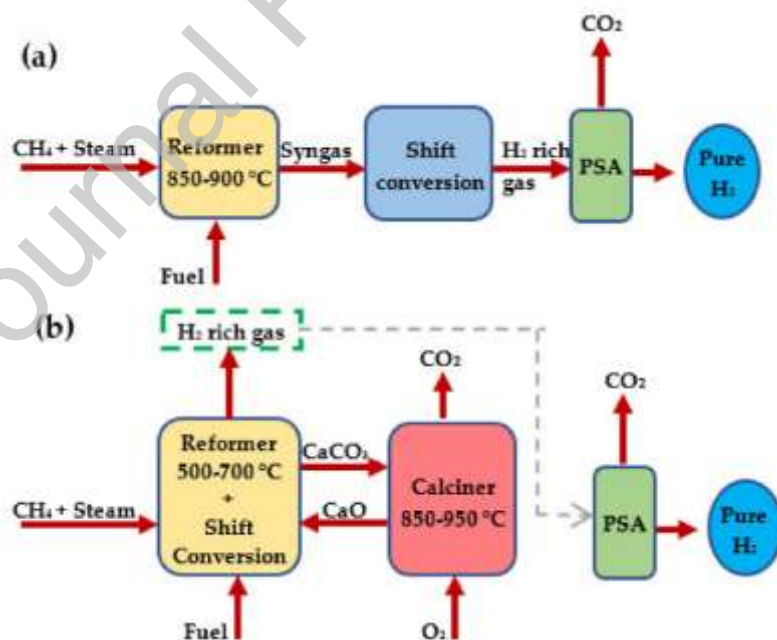
The commercial technologies based on the fuels reforming and gasification processes involve the production of syngas (H<sub>2</sub>, CO, CO<sub>2</sub>, and some CH<sub>4</sub> and hydrocarbons).(Han, R. et al., 2022; Madejski et al., 2022; Yang, Y. et al., 2021) Downstream applications of molecular H<sub>2</sub> usually demand high purity

with 99.99% and CO-free composition. This purpose has been achieved through water gas shift reaction (WGS), where CO reacts with water vapor to produce additional H<sub>2</sub> and CO<sub>2</sub>. However, this reaction (Reaction 3.12) is equilibrium-limited, but if CO<sub>2</sub> is continuously removed, the reaction will be shifted in favor of increased H<sub>2</sub> production.



Consequently, the syngas produced during the reforming or gasification (>600 °C) is upgraded in an independent WGS reactor (250-500 °C). The capture of CO<sub>2</sub> generated in-situ during the reforming and gasification processes, or syngas upgrade in a separate reactor, can favorably shift the thermodynamic equilibrium of the above-mentioned reactions toward a higher efficiency of H<sub>2</sub> production.

Another advanced energy efficient technique is called sorption-enhanced steam reforming. CaO is incorporated in this process in sorbents and immobilized with active metallic catalytic materials to enhance the overall the economics of CO<sub>2</sub> capture. Ni-based reforming catalysts, synergistically working with trace amounts of noble Rh, Pt, Pd and Ru have better performances in coke resistance for converting natural gas into highly purified molecular H<sub>2</sub>. The flow scheme is present in Figure 3.45, where reformer/shift reactors are working with calciner in a synchronizing fashion, coupled with pressure swing adsorption (PSA) for producing high quality H<sub>2</sub>. Life cycle assessment has confirmed that, such novel combination could lower the H<sub>2</sub> production cost by 3%-5% comparatively with no capture conventional reforming (approximately \$40/MWh capacity).



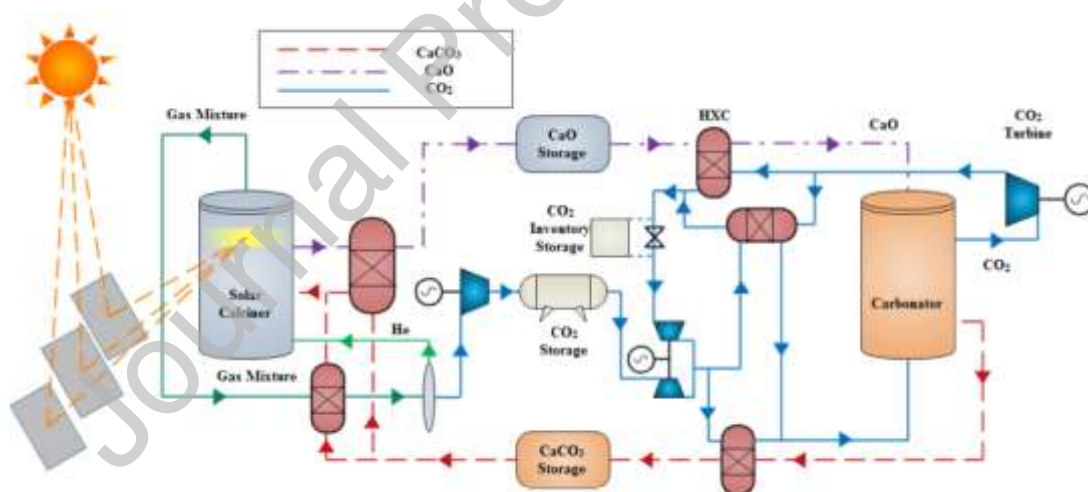
**Figure 3.45.** Flow diagram of (a) steam methane reforming and (b) sorption-enhanced steam methane reforming (CaCO<sub>3</sub> as sorbent)

(2) Solar thermal calcium looping

Grey H<sub>2</sub> production from natural gas conversion, or dry reforming of CH<sub>4</sub> and CO<sub>2</sub> could enhance the overall sustainability of CO<sub>2</sub> capture processes. However, carbon footprint analysis shows that, using solar energy as primary source could potentially reduce process cost by almost 12-25%, simply using solar heat as energy carrier. (Khosa et al., 2019; Salaudeen et al., 2018; Valverde, 2018)

An earlier version of solar thermal-assisted calcium looping has been involving compressed CO<sub>2</sub> and high-pressure air in carbonation stage. It assumed that CO<sub>2</sub> was completely converted in the carbonator, and then only high-temperature and high-pressure air was sent to the turbine to generate work. The power generation efficiency of the system was maximum, as high as 40-43%. It is worth mentioning that the complete consumption of CO<sub>2</sub> in the carbonator is an ideal situation.

Heat storage would favor the efficiency enhancement for calcium looping. An indirect integration of the steam Rankine cycle in calcium looping can be optimized from both energy and economic aspects, which determined the size and operating conditions of the main components. A complete exergy analysis show that, exergy loss occurs in the solar receiver (about 37%), the calcination section (26%), and the steam Rankine cycle (about 21%). (Erans et al., 2016; Perejon et al., 2016) In sharp contrast, the exergy loss that occurred in the carbonation section was relatively small, lower than 5%. The improved solar thermal-assisted calcium looping (shown in Figure 3.46) leads to a much higher process efficiency of 51%. (Ortiz et al., 2019; Tregambi et al., 2021)



**Figure 3.46.** Solar thermal calcium looping (Chacartegui et al., 2016)

### (3) Nanomaterials

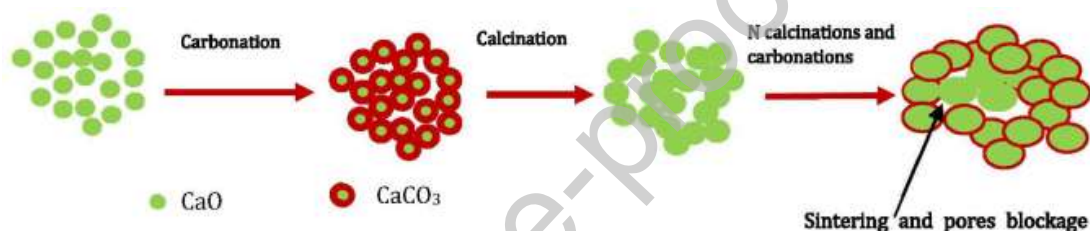
The use of functionalized materials not only could reduce the carbon footprint by combining H<sub>2</sub> generation technologies with calcium looping, in addition, nanomaterials with high surface areas would significantly enhance heat transfer in carbonation and calcination, leading to lowered loss of exergy. Experimental studies have suggested that the coupling of a solid looping cycle, for example, Fe/FeO



and Cu/CuO, can deliver the heat required in the calcination step in a faster way. The improvement is achieved by the exothermic oxidation of the Fe (Cu) to FeO (CuO) with air, which took place in the same fixed bed reactor as the calcination. (Santos and Hanak, 2022)

Nanostructured CaO and CaCO<sub>3</sub> materials could also slow sorbent and catalyst deactivation during high temperature looping. In earlier stages of looping operation, reactions occur in a kinetic controlled regime. In this stage, catalyst size is small thus reactions are considered as rate limiting step. However, catalyst size has been enhanced significantly after several cycles, leading to poor surface area and loss of sorbent reactivity by particle sintering and pore blockage (Figure 3.47).

Recent experimental studies have demonstrated the advantages of using nano-sized CaO and CaCO<sub>3</sub> materials in calcium looping. Unfortunately, no life cycle assessment has been conducted to quantitatively evaluate the environmental impact of preparation steps on the overall sustainability in calcium looping. (Li, K. et al., 2022; Xu, Y. et al., 2021)



**Figure 3.47.** Particle sintering during carbonation-calcination cycles (Teixeira et al., 2022)

### 3.5.3 Li-, Na-, Sr-, and Ba-based sorbents

Unlike MgCO<sub>3</sub> and CaCO<sub>3</sub>, other carbonates of alkali metal or alkaline earth metals, e.g., Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, SrCO<sub>3</sub> and BaCO<sub>3</sub>, are hard to decompose in practically achievable conditions, making them unsuitable for reversible CO<sub>2</sub> capture in their monometallic forms. To address this issue, transition metals and/or semi-metals are often incorporated into oxides of Li, Na, Sr and Ba to form ternary oxide sorbents. The incorporation of the transition metals modifies the basicity of the oxides, thus rendering their regenerability over CO<sub>2</sub> capture cycles. This section discusses some developments in Li, Na, Sr and Ba based CO<sub>2</sub> sorbents. Table 3.19 summarises the stoichiometric CO<sub>2</sub> capacities and experimental CO<sub>2</sub> uptakes of these sorbents.

**Table 3.19.** Stoichiometric CO<sub>2</sub> capacities and experimental CO<sub>2</sub> uptakes of Li, Na, Sr and Ba based sorbents.

Sorbent	Stoichiometric CO <sub>2</sub> capacity [wt.%]	Experimental CO <sub>2</sub> uptake [wt.%]	Carbonation Temperature [°C]	Calcination Temperature [°C]	Carbonation CO <sub>2</sub> partial pressure [bar]	Calcination CO <sub>2</sub> partial pressure [bar]	Max No. of Cycles	Ref
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<b>Li<sub>4</sub>SiO<sub>4</sub></b>	36.7	1.8-36.0	RT-700*	550-900	0.04-1.0	0	250	(Chen, X. et al., 2016; Lara-García et al., 2019; Seggiani et al., 2018; Wang, Haiyang et al., 2018; Wang, K. et al., 2019; Yang, Xinwei et al., 2016a, b)
<b>Li<sub>8</sub>SiO<sub>6</sub></b>	98.0	0-42.0	25-776*	-	1.5	-	-	(Cova et al., 2019)
<b>Li<sub>2</sub>ZrO<sub>3</sub></b>	28.7	0.01-23.0	500-575	600-700	0.10-2.0	0-0.585	30	(Gómez-Garduño and Pfeiffer, 2019; Peltzer et al., 2019; Peltzer et al., 2018)
<b>Li<sub>6</sub>WO<sub>6</sub></b>	41.1	3.6-25.9	30-710*	730-760	0.60	0	4	(Gaultois et al., 2018)
<b>Li<sub>6</sub>CoO<sub>4</sub></b>	80.0	5.0-76.4	300-700	700-750	0.20-1.0	0	10	(Bernabé-Pablo et al., 2020)
<b>Li<sub>3</sub>BO<sub>3</sub></b>	69.1	0-47.2	500-650	650	0.20-1.0	0	10	(Harada and Hatton, 2017)
<b>Li<sub>2</sub>CuO<sub>2</sub></b>	40.2	3.6-37.4	30-750*	750-850	1.0-5.0	0	-	(Martínez-Cruz et al., 2020; Yañez-Aulestia et al., 2020)
<b>Li<sub>5</sub>FeO<sub>4</sub></b>	71.2	0-62.0	30-700*	-	1.0	-	-	(Blanco et al., 2018)
<b>Li<sub>4</sub>TiO<sub>4</sub></b>	47.3	0-42.0	300-856	-	1.0	-	-	(Togashi et al., 2007)

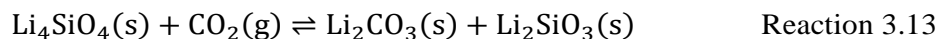
<b>Na<sub>4</sub>SiO<sub>4</sub></b>	23.9	7.7-19.2	50-840*	-	0.80	-	-	(Liu, J. et al., 2019)
<b>Na<sub>2</sub>ZrO<sub>3</sub></b>	23.8	4.5-23.8	150-800	680-900	0.025-1.0	0	70	(Ji et al., 2017; Martínez-dlCruz and Pfeiffer, 2012; Munro et al., 2020; Zhao et al., 2007)
<b>NaCoO<sub>2</sub></b>	15.0	3.3-11.1	100-800	-	0.050-1.0	-	-	(Vera et al., 2019)
<b>SrO</b>	42.5	3.0-37.1	1100-1200	1100-1200	0.30-0.50	0	10	(Miccio et al., 2016)
<b>La<sub>0.1</sub>Sr<sub>0.9</sub>Co<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3-δ</sub></b>	20.7	0-17.3	600-800	-	0.10-1.0	-	-	(Yang and Lin, 2006)
<b>Sr<sub>x</sub>Ca<sub>1-x</sub>Fe<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3-δ</sub></b>	15.1	0.4-17.0	RT-950*	-	1.0	-	-	(Homonay et al., 2002; Juhasz et al., 2001; Nomura et al., 1996)
<b>SrCo<sub>1-2x</sub>(Fe,Nb)<sub>x</sub>O<sub>3-δ</sub></b>	11.6	0-13.1	925	-	0.75	-	-	(Lu et al., 2011)
<b>Li<sub>2</sub>SrTa<sub>2</sub>O<sub>7</sub></b>	5.1	0-4.9	140	700	-	-	6	(Galven et al., 2010)
<b>Ba<sub>0.95</sub>Ca<sub>0.05</sub>Co<sub>1-x</sub>Fe<sub>x</sub>O<sub>3-δ</sub></b>	9.3	2.8-12.0	850	-	0.10	-	-	(Nomura et al., 1996)
<b>Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub></b>	10.1	0-14.9	RT-950*	-	1.0	-	-	(Lu et al., 2011)
<b>Ba<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub></b>	9.4	0-9.4	1000	1000	1.0	0	-	(Fujishiro et al., 2011; Yi et al., 2013)
<b>BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>2.95</sub></b>	13.8	0-13.1	600-1000	-	1.0	-	-	(Sneha and Thangadurai, 2007)
<b>Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub></b>	14.1	9.5-14.0	650-750	950	0.42	1	100	(Dunstan et al., 2013)

\* indicates temperature programmed CO<sub>2</sub> capture experiments in a TGA.

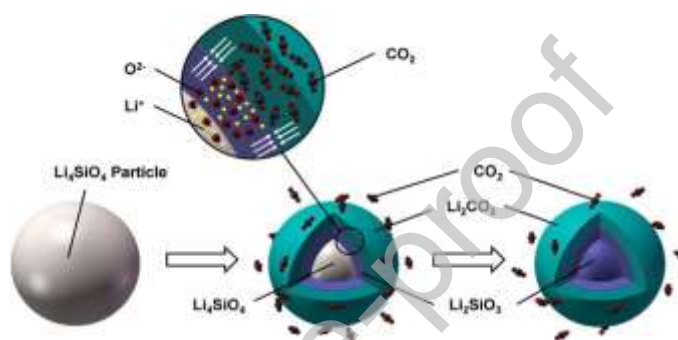
### 3.5.3.1 Li-based sorbents

#### 3.5.3.1.1 Lithium silicates

Lithium silicates, including  $\text{Li}_4\text{SiO}_4$  and  $\text{Li}_8\text{SiO}_6$ , are the most often studied lithium based sorbents.  $\text{Li}_4\text{SiO}_4$  reacts with  $\text{CO}_2$  between 450 and 700 °C with a stoichiometric  $\text{CO}_2$  capacity of 36.7 wt.%:



The carbonation mechanism of these ternary oxides is different from simple oxides like CaO or MgO, because more than one solid phase will be produced. The two solid products,  $\text{Li}_2\text{CO}_3$  and  $\text{Li}_2\text{SiO}_3$ , form an outer shell and an inner shell surrounding the unreacted  $\text{Li}_4\text{SiO}_4$  core, respectively, generating a double-shell structure, as shown in 8 (Yang, Xinwei et al., 2016b).

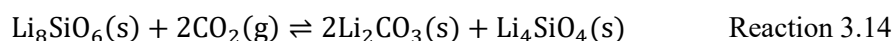


**Figure 3.48.** Schematic illustration of the “double shell” model describing  $\text{Li}_4\text{SiO}_4$  carbonation.

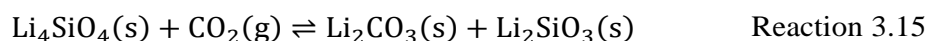
Reprinted with permission (Yang, Xinwei et al., 2016b).

The subsequent carbonation requires the transport of  $\text{CO}_2$  through the  $\text{Li}_2\text{CO}_3$  layer, and the migration of  $\text{Li}^+$  and  $\text{O}_2^-$  ions out of the  $\text{Li}_2\text{SiO}_3$  layer. As the shells grow thicker during carbonation, the diffusion resistances of both  $\text{CO}_2$  and ions will increase, slowing down the carbonation. It is believed that the rate limiting step is the  $\text{CO}_2$  gas diffusion through the  $\text{Li}_2\text{CO}_3$  layer. Owing to these product layer diffusion resistances, the experimental  $\text{CO}_2$  uptake capacity of  $\text{Li}_4\text{SiO}_4$  is always lower than the stoichiometric value. Increasing the surface area of the chemically unmodified lithium silicates is one of the most effective means to enhance the  $\text{CO}_2$  uptake performance of  $\text{Li}_4\text{SiO}_4$ .

$\text{Li}_8\text{SiO}_6$ , as a  $\text{CO}_2$  sorbent with higher Li contents than  $\text{Li}_4\text{SiO}_4$ , also has a higher theoretical  $\text{CO}_2$  uptake of 98 wt.%. The process of  $\text{Li}_8\text{SiO}_6$  carbonation consists of 3 steps (Cova et al., 2019). Steps 1 and 2 involve the  $\text{CO}_2$  adsorption on the surface and in bulk:



Step 3 involves the reaction between  $\text{CO}_2$  and the formed  $\text{Li}_4\text{SiO}_4$ :



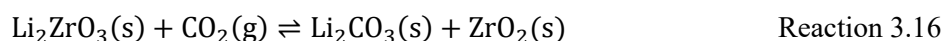
Lithium silicates can be synthesised by mechanically mixing solid particles of lithium and silicon precursors at stoichiometric ratios, followed by drying and calcination. Commonly used lithium precursors include  $\text{Li}_2\text{CO}_3$  (Chen, X. et al., 2016; Wang, Haiyang et al., 2018),  $\text{Li}_2\text{O}$  (Lara-García et al., 2019), and  $\text{LiNO}_3$  (Wang, K. et al., 2019), while the silicon precursor is almost always  $\text{SiO}_2$ . However, the lithium silicates obtained by solid-state reactions typically have low surface areas ( $<1 \text{ m}^2/\text{g}$ ) and low experimental  $\text{CO}_2$  uptakes (28-35 wt.% for  $\text{Li}_4\text{SiO}_4$  (Chen, X. et al., 2016; Wang, Haiyang et al., 2018) and 42 wt.% for  $\text{Li}_8\text{SiO}_6$ ) (Cova et al., 2019). Additionally, the poor sintering resistance of the  $\text{Li}_2\text{SiO}_3$  results in a rapid decrease in  $\text{CO}_2$  capture capacity over carbonation cycles (Chen, X. et al., 2016; Yang, Xinwei et al., 2016b).

To overcome the product layer diffusion resistances during carbonation, wet chemistry methods (e.g., impregnation suspension) are applied to synthesise  $\text{Li}_4\text{SiO}_4$  with high surface areas (Yang, Xinwei et al., 2016a, b). With improved specific surface areas (1.65-2.09  $\text{m}^2/\text{g}$ ),  $\text{Li}_4\text{SiO}_4$  prepared by impregnation suspension afforded higher  $\text{CO}_2$  uptake (up to 37 wt.%) and better cyclability (over 40 cycles) than those prepared by solid-state reactions (Yang, Xinwei et al., 2016b).

The  $\text{CO}_2$  capture performance of  $\text{Li}_4\text{SiO}_4$  can also be improved by metal doping. Low melting-point dopants, e.g.  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$ , can accelerate the migration of  $\text{CO}_2$  through the  $\text{Li}_2\text{CO}_3$  product layer (Seggiani et al., 2018; Wang, K. et al., 2019; Yang, Xinwei et al., 2016a). Alternatively, redox-active dopants, such as salts containing  $\text{Fe}^{3+}$ , are able to promote the transport of  $\text{O}^{2-}$  through the  $\text{Li}_2\text{SiO}_3$  shell (Lara-García et al., 2019). Some practical methods to introduce the dopants into  $\text{Li}_4\text{SiO}_4$  sorbents include adding dopant precursors during the solid-state reactions (Chen, X. et al., 2016; Wang, Haiyang et al., 2018), impregnating the solid-state synthesised  $\text{Li}_4\text{SiO}_4$  with soluble dopants, and conducting further solid-state synthesis between  $\text{Li}_4\text{SiO}_4$  particles and the dopant precursors (Lara-García et al., 2019). Wang et al. chose acid-leached blast furnace slag, which contains  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{K}_2\text{O}$ , as an economic and sustainable alternative for silicon precursor of  $\text{Li}_4\text{SiO}_4$  (Wang, Haiyang et al., 2018). In many cases, doped  $\text{Li}_4\text{SiO}_4$  showed many improvements, including higher specific surface area, enhanced  $\text{CO}_2$  uptake (up to 35 wt.%) (Chen, X. et al., 2016), improved cyclic stability (for up to 250 cycles) (Seggiani et al., 2018) and faster carbonation rate at lower temperatures and/or in lower  $\text{CO}_2$  concentrations (Lara-García et al., 2019).

### 3.5.3.1.2 Other Li-based sorbents

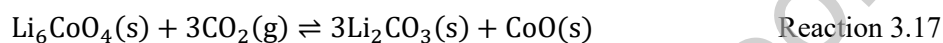
Lithium zirconate ( $\text{Li}_2\text{ZrO}_3$ ) is the second most studied Li based sorbent. It has a stoichiometric  $\text{CO}_2$  capacity of 28.7 wt.% when used within a temperature range of 450-650 °C:



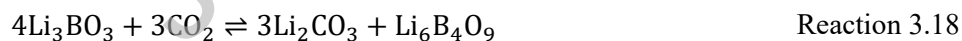
Like lithium silicates, the carbonated  $\text{Li}_2\text{ZrO}_3$  also exhibit a double-shell structure, with  $\text{ZrO}_2$  and  $\text{Li}_2\text{CO}_3$  forming the inner layer and the outer layer, respectively. Similarly, the  $\text{CO}_2$  diffusion through the  $\text{Li}_2\text{CO}_3$  layer is believed to be rate limiting.  $\text{Li}_2\text{ZrO}_3$  can be prepared by a solid-state reaction

between  $\text{Li}_2\text{CO}_3$  and  $\text{ZrO}_2$ . However, solid-state synthesised  $\text{Li}_2\text{ZrO}_3$  shows relatively slow carbonation and low capacities (5.9 - 10 wt.%) (Gómez-Garduño and Pfeiffer, 2019; Peltzer et al., 2018). Likewise, metal doping methods e.g. (i) doping low-melting point salts (Peltzer et al., 2018) (ii) doping redox-active  $\text{Fe}^{3+}$  chemicals (Gómez-Garduño and Pfeiffer, 2019), and (iii) impregnation suspension method (Peltzer et al., 2019) have been adopted to improve the performance of  $\text{Li}_2\text{ZrO}_3$  sorbents. Both (i) and (iii) could effectively improve  $\text{CO}_2$  uptake (20 - 22 wt.%), whereas the Fe-doping method gives marginal enhancements (7.0 - 9.2 wt.%).

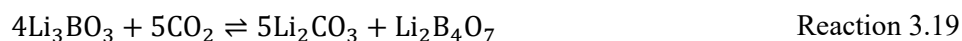
Other Li-based ternary oxide phases have also been studied for  $\text{CO}_2$  capture (Bernabé-Pablo et al., 2020; Blanco et al., 2018; Gaultois et al., 2018; Martínez-Cruz et al., 2020; Togashi et al., 2007; Yañez-Aulestia et al., 2020). Among these ternary oxides,  $\text{Li}_6\text{CoO}_4$  shows the highest stoichiometric  $\text{CO}_2$  capacity and experimental uptake of 80.0 and 74.5 wt.%, respectively (Bernabé-Pablo et al., 2020).  $\text{Li}_6\text{CoO}_4$  reacts with  $\text{CO}_2$  according to:



However, the  $\text{CO}_2$  capture uptake of  $\text{Li}_6\text{CoO}_4$  decreases quickly over cycles in the presence of  $\text{O}_2$ , reaching 30.5 wt.% after 10 cycles. This deterioration is attributed to the irreversible oxidation of  $\text{Co}^{2+}$  to  $\text{Co}^{3+}$  (Bernabé-Pablo et al., 2020). In contrast, for  $\text{Li}_5\text{FeO}_4$ ,  $\text{O}_2$  appears to accelerate the ion diffusion through the  $\text{LiFeO}_2$  layer, improving its  $\text{CO}_2$  capture performance (Lara-García et al., 2019). Similar to lithium silicates and lithium zirconates, doping is an effective strategy to enhance the  $\text{CO}_2$  capture performance of lithium-transition metal oxides. Several dopants, including second transition metal salts (e.g. Mn, Fe or Ni) (Martínez-Cruz et al., 2020) or alkali metal nitrates ( $\text{MNO}_3$ ,  $\text{M}=\text{Li, Na, K}$ ) (Yañez-Aulestia et al., 2020), were found to increase the  $\text{CO}_2$  uptake and cyclic stability of  $\text{Li}_2\text{CuO}_2$ . Recently,  $\text{Li}_6\text{WO}_6$  nanowires were developed and showed the capability to capture  $\text{CO}_2$  at ambient temperatures in the presence of moisture, owing to the hydration and activation of  $\text{Li}_6\text{WO}_6$ , which promoted the carbonation kinetics. At 30 °C and with a relative humidity =  $58 \pm 3\%$ ,  $\text{Li}_6\text{WO}_6$  was able to achieve a  $\text{CO}_2$  uptake of 7.6 wt.% within 1 min (Bernabé-Pablo et al., 2020).

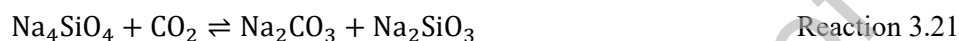


Lastly,  $\text{Li}_3\text{BO}_3$ , with a stoichiometric  $\text{CO}_2$  uptake capacity of  $\text{Li}_3\text{BO}_3$  of 41.4 wt.% has shown an experimental  $\text{CO}_2$  uptake of 35.4 wt.% (Harada and Hatton, 2017), through Reaction 3.17. However, the cyclic stability of  $\text{Li}_3\text{BO}_3$  is inferior. Doping with  $\text{NaNO}_2$  or  $\text{KNO}_2$ , which facilitates the formation of a molten layer, could accelerate product layer diffusion and the carbonation of  $\text{Li}_3\text{BO}_3$ . Interestingly, adding 10 mol% (Na-K) $\text{NO}_2$  achieved an experimental uptake of 47.2 wt.%, exceeding the stoichiometric capacity. The enhanced  $\text{CO}_2$  uptake may have originated from the deeper carbonation, which was induced by the incorporation of alkali metal nitrites. Accordingly, Reactions 3.18 and 3.19 corresponds to improved stoichiometric uptake capacities of 69.1 and 55.4 wt.%, respectively.



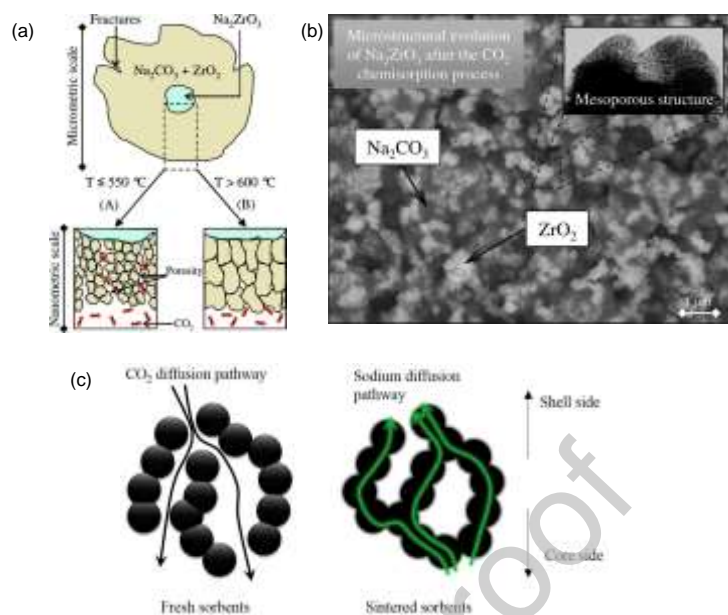
### 3.5.3.2 Na-based sorbents

Na-based sorbents share similar chemical formulae with Li based ones. On one hand, Na-based sorbents are cheaper as Na is more earth abundant. On the other hand, Na based sorbents generally have lower stoichiometric CO<sub>2</sub> capacities than the Li equivalents in terms of weight percentage because Na is a heavier element. Experimentally, Na<sub>4</sub>SiO<sub>4</sub>, Na<sub>2</sub>ZrO<sub>3</sub> and other Na based ternary oxides have shown promising CO<sub>2</sub> capture performance up to 850 °C:



Similarly, Na based sorbents can be obtained by either solid-state reactions or wet-chemistry methods, e.g., sol-gel synthesis (Ji et al., 2017; Zhao et al., 2007), using several combinations of precursors, e.g. Na<sub>2</sub>SiO<sub>3</sub> + NaOH (Liu, J. et al., 2019), Na<sub>2</sub>CO<sub>3</sub> + ZrO<sub>2</sub> (Martínez-dlCruz and Pfeiffer, 2012), and Na<sub>2</sub>CO<sub>3</sub> + CoCO<sub>3</sub> (Vera et al., 2019). Na<sub>4</sub>SiO<sub>4</sub> has a stoichiometric capacity of 23.9 wt.%, an experimental uptake of 19.2 wt.% at 840 °C, and a generally good performance above 750 °C (Liu, J. et al., 2019). To improve the capture performance of Na<sub>4</sub>SiO<sub>4</sub> at lower temperatures (< 700 °C), modification with alkali carbonates (M<sub>2</sub>CO<sub>3</sub>, M=Li, Na, K) could be a good choice, because the molten can accelerate the diffusion of O<sub>2</sub><sup>-</sup> through the product layer (Liu, J. et al., 2019). In particular, K<sub>2</sub>CO<sub>3</sub>-doped Na<sub>4</sub>SiO<sub>4</sub> has shown a CO<sub>2</sub> uptake of 4.7 wt.% at 300 °C, doubling that of undoped Na<sub>4</sub>SiO<sub>4</sub>.

Unlike the silicates, the gas permeability through the product layer during the carbonation of Na<sub>2</sub>ZrO<sub>3</sub> is higher. Therefore, the Na<sub>2</sub>ZrO<sub>3</sub> sorbents do not appear to encounter serious product layer diffusion resistance, as shown in **Error! Reference source not found.**(a) and (b). Ji et al. prepared Na<sub>2</sub>ZrO<sub>3</sub> by a sol-gel method, and achieved an experimental uptake of 22.6 wt.%, (stoichiometric uptake = 23.8 wt.%), which lasted over 5 cycles (Ji et al., 2017). The authors attributed the high performance of Na<sub>2</sub>ZrO<sub>3</sub> to the partly sintered product layer, which could form channels to facilitate fast sodium diffusion, as illustrated in **Error! Reference source not found.**(c). For NaCoO<sub>2</sub>, partially doping the Co sites with Fe could increase the CO<sub>2</sub> capture performance by enhancing the redox activity and ionic conductivity of the sorbent. For instance, NaCo<sub>0.7</sub>Fe<sub>0.3</sub>O<sub>2</sub> showed increased uptake of 10.6 wt.% in 20% CO<sub>2</sub> at 700 °C, while undoped NaCoO<sub>2</sub> could only achieve 3.3 wt.% (Vera et al., 2019).

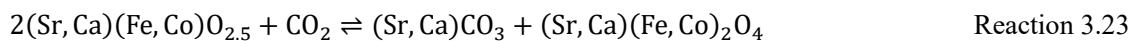


**Figure 3.49.** (a) Scheme of the carbonation of  $\text{Na}_2\text{ZrO}_3$  at different temperatures. Reprinted with permission (Martínez-dlCruz and Pfeiffer, 2012) (b) SEM image of growth of  $\text{ZrO}_2$  and  $\text{Na}_2\text{CO}_3$  after the carbonation of  $\text{Na}_2\text{ZrO}_3$ . Reprinted with permission (Martínez-dlCruz and Pfeiffer, 2012) (c) Scheme of the  $\text{CO}_2$  and  $\text{Na}^+$  diffusion in fresh and sintered  $\text{Na}_2\text{ZrO}_3$  sorbents. Reprinted with permission (Ji et al., 2017)

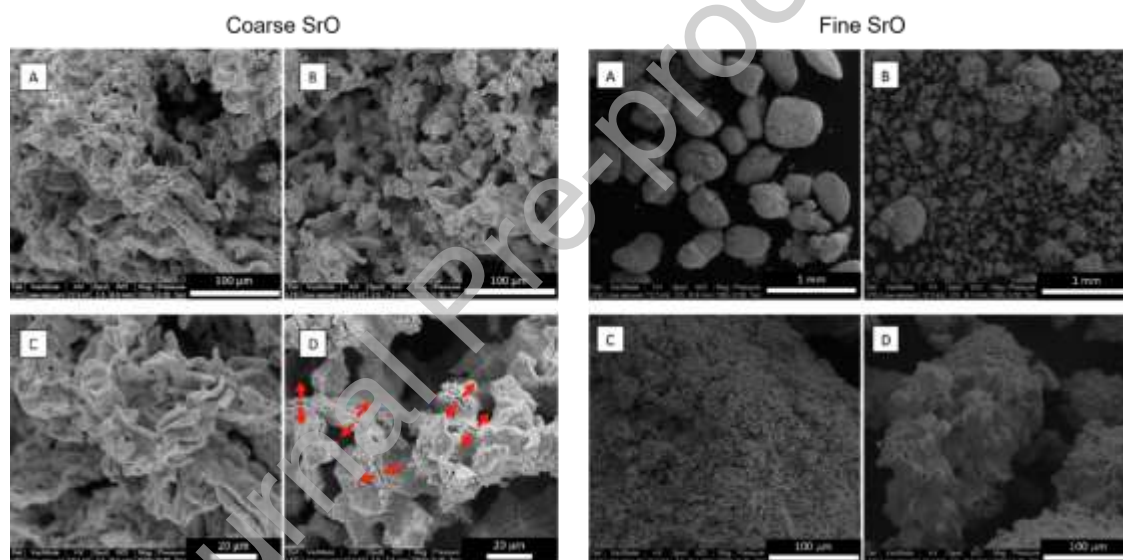
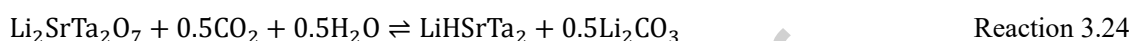
### 3.5.3.3 Sr-based sorbents

$\text{SrO}$  itself can be directly used as a  $\text{CO}_2$  sorbent, functioning at temperatures  $> 1000^\circ\text{C}$ . Miccio et al. (Miccio et al., 2016) synthesised coarse  $\text{SrO}$  particles by calcining  $\text{SrCO}_3$  and fine  $\text{SrO}$  particles by wet-granulation method (Figure 3.50). Both  $\text{SrO}$  sorbents showed relatively high initial  $\text{CO}_2$  uptakes of 37.1 and 30.5 wt.%, respectively. On the other hand, the capture capacities dramatically dropped after 5 cycles due to severe sintering. To increase the cyclic durability, it could be helpful to load  $\text{SrO}$  onto  $\text{Al}_2\text{O}_3$  to form the thermally stable  $\text{Sr}_3\text{Al}_2\text{O}_6$  and/or  $\text{SrAl}_2\text{O}_4$  sorbents.

In fact, Sr-containing  $\text{CO}_2$  sorbents are more often perovskite structured, where Sr occupies the A sites in the  $\text{ABO}_3$  lattice. The  $\text{CO}_2$  capture performance of the perovskites are greatly affected by both A and B site metals, which can be adjusted by changing the compositions of precursors during the sol-gel synthesis (Yang and Lin, 2006). For example,  $\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$  is able to adsorb more  $\text{CO}_2$  (17.3 wt.%) than  $\text{Sr}_{0.95}\text{Ca}_{0.05}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$  (4.37 - 8 wt.%) (Homonnay et al., 2002; Juhasz et al., 2001). Further changing Sr:Ca ratio to  $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$  could improve the uptake to 17 wt.% (Juhasz et al., 2001), owing to the formation of more ordered oxygen vacancies, which is considered to be helpful for  $\text{CO}_2$  uptake (Homonnay et al., 2002; Nomura et al., 1996):



Lu et al. (Lu et al., 2011) studied the effects of B-site occupancies for Sr based, perovskite structures. They prepared  $\text{SrCo}_{1-2x}(\text{Fe, Nb})_x\text{O}_{3-\delta}$  with equimolar Fe and Nb. The fresh  $\text{SrCo}_{1-2x}(\text{Fe, Nb})_x\text{O}_{3-\delta}$  sorbents had  $\text{CO}_2$  uptake of 13.1 wt.% and 11.1 wt.%, when  $x = 0.05$  and 0.10 respectively. The increased Nb occupancy of the B sites would reduce the carbonation activity due the weakened basicity of the perovskite (Yi et al., 2010). Besides the perovskite-structured Sr-based sorbents, a  $\text{Li}_2\text{SrTa}_2\text{O}_7$  sorbent having a Ruddlesden–Popper (RP) phase ( $A'_2[A_{n-1}B_nO_{3n+1}]$ ) was reported by Galven et al. (Galven et al., 2010) to achieve 4.90 wt.% experimental uptake (with a stoichiometric capacity of 5.11 wt.%) at 140 °C, 30 bar. Additionally, the  $\text{Li}_2\text{SrTa}_2\text{O}_7$  sorbent exhibited good cyclability after 5 carbonation-regeneration cycles.



**Figure 3.50.** SEM images of coarse and fine SrO particles before (A & C) and after (B & D) five cycles of carbonation–calcination at 1100 °C. Reprinted with permission (Miccio et al., 2016)

### 3.5.3.4 Ba-based sorbents

Similar to Sr based sorbents, most Ba based sorbents are perovskite-structured oxides with Ba occupying the A sites. These sorbents can be prepared by either state reactions (Sneha and Thangadurai, 2007) or sol-gel synthesis (Nomura et al., 1996). The capture performance of the Ba based perovskites also depends on the metal site occupancies. For example, Nomura et al. (Nomura et al., 1996) discovered that if the Fe contents in  $(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Co}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$  is increased from 0.2 to 0.9, the  $\text{CO}_2$  uptake will drop from 10.0 wt.% to 8.7 wt.%. The  $\text{BaFeO}_{3-\delta}$  ( $0 < \delta < 0.5$ ) structures could switch phases between perovskite ( $\text{ABO}_3$ ) and brownmillerite ( $\text{A}_2\text{B}_2\text{O}_5$ ), representing oxygen uptake and release. It is

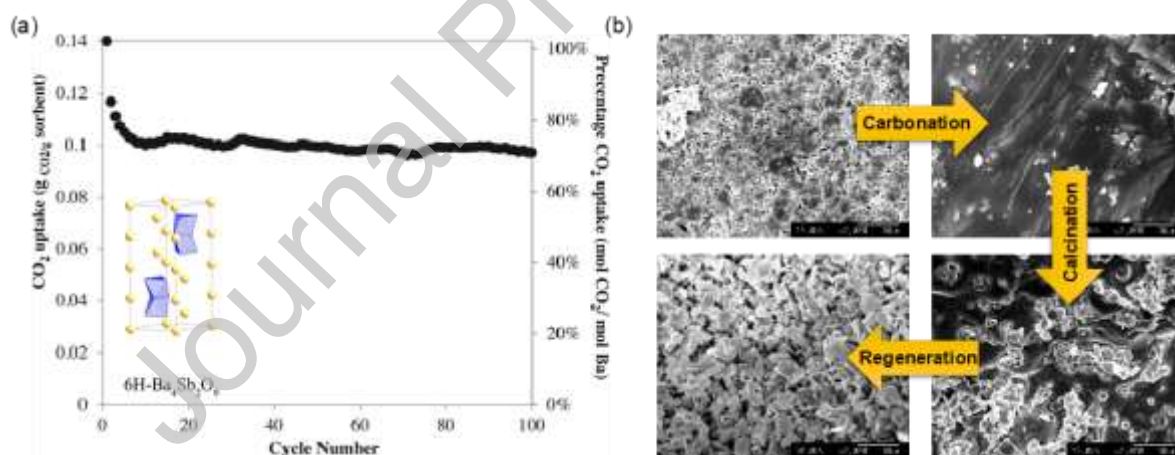


believed that these phase changes are beneficial to the CO<sub>2</sub> capture performance. For instance, the thermal decomposition of perovskite structured Ba<sub>0.95</sub>Ca<sub>0.05</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> to brownmillerite in the absence of O<sub>2</sub> would improve CO<sub>2</sub> uptake of 12 wt.%; this phenomenon is in line with the findings of Lu et al. (Lu et al., 2011) and Fujishiro et al. (Fujishiro et al., 2011) Like Sr based perovskites, doping B-sites with Nb will hinder the carbonation of Ba based perovskites as well. Yi et al. (Yi et al., 2013) reported low CO<sub>2</sub> uptake (0 – 1.3 wt.%) of the Nb-doped BaFeO<sub>3-δ</sub>. It is possible that the reduced performance may be related to the electron-donating behaviour of Nb dopant, which makes the perovskite sorbents more thermodynamically inert towards CO<sub>2</sub>.

The most outstanding Ba based sorbent so far is probably be the 6H-perovskite Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> reported by Dunstan et al. (Dunstan et al., 2013) Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> has a stoichiometric capacity of 14.1 wt.%:



Experimentally, a near-stoichiometric CO<sub>2</sub> uptake of 13.8 wt.% was achieved at 750 °C. During cyclic carbonation-regeneration, Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> exhibited >10 wt.% CO<sub>2</sub> uptake over 100 cycles (Figure 3.51a). The excellent cyclic stability of Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> was attributed to its outstanding regenerability: its pore structure could be fully recovered after calcination in each cycle (Figure 3.51b). The authors also discovered that Ba<sub>4</sub>Nb<sub>2-x</sub>Ta<sub>x</sub>O<sub>9</sub> is a poor CO<sub>2</sub> sorbent, with only <0.07 wt.% in 100% CO<sub>2</sub> at 1000 °C (Dunstan et al., 2011).



**Figure 3.51.** (a) CO<sub>2</sub> uptake by 6H perovskite Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> over 100 carbonation-calcination cycles in at TGA. (b) surface morphology Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> as it evolves over carbonation-calcination cycles. Reprinted with permission (Dunstan et al., 2013)

## 4. Membrane based CO<sub>2</sub> capture

### 4.1 Polymeric membranes

#### 4.1.1 Introduction for polymeric membranes CO<sub>2</sub> capture

Membrane technology (a thin interface that acts as a permselective for two-phase separation, typically in a range of 100 nm to a few micrometers) has emerged as one of the promising alternative technologies in CO<sub>2</sub> capture compared to the conventional gas-liquid contractors, due to their inherent attribution such as smaller footprint, simpler setup, and operation, energy-saving and do not involve in phase transformation (Fujikawa et al., 2020; Ramasubramanian et al., 2013). But still, the highly permeable membrane is a big challenge for efficient CO<sub>2</sub> capture. Thanks to the unique architectural properties of polymeric chemistry, it has great potential to design a versatile membrane with outstanding properties for gas separation, especially for CO<sub>2</sub> capture (Robeson et al., 2009; Wang, S. et al., 2016). Polymeric membrane technology has been used widely for CO<sub>2</sub> capture and is considered a next-generation technology for CO<sub>2</sub> capture due to its inherent properties such as cost-effectiveness, efficiency, separation performance, mechanical stability, and applicability for large scale-manufacturing (Feron and Jansen, 2002). Over the past decade, an extensive research quest has been devoted to the polymeric membrane with unprecedented transport properties for CO<sub>2</sub> capture from post-combustion (CO<sub>2</sub>/N<sub>2</sub>), syngas processing (CO<sub>2</sub>/H<sub>2</sub>), and natural gas sweetening (CO<sub>2</sub>/CH<sub>4</sub>).

One of the major challenges associated with the commercialization of membrane technology is the permeability and selectivity trade-off, i.e., high permeability is achieved always at the cost of lower selectivity and vice versa, for a specific component of the mixture. Robeson's proposed the empirical upper bounds limit in 1991 and updated the upper bounds in 2008 to explain such a limiting behavior (Robeson, 1991; Robeson, Lloyd M., 2008). The paradigm shift is desirable in developing a new polymer-based membrane to outreach the Robeson's upper bounds limit along with long-term stability to be able to mitigate a massive volume of CO<sub>2</sub> emission.

In this section, we will review the recent efforts of the membrane's main research theme to surpass Robeson's upper bond limit focusing on polymeric materials. The unique structural properties of polymeric

materials exhibit high permeability of CO<sub>2</sub> with sufficient selectivity. We categorized polymeric-based membranes into two categories based on the transport mechanism, 1) solution-diffusion membranes, including polyethylene oxide (PEO) (copolymer membranes, blend membranes, crosslinking membranes), perfluoro polymers, polymers of intrinsic microporosity, thermally rearrange polymers; and 2) facilitated transport membranes, including Amin based membranes, RTIL and other carriers for facilitated transport membranes.

#### 4.1.2 Solution - diffusion transport mechanism

The driving force in membrane separation is pressure or concentration gradient. Firstly, the gas molecules dissolve in the dense polymeric membrane at the higher-pressure side for non-reactive polymer, then diffuse across the membrane and desorb at the lower-pressure side. This simple approach to gas transportation is known as the solution diffusion transport mechanism. This mechanism can be expressed as a product of the solubility coefficient ( $S_x$ ) and diffusion coefficient ( $D_x$ ) term as permeability coefficient ( $P_x$ ) (Doong et al., 1995).

$$P_x = S_x \times D_x \quad \text{eq. 4.1}$$

The permeability is commonly expressed in terms of Barrer, whereas 1 Barrer = 1 Barrer =  $1 \times 10^{-10} \text{ cm}^3$  (STP)·cm·cm<sup>-2</sup>·s<sup>-1</sup>·(cm Hg)<sup>-1</sup>. The permeability is an inherent property of polymeric materials, as solubility is the thermodynamic affinity of materials toward gas and diffusivity is dependent upon the morphology of the material and the size of gas molecules. The separation performance of the membrane can be expressed in terms of the permeability of the membrane divided by the thickness of the membrane.

The separation efficiency of the membrane is described by selectivity. The selectivity of the membrane is termed as the ability of a membrane to separate one component from another component of the mixture. The ideal selectivity is the ratio of two gas (x, y) permeability as shown in the equation below, which can further be extended in terms of solubility selectivity and diffusivity selectivity as:

$$\alpha_{x/y} = \frac{S_x}{S_y} \times \frac{D_x}{D_y} \quad \text{eq. 4.2}$$

The perm selectivity is deeply rooted in the solubility or diffusivity of gas molecules into the polymeric membrane. The solubility selectivity is enthalpy driven, dependent upon the condensability (increase with the increasing critical temperature) of penetrant gas molecules in the polymer and the affinity of penetrant gas toward the polymeric membrane (Frisch, 1970; Zydney, 1995). The solubility of CO<sub>2</sub> is higher as compared to other gases due to its significantly high critical temperature,  $T_{c, CO_2} = 304.1$  K shown in Table 4.1 (Bondar *et al.*, 2000). The diffusivity selectivity kinetic diameter of penetrant gas molecules is dependent, and the gas molecules migrate through the free voids of polymer, which is the inherent characteristic of the polymer. The diffusivity selectivity of CO<sub>2</sub> is also higher as compared to other gases due to its smallest kinetic diameter,  $d_k = 0.330$  nm. The less packing density and chain to chain spacing allows penetrant molecules to diffuse. Typically, the diffusivity increases with the decreasing in the kinetic diameter of gas molecules as well as increasing in free voids.

**Table 4.1: physical properties of CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>**

Gas	Kinetic diameter/nm	Critical temperature/K
CO <sub>2</sub>	0.330	304.1
N <sub>2</sub>	0.364	126.2
CH <sub>4</sub>	0.380	190.6

The fractional free volume (FFV) plays a vital role in the gas transport phenomenon in glassy polymeric membranes. Free volume is obtained during the condensation, as the less packing density leads to a more void not occupied by the polymer chain. Contrary to glassy polymer in rubbery polymer, solubility selectivity is more favorable (Lee, 1980). But the aging and plasticization of the membrane limit the fractional free volume and decrease the performance of the membrane (Du *et al.*, 2011). It is required to mitigate such a challenge to fabricate an efficient and long-term durable membrane to move forward toward commercial applications.

#### 4.1.2.1 PEO based polymeric membrane

Poly (ethylene oxide) (PEO) containing polymers have been extensively studied and shown a great potential to capture CO<sub>2</sub> due to their outstanding affinity toward CO<sub>2</sub> attributed to its dipole- quadrupole interaction between ethylene oxide (EO) group and CO<sub>2</sub> (Rindfleisch *et al.*, 1996). Due to the inherent property of

polar ether linkage (-c-c-o-) in PEO (rubbery polymer), it has a reasonable separation performance of CO<sub>2</sub> from other light gases. However, the limitation of PEO is its tendency toward crystallinity and film-forming ability due to its polar oxygen atoms, which are prone to reduce the free volume leading to the poor separation performance of CO<sub>2</sub>, poor mechanical strength, and ultimately hampering their commercial applications (Sangroniz et al., 2021). Therefore the current effort of the researchers is to overcome the crystallinity constrain by cross-linking to form a highly branched polymeric network, copolymerization with the hard segment, and blending with the low MW polymer PEG, to enhance the separation performance as well as the thermal stability of the PEO based membrane. The PEO based membranes have been widely investigated via different synthesis approaches and some examples are summarized in Table 4.2.

**PEO based copolymeric membrane.** To overcome the limitation of crystallinity in the PEO based membrane is the copolymerization approach with the different rigid segments (Han and Ho, 2018). The transport properties of these membranes are controlled by altering the PEO phase and the unit length of soft and rigid segments (Yave et al., 2010). Luo et al. investigated the copolymer membranes of commercial polyether amines, pentiptycene-based diamine, and 6FDA, which exhibited high CO<sub>2</sub> gas permeability of 39 Barrer with CO<sub>2</sub>/H<sub>2</sub> selectivity of 4.1 and CO<sub>2</sub>/N<sub>2</sub> of 46 (Luo, S. et al., 2016). The supramolecular chain threading and interlocking induced by the pentiptycene structures, effectively minimize the inherent crystallization ability of PEO, leading to an amorphous structure. Jankowski et al. synthesized a series of PEO based copolyimides with varying hard segment structures and found OPDA-ODA-PEO is the best copolyimide, with CO<sub>2</sub> permeability of 52 Barrer with CO<sub>2</sub>/N<sub>2</sub> selectivity of 63 (Jankowski et al., 2021). A CO<sub>2</sub> selective copolymer based on aromatic poly ethers tethered with flexible PEO side chains was synthesized via polycondensation by Ioannidi et al. showing maximum CO<sub>2</sub> permeability of 11.2 Barrer along with CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> ideal selectivity of 9.6 and 68 respectively surpassing the upper bond limit for H<sub>2</sub> (Ioannidi et al., 2021). An asymmetric TF-MMM with ZIF-8 in the copolymer of PVI-POEM was synthesized by Lee et al. observed high CO<sub>2</sub> performance of 4474 GPU with high CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> ideal selectivity of 32 and 12.4, respectively (Lee et al., 2022).

**PEO based crosslinked membrane.** The crosslinking approach is also the best alternative to overcome the crystallinity limitation of PEO based membranes. The crosslinking strategy is the transformation to a highly

branched polymer by the free radical polymerization of ethylene oxide monomers and oligomers. At the incipient, the crosslinked PEO based polymers were designed by the free radical polymerization of different methyl acrylate monomers. Another noticeable building block for designing of PEO crosslink network is the addition reaction of amino and epoxy groups shows a high separation performance as well as thermal stability (Lin et al., 2006). Zhang et al. explored the crosslinking of PEO with nitrogen-rich polyamines network (PAN-NH<sub>2</sub>) to synthesized CO<sub>2</sub>-philic mixed matrix membrane, showing the excellent separation performance of CO<sub>2</sub> 1160 Barrer along with CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub> selectivity of 73, 19.7 respectively, surpassing the Robeson's upper bond (2019) limit (Zhang, Xiaoxia et al., 2022). Recently, a highway built up in PEO based membrane via a solvothermal annealing approach, offered a superior CO<sub>2</sub> permeability of 1299 Barrer with CO<sub>2</sub>/N<sub>2</sub> selectivity of 50 along with long-term stability of 110 h, beyond the Robeson's upper bond line (Li, S. et al., 2022). The solvothermal annealing approach enhances the flexibility of PEO chain and rearranges the side chain, which is an essential tuning parameter to boost the membrane performance, opening a new dimension for PEO based membrane for CO<sub>2</sub> capture towards industrialization.

**PEO based blended membrane.** The blending approach with a low molecular weight (100-200) polymer like PEG is also a suitable strategy not only to circumvent the limitations of crystallinity but also to obtain superior separation performance and thermal stability (Chen, Y. et al., 2016b). The introduction of low MW polymer in the backbone of PEO leads the crystalline PEO to the amorphous materials with outstanding separation performance. In addition it provides another tuning parameter to reduce the strong hydrogen bonding among the ether groups. Kang et al. synthesized an amphiphilic combo copolymer PDMS-PEGBEM via free radical polymerization and incorporated it into commercially available polymer PEO, resulting in extremely enhanced selectivity of CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> from 0.78 and 0.71 to 41.7 and 13.3 respectively (Kang et al., 2021a)

**Table 4.2: Examples of polymeric-based membranes with their performances (solution diffusion mechanism).**

Material	$p$ (CO <sub>2</sub> )/atm	$T$ /°C	$P$ (CO <sub>2</sub> )/Barrer	$\alpha$ (CO <sub>2</sub> /N <sub>2</sub> )	$\alpha$ (CO <sub>2</sub> /CH <sub>4</sub> )	References
<b>PEO based polymeric membrane</b>						
HPEO <sub>2</sub> -800	30 psig	35	540	43	14	(Zhang, Gengyi et al., 2022)

PAN-NH <sub>2</sub> /PEO	5bar	35	1160	73	19.7	(Zhang, Xiaoxia et al., 2022)
DME240-45	3bar	35	1400	45	-	(Guo, W. et al., 2022)
STA-PEO	0.5MPa	35	1294	50	-	(Li, S. et al., 2022)
PEO/PDMS-PEGBEM	1 bar	35	240	34.6	12.2	(Kang et al., 2021b)
PEO/PEGDEI 37	1 bar	35	201.1	49.3	15.7	(Min et al., 2021)
OPDA-ODA-PEO	6 bar	30	52	63		(Jankowski et al., 2021)
PEGDME-500			2281.1	48.1		(Li, Songwei et al., 2019)
XLPP3-30	5 bar	25	92	92		(Motahari and Raisi, 2020)
PEO/PGP-POEM	1 bar	35	120.9	44.9	14.5	(Kim et al., 2020)
XLPEO/C6-60	30 psig	35	1340	48		(Huang et al., 2020)
1-GEF-M	4 bar	35	460	57	18	(Liu, N. et al., 2022)
PVI-POEM -PZ-50	1bar	30	4474	32	12.4	(Lee et al., 2022)
PEO/PTMSP EFCM	0.3MPa	25	281	32.94		(Zheng, W. et al., 2022)
XLPEO		35	761.9	40.3	11.5	(Cheng et al., 2020a)
<b>Perfluoro based polymeric membrane</b>						
Teflon AF1600	1000kPa	35	489		12	(Scholes et al., 2016)
Poly (PFMMD-co-CTFE)	50psig	22	44.3		49	(Fang et al., 2018)
PEBAXs 2533	350kpa	35	1860	22		(Scofield et al., 2016b)
F-SPEEK/Matrimid	10 bar	25	33.2	51.11	47.45	(Asghar et al., 2018)
PEBAX 1657/P1 (60 wt %)	350kpa	35	226	39		(Scofield et al., 2016a)
PIM-COOH-360h		30	96.43	53.6	25.2	(Jeon et al., 2017)
PIM-1/SNW-1	2 bar	30	7553	22.7	13.5	(Wu et al., 2017)
PIM-1/PEG-POSS-10	1 bar	30	1300	31	30	(Yang, L. et al., 2017)
PIM-TMN-Trip		31	16,500	11		(Stanovsky et al., 2020)
PIM-SBI-Trip	1bar	25	35 600	15.4	7.74	(Bezzu et al., 2021)
PIM-1/SBI-Trip	1bar	25	24 410	18.8	9.69	(Wang, Z. et al., 2017)
PAO-PIM-1/NH <sub>2</sub> -UiO-66 (30%)	1bar	35	8425	27.5	23.0	(Wang, Z. et al., 2017)

3-SCPIM-6/24	1 atm	25	4008	58.1	40.9	(Zhou, S. et al., 2020b)
PIM-BM-70	50psi	25	48.3	30.1	43.9	(Chen, X. et al., 2020)
PIM-MP-TB	1 bar	25	633	29.6	24.4	(Williams et al., 2018)
PIM-1-450	3.5 atm	35	40	40	110	(He et al., 2020)
AOPIM-1-9	1 atm	35	2483.6	31.2	30.1	(Wang, Z. et al., 2020)
PIM-1/sPPSU-3.5 (98:2)	3.5atm	35	3003	22.9	18.0	(Kammakakam et al., 2021)
<b>TR polymeric based membrane</b>						
Im-PBOlonene] <sup>+</sup> [2-IL]	2 atm	20	44.7	34.1	51.9	(Kammakakam et al., 2021)
TR400-0	76cmhg	25	184	26	63	(Suzuki, 2021)
6F-AP-450	100 psi	35	200.3		28	(Suzuki, 2021)
TR-coated PBOA	0.5 Mpa	25	24.0 gpu	18.9	18.2	(Ye et al., 2021)
ODA/APAF (3:7)			127.4	20.6	34.2	(Jia, P. et al., 2022)
PIOAc30	3 bars	30	1036	23	28	(Aguilar-Lugo et al., 2021)
XTR-PBOI	3 bars	75	400 GPU	20		(Lee et al., 2017)
TR-PBOI-AD5		25	481 GPU	17.7		(Woo et al., 2016a)
XTR425	1 atm	35	271	20		(Lee, J. et al., 2019)
TR-PBOI-375			560 GPU	16.8		(Woo et al., 2016b)
2D-diXTR	3 bar	35	4,590 GPU	18.0		(Lee, Jongmyeong et al., 2020)
6F-TM-Ac-425	1 bar	35	205	25	33	(Hu, Xiaofan et al., 2020)
rGO-PBOI	1 atm	25	1784 GPU	17.7	32.4	(Kim, S. et al., 2018)

#### 4.1.2.2 Perfluoro based polymeric membrane

Perfluoro polymers are a fluorinated polymeric family, which attracted the most attention because of its mostly or all hydrogen atoms are replaced by fluorine atoms. The enrichment in strong C-F and C-C covalent bonds, transformed the per fluoropolymers to extremely thermally and chemically stable, which is the beneficial trait of this class of polymer to be a prospective candidate for commercial application



(Merkel et al.) Although it has a low tendency toward swelling because of its insolubility in many organic compounds and its semi-crystalline nature, it limits the applicability of perfluoro polymer in membrane advancement for gas separation (Prabhakar and Freeman, 2002). Since 1980, a new family of perfluoro polymers like Teflon AF, Hyflon AD, and Cytop polymers have been designed for gas separation. The bulky dioxole monomer as a copolymer or cyclic homopolymer in these polymers reduces the chain mobility and crystallinity, leading to an amorphous polymer with exponential FFV, which renders the superior gas separation performance (Hellums et al., 1989; Tanaka et al., 1992). Fang et al. reported a new class of amorphous perfluorinated polymeric membranes to exhibit tuneable transport properties, which showed excellent separation performance for important gas pairs including CO<sub>2</sub>/CH<sub>4</sub> (Wang, Xuerui et al., 2019). The summarized membrane performance mentioned is in Table 4.2.

#### 4.1.2.3 Polymer of intrinsic microporosity-based membrane

In 2004 Budd and McKeown et al. introduced a new family of glassy polymers with a unique backbone feature having rigid ladder-like and contorted macromolecular structures, which are called polymers of intrinsic microporosity (PIMs) (Budd et al., 2004). The restricted chain rotation due to the absence of a single bonded chain in the backbone, kink chain, and their three-dimensional contorted conformation due to the tetrahedral carbon atom interaction with five-membered carbon rings, inhibit the macromolecules to effectively compact packing leads to the higher fractional free volume of typically 20% FFV (McKeown, 2012; Rose et al., 2017). Therefore, PIM exhibits unprecedented permeability with moderate selectivity of CO<sub>2</sub> in a CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> mixture. These versatile features of PIM attract the attention of researchers to focus on the designing of highly permeable and selective membranes. In recent years many efforts have been employed to enhance the CO<sub>2</sub> selectivity of PIM-based membranes. Some are summarized in Table 4.2. Bezzu et al. synthesized polymer of intrinsic microporosity (PIMs) by blending with rigid and bulky triptycene to the spirobisindane (SBI) and showed excellent permselective for the CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> gas pairs (Bezzu et al., 2021). A hybrid mixed matrix membrane of PIM with the metal-organic framework synthesized by Wang et al. exhibited excellent performance with CO<sub>2</sub> permeability of 8425 Barrer and CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivity of 27.5 and 23, respectively, surpassing the 2008 Robeson's upper bound

(Bandeali et al., 2021). Recently, thermally self-crosslinked Bromo alkylated PIM-based membranes were constructed by Xiuling Chen and co-workers and treated for gas separation, indicating superior CO<sub>2</sub> permeability of 48.3 Barrer along with CO<sub>2</sub>/CH<sub>4</sub> selectivity of 43.9 (Halder et al., 2018). Jeon et al. reported, highly carboxylate functionalized PIMs (HCPIMs), due to their smaller interchain distance and CO<sub>2</sub> affinity exhibited high separation performance for CO<sub>2</sub> separation with a selectivity of 53.6 for CO<sub>2</sub>/N<sub>2</sub> separation (Zhou, S. et al., 2019).

#### 4.1.2.4 Thermally rearranged (TR) polymeric-based membrane

Park et al. first introduced a new concept of more rigid and planer macromolecules from ortho-functionalized polyimides or polyamides by thermal rearrangement, named thermally rearranged (TR) polymer (Park et al., 2007). The TR polymer engineered with an unprecedented inherent feature of bimodal narrow cavity distribution (3-10 Å) and structural rigidity led to a high free volume, which was attributed to the excellent gas separation performance of TR-based polymeric membranes (Chern et al., 1983; Zhuang et al., 2015). Several examples TR based polymeric membranes are listed in Table 4.2 with their transport properties for lighter gas pairs. The ortho-position hydroxy group of polyimides or polyamides thermally rearranged via polycondensation reaction and formed twisted rigid-rod structure with a uniform microporosity, i.e., Poly benzoxazole (PBO) or polybenzimidazole (PBI) (Calle et al., 2015; Kim and Lee, 2015). The intrinsic uniform and small size micropores, result in the TR polymer to outstanding rapid gas transportation along with high selectivity for lighter gas pairs (Budd and McKeown, 2010). These inherent properties of TR polymer can further modify by tuning the thermal treatment protocol to surpass Robeson's upper bound along with the major bottleneck of TR polymer such as fragility and brittleness for gas separation.

Many research endeavors have been done due to the unprecedented intrinsic property of TR polymer. Recently, a new TR polymer incorporation of ionic components to obtain a novel imidazolium mediated poly benzoxazole by Kammakam et al. in order to enhance the gas separation performance (Kammakam et al., 2021). Suzuki et al. synthesized a novel TR-PBI-silica hybrid membrane and found an outstanding gas separation performance for CO<sub>2</sub>/CH<sub>4</sub> due to the enlargement in the FFV and d-spacing

with size-selective CO<sub>2</sub>/CH<sub>4</sub> free volume holes at polymer-silica interfacial region (Suzuki, 2021). Lugo et al. synthesized mixed matrix membrane (TROH and TROAc-MMMs), notably increasing the permeation of CO<sub>2</sub> with 1036 Barrer CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> surpassing the 2008 Robison's upper bound limit, with a selectivity of 28 for CO<sub>2</sub>/CH<sub>4</sub> bit lower than the pristine TR-PBO membrane (Aguilar-Lugo et al., 2021). The thermal densification of the skin layer in the hollow fiber membrane of TR polymer hindered the permeance, and Lee et al. exploited this limitation by ultrathin skin layer. The crosslinking thermally rearranged diXTR hollow fiber, exhibits remarkable permeance of 4600 GPU with CO<sub>2</sub>/N<sub>2</sub> selectivity of 18 (Lee, Jongmyeong et al., 2020).

#### 4.1.3 Facilitated transport mechanism

Contrary to the solution-diffusion transport mechanism, membranes with a reactive carrier (amino group, -NH<sub>2</sub>) which enhanced the reversible reaction between CO<sub>2</sub> and reactive carriers, refer to facilitated transport membranes (Schultz et al., 1974; Tong et al., 2017). The reactive carriers either be chemically embedded onto a backbone (fixed site carrier) or in the form of mobile carriers (mobile carriers) in a polymer matrix (Noble, 1990). Initially, CO<sub>2</sub> diffused into the polymer metrics, herein CO<sub>2</sub> reacts with the carrier and forms a CO<sub>2</sub>-carrier complex at the high-pressure side, as due to the concentration gradient, it transports towards the low-pressure side by intramolecular diffusion (fixed-site carrier) or intermolecular diffusion (mobile carrier) where it released CO<sub>2</sub> and the reactive-carrier been regenerated back (Meldon et al., 1982).

While on the other hand, the small magnitude of inert gas molecules to the carrier transports through the membrane by the phenomenon of solution-diffusion mechanism. Worth noticeable that in the facilitated transport mechanism, the solution-diffusion mechanism is important. In general, the total CO<sub>2</sub> flux through the membrane is the combination of facilitated transport and solution diffusion transport mechanism, which can be represented by the following equation:

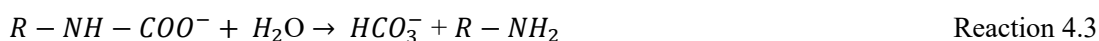
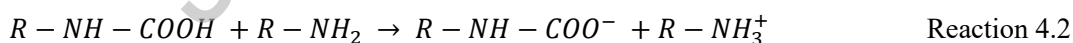
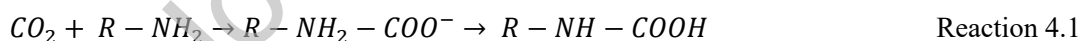
$$J_{CO_2} = \frac{D_{CO_2}}{l} (\Delta C_{CO_2}) + \frac{D_{Carrier+CO_2}}{l} (\Delta C_{Carrier+CO_2}) \quad \text{eq. 4.3}$$

Where,  $D_{CO_2}$  and  $D_{Carrier+CO_2}$  are the diffusion coefficient of Fick's diffusion (solution-diffusion) and carrier-CO<sub>2</sub> complex diffusion (facilitated diffusion), respectively. The thickness of the membrane is represented

as  $l$ . The above equation clearly shows that the reactive carrier can drastically increase the total flux in addition to the solution diffusion, which can be attributed to the outstanding performance of facilitated transport-based membranes. However, the strong interaction between carrier and  $\text{CO}_2$  hindered the desorption of  $\text{CO}_2$  at permeate side. Contrary to this weak interaction between carrier and  $\text{CO}_2$ , it induced additional  $\text{CO}_2$  partial pressure due to the  $\text{CO}_2$  saturation in the membrane, consequently having an adverse effect on the performance of the membrane. Therefore, it is required to optimize reaction kinetics and  $\text{CO}_2$  loading capacity for the outstanding separation performance of facilitated transport-based membranes.

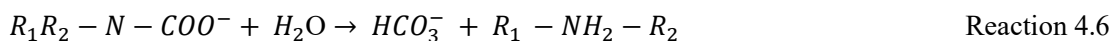
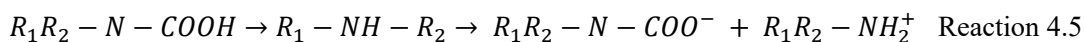
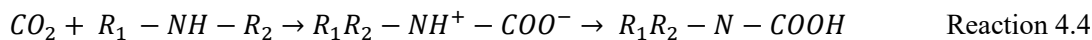
#### 4.1.3.1 Amine-based polymeric membranes

The most investigated reactive carrier in the facilitated transport of  $\text{CO}_2$  captures is amines. The inherent features of amines provide structural versatility with tuneable of fast reaction kinetics and the extraordinary capacity of  $\text{CO}_2$  loading (Perinu et al., 2017). The chemistry of  $\text{CO}_2$  and amines is shortly explained in this section. Primary and secondary amine (electron-rich) acts as a nucleophile and attacks the electron-deficient carbonyl group  $\text{CO}_2$  from zwitterion as shown in the below Equation (Caplow, M.J.J.o.t.A.C.S., 1968). The immediate proton transformation of another amine zwitterions transforms to a stable carbamate and ammonium ion as shown in Reactions 4.1, 4.2 and 4.3, in the nutshell 2 mol of amines are required for 1 mol of  $\text{CO}_2$  (Danckwerts, 1979). Hydrolysis of carbamate ions can occur at low PH to produce bicarbonate regenerating free amine. However, it is not favorable due to the stability of carbamate, as shown in the below Equation.



The sterically hindered amino group effectively contributes to fasting reaction kinetics with  $\text{CO}_2$ , leading to an equimolar stoichiometry between  $\text{CO}_2$  and amine. Consequently, it increases the  $\text{CO}_2$  loading capacity of amine (Sartori et al., 1983). The sterically hindered destabilized the carbamate intermediate by restricting

the C-N bond in carbamate. As the carbamate is destabilized by the bulky substituted amino group, it forms bicarbonate, releasing the free amine as shown in the Reactions 4.4, 4.5 and 4.6.



A common polymer matrix that attracted much attention from a researcher is poly (vinyl alcohol) (PVA), polyvinyl amine (PVAm), and polyallylamine (PAA) for facilitated-based membranes. Some examples are summarized in Table 4.3. Chen et al. synthesized a polyvinyl amine (PVAm) based membrane featuring the fixed-site carrier also with different amino acid salts mobile carries for CO<sub>2</sub> facilitated transport, demonstrated a CO<sub>2</sub> permeance of 1100 GPU and selectivity of 200 for CO<sub>2</sub>/N<sub>2</sub> (Chen, Y. et al., 2016b). Zhao et al. studied the steric hindrance effect on amine and observed that it has a great advantage to enhance CO<sub>2</sub> transport (Zhao and Winston Ho, 2012). A hindered polyamines cross-linked with polyvinyl alcohol and obtained polymeric membrane of the fixed-site carrier, which exhibits an outstanding transport property of 440% enhancement in CO<sub>2</sub> permeability along with 311% increment in CO<sub>2</sub>/N<sub>2</sub> selectivity. The same group studied again a sterically hindered polyvinyl amine effect more comprehensively by Tong et al. the modified poly(N-methyl-N-vinylamine) demonstrated superior performance of CO<sub>2</sub> permeability of 6804 Barrer with a selectivity of 350 for CO<sub>2</sub>/N<sub>2</sub> and 162 for CO<sub>2</sub>/H<sub>2</sub> (Tong, Z. and Ho, W.S.W., 2017b). Polyvinyl amine/piperazine glycinate membrane is fabricated by Chen and co-workers, consequently achieving the excellent performance of about 1100 GPU of CO<sub>2</sub> permeability and selectivity of 140 for CO<sub>2</sub>/N<sub>2</sub> mixture, such high performance is attributed to the PVAm fixed-site-carrier whereas piperazine glycinate mobile carrier (Chen, Y. and Ho, W.S.W., 2016).

**Table 4.3: Examples of polymeric based membranes with their performances (facilitated transport mechanism).**

Material	$p(CO_2)/atm$	$T/^\circ C$	$P(CO_2)/Barrer$	$\alpha(CO_2/N_2)$	$\alpha(CO_2/CH_4)$	Reference
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Amine-based polymeric membranes						
65/35 PG/PVAm	1.5 psig	57	1100 GPU	200		(Chen, Y. et al., 2016a)
TFC-a-Tertiary amine	0.11 Mpa feed pressure	70	173 GPU	70	37	(Yu et al., 2010)
PEBAX/AFS-15	2 bar	25	145		28	(Isanejad et al., 2018)
PAA-C3H7/PVA	2atm F	110	308.6	346.9		(Zhao and Ho, 2012)
zeolite Y/Biomax PES	1atm	57	745 GPU	25.4		(Zhao, L. et al., 2016)
PVAm/PG		57	1100 GPU	140		(Chen, Y. and Ho, W.W.J.J.o.M.S., 2016)
poly(N-methyl-N-vinylamine)	1atm	102	6804	350		(Tong, Z. and Ho, W.W.J.J.o.M.S., 2017)
PES	4atm	67	1451 GPU	165		(Han et al., 2019c)
HMMP-1	0.2 MPa	298 K	1544 GPU	252		(Yuan et al., 2021)

#### 4.1.3.2 RTIL and other carrier based facilitated polymeric membranes

The designer solvent, room temperature ionic liquids (RTIL), nowadays are highly investigated as a potential candidate to replace other conventional materials, especially in CO<sub>2</sub> capture, due to its extraordinary features, such as low vapor pressure, high CO<sub>2</sub> uptake capacity, task-specific tuneable features, high thermally and chemical stability (Gan et al., 2011). These unique features supported ionic liquid-based membranes (SILMs) attracted much attention from a researcher for light gas separation. For instance, supported ionic liquid-based membranes have been investigated by Scovazzo et al. and exhibited an excellent separation with CO<sub>2</sub> permeability of 1000 Barrer along with the selectivity of 22 for CO<sub>2</sub>/N<sub>2</sub>. The major challenges for SILMs are the leaching of ionic liquids at the low-pressure difference from the polymer matrix due to its weak interactions limiting their mechanical stability (Tomé and Marrucho, 2016). To minimize these limitations, different approaches have been applied such as poly (ionic liquids) PIL by direct polymerization of IL monomers, embedding of IL into a compatible polymer matrix, and ion-gel membranes showing robust mechanical stability along with outstanding separation performance. For

instance, Mannan et al. reported polyether sulfone/emim (Tf2N) ionic liquid polymeric membrane, observed 124-fold enhancement than the neat PES membrane, CO<sub>2</sub> permeability of 298.84 Barrer with 57.53 (3.6-fold enhancement) selectivity of CO<sub>2</sub>/CH<sub>4</sub> (Mannan et al., 2016).

A small molecule of diamine and polyamine-based ionic liquid is used by Dai et al. to cross-link PEG diglycidyl ether (PEGDE) to obtain poly (ethylene glycol)-based epoxy-amine networks, exhibiting good separation performance due to CO<sub>2</sub>-philic ionic liquids along with robust mechanical strength due to the cross-linking. Moghadam et al. fabricated an interesting double-network ion-gel membrane of triethyl(2-methoxymethyl) phosphonium indazole ([P222(101)] [Inda]), displaying an excellent CO<sub>2</sub> separation performance and excellent mechanical strength. By tuning the cross-linking loading, the impact of CO<sub>2</sub> separation performance significantly increases such as 4 mol% loading showing CO<sub>2</sub> permeability of 2254 Barrer with 210 selectivity of CO<sub>2</sub>/N<sub>2</sub> (Moghadam et al., 2017). Ionic liquid based epoxy-amine ion gel membrane designed by M.McDanel et al. for fixed-site-carrier facilitated transport of CO<sub>2</sub> (Kasahara et al., 2014). The CO<sub>2</sub>-philic free RTIL carrier in membranes enhances the CO<sub>2</sub>/N<sub>2</sub> separation performance of epoxy-amine ion-gel membrane drastically and surpasses the 2008 Robeson's upper bound limit. Ionic liquids featured with highly CO<sub>2</sub>-philic functional groups make them more interesting alternatives for CO<sub>2</sub> separation. Its CO<sub>2</sub>-philic functional groups lead it to a highly facilitated transport for CO<sub>2</sub> as well as also provide a solution-diffusion transport effect. Zhang et al. first introduced diamine-monocarboxylate-based protic ionic liquids (PILs) as a supported ionic liquid membrane (SILMs), exhibit an excellent separation performance of CO<sub>2</sub> permeability of 3028 Barrer with ideal selectivity of CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> is 151 and 72 respectively (Zhang, X.-M. et al., 2017a). A series of imidazolium based phenolate ionic liquid feature with dual sites of interaction with CO<sub>2</sub> reported by Zhang et al. The outstanding separation performance of CO<sub>2</sub> permeability of 2540 Barrer with ideal selectivity of CO<sub>2</sub>/N<sub>2</sub> of 127, such an excellent performance is attributed to facilitated transport of CO<sub>2</sub> from carbene to phenolated anion based on theoretical calculations (Zhang, Xiaomin et al., 2019).

Beyond the amine and RTIL, many other carriers also have been widely investigated for CO<sub>2</sub> separation and show a vibrant separation performance with mechanically stable such as nanotube, GO, nanoparticles, etc. A novel nanotube-reinforced facilitated transport membrane is fabricated by Han et al., a selective layer

of 170nm coated on the polyether sulfone substrate demonstrates a CO<sub>2</sub> permeance of 975 GPU along with a CO<sub>2</sub>/N<sub>2</sub> ideal selectivity of 140 (Han et al., 2018). This excellent separation performance is attributed to the amino group bound to the polymer backbone acting as a fixed-site carrier and 2-(1-piperazinyl) ethylamine as a mobile carrier. Zhang et al. reported a mixed matrix membrane (MMMs) by introducing amino silane functionalized graphene oxides (f-GO) nanosheet into the Pebax polymer matrix, demonstrating a high CO<sub>2</sub> permeability of 934.3 Barrer along with CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> ideal selectivity of 40.9 and 71.1 respectively (Zhang, J. et al., 2019b). The amino groups on graphene oxides introduce facilitated transport effects in the MMMs, leading to surpassing Robeson's upper bound limit. An interesting hollow fiber thin film composite membrane with a three-phase hybrid facilitated transport effect (host polymeric matrix feature with fixed-site carriers, 2D-GO filler, CO<sub>2</sub>-reactive mobile carrier) is investigated by Janakiram, showed a CO<sub>2</sub> permeance of 825 GPU with CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation factor of 31 and 20 respectively (Janakiram et al., 2020).

Although much research focus has been made to explore the efficient membrane for CO<sub>2</sub> separation still far to make it applicable for industrial applications. In view of the exponential increment of carbon dioxide levels in the atmosphere, a high efficiency, low cost, energy effective, and stable membrane is required urgency.

#### 4.2 Mixed matrix membranes

Although polymeric membranes have been extensively investigated for gas separation due to their inherent features such as low costs, mechanical stability and easy processability, they are hindered due to their trade-off relationship between selectivity and permeability for industrial application (Sanders et al., 2013). Many researchers have devoted an effort to the advancement of polymeric materials like thermally rearranged polymer (TR) (Meis et al., 2022) and polymer of intrinsic microporosity (PIMs) (Zhou, S. et al., 2020a) as discussed in the above section, proved its potential to surpass Robeson's upper bound.

However, in the past few decades, mixed matrix membranes (MMMs) gained much attention from researchers due to their outstanding property to surpass Robeson's upper bound limit (Katare et al., 2023). In 1970, Paul and Kemp reported MMMs of zeolite 5 Å into polydimethylsiloxane (PDMS) for the first



time (Paul and Kemp, 1973). MMMs generally comprise inorganic fillers dispersed into a polymeric matrix that exhibit excellent permeability and selectivity for gas separation (Zornoza et al., 2015). MMMs featured with the dispersed phase (inorganic-fillers) provide the selectivity and continuous phase (polymer matrix) enhanced permeability and mechanical strength. MMMs are potential alternatives to a conventional polymeric membrane to overcome the trade-off between permeability and selectivity for gas separation.

Generally, the transport behaviour of small gas molecules through membranes depends upon the pore size of the porous membrane and solubility or reactivity in the case of the dense membrane, as explained in the above section (Kanehashi and Nagai, 2005). However, the transport property of MMMs is dependent upon many factors such as the compatibility of filler and polymer matrix, loading of filler, size, and shape of filler, etc. Maxwell model is a well-known model for the prediction of the transport mechanism of gas through MMMs for low loading and good compatibility between polymer and filler (Kanehashi et al., 2015). For higher loading and ideal morphology, Lewis-Nielsen models are more appropriate (Lewis and Nielsen, 1970). Many inorganic fillers such as carbon molecular sieves (CMS) (Rafizah and Ismail, 2008), graphene oxides (GOs) (Li, X. et al., 2015), zeolite imidazolate framework (ZIFs) (Yuan et al., 2017), metal-organic framework (MOFs) (Fu et al., 2016), covalent organic framework (COFs) (Fan et al., 2021) are investigated as filler into a polymeric matrix for gas separation. Recently, Fan et al. reported an interesting approach to enhance MOF/polymer interaction. However, it affects the permeability and selectivity of MMMs (Fan et al., 2022b). Deng et al. reported the effect of the morphology of filler (ZIFs 0D, ZIFs 1D, and ZIFs 2D) on the performance of MMMs (Deng et al., 2020a). Zhang et al. investigated 2D MFI nanosheet as a filler in Pebax polymeric matrix showing an excellent CO<sub>2</sub> permeability of 159.1 Barrer with a selectivity of 27.4 for CO<sub>2</sub>/CH<sub>4</sub> (Zhang, Q. et al., 2021b). Yoo et al. studied defects in metal-organic frameworks, a highly porous defect-engineered UiO-66 incorporated into PEGDA exhibit superior CO<sub>2</sub> permeability of 470 Barrer with CO<sub>2</sub>/N<sub>2</sub> selectivity of 41 (Lee et al., 2021b). Although by incorporating different and effective fillers into an appropriate polymer matrix we can achieve high separation performance, the defects exist at the polymer and filler interface. Therefore, evenly dispersion of fillers and appropriate fillers are still existing challenges for the researchers.

The separation of  $H_2/CO_2$  is extremely difficult due to its kinetic diameters (Zhu, Lingxiang et al., 2019). However, the exponential separation performance, sieving effects, high thermal, chemical, and mechanical stability of MMMs is extensively investigated for  $H_2/CO_2$  or  $CO_2/H_2$  separation. In this section, we discussed the pre-combustion and post-combustion  $CO_2$  capture through MMMs.

#### 4.2.1 Mixed matrix membranes for pre-combustion $CO_2$ capture

The separation of  $CO_2$  or  $H_2$  before the combustion is an effective strategy to limit the  $CO_2$  concentration level in the atmosphere, generally termed pre-combustion  $CO_2$  capture (Babu et al., 2016). After the water gas shift reaction, a mixture of  $CO_2/H_2$  is obtained with high temperature and high pressure from the IGCC system (Kanniche et al., 2010). Membrane technology is a promising alternative to the conventional separation technologies such as cryogenic distillation, chemical absorption, and physical sorption. Membrane materials must be considered especially for pre-combustion separation. MMMs have the potential to sustain such extreme conditions due to their thermal and mechanical stability. For precombustion  $CO_2$  capture, the membrane must either be  $H_2$  selective or  $CO_2$  selective (Al-Rowaili et al., 2023). We categorized MMMs as  $H_2$  selective and  $CO_2$  selective.  $H_2$  selective membranes have been investigated mostly, which might be due to the increasing demand for pure hydrogen fuel. Among the polymer classes polybenzimidazole (PBI) exhibit excellent  $H_2/CO_2$  selectivity. However, permeation is not significant (Zhu, L. et al., 2017). MMMs provide an interesting window for such a polymer to enhance the permeability along with reasonable selectivity by incorporation of suitable fillers. For example, recently, Etxeberria-Benavides et al. studied the effect of zeolitic-imidazolate framework (ZIF-8) filler into the polybenzimidazole (PBI) matrix, found superior  $H_2$  permeance of 65 GPU to 170 GPU with ideal selectivity of 18 for  $H_2/CO_2$  at 150 °C and 7 bar (Etxeberria-Benavides et al., 2020). Asymmetric PBI/ZIF-8 MMMs with 1  $\mu m$  skin layer designed by Sanchez-Lainez et al. exhibit unprecedented  $H_2$  permeability of 20.3 GPU and  $H_2/CO_2$  ideal selectivity of 35.6 at 250 °C and 6 bar (Sánchez-Laínez et al., 2018). Cheng et al. work on Zn/CO zeolitic imidazolate framework filler into a PEBAX polymer matrix to fabricate  $CO_2$  selective MMMs showing  $CO_2$  permeability of 102.5 Barrer along with 9.4  $CO_2/H_2$  selectivity (Cheng et al., 2020b).

Metal-organic frameworks (MOFs) are also emerging material that has been reported as filler due to their pore size and functional groups giving superior gas transportation property (Lin et al., 2018). Friebe et al. fabricated NH<sub>2</sub>-MIL-125 MOF layer MMMs for shown enhanced selectivity and H<sub>2</sub> permeability (Friebe et al., 2016). The morphology of fillers is also a good tuning property to enhance the separation performance of MMMs. Kang et al. reported an effect of filler morphology on membrane performance. PBI/[Cu<sub>2</sub>(ndc)<sub>2</sub>(dabci)]<sub>n</sub> MMMs with different morphology (bulk crystal (BC), nanocube (NC), and nanosheet (NS)), stacking orientation of NS MOF in MMMs provide a CO<sub>2</sub> barrier and enhance the H<sub>2</sub>/CO<sub>2</sub> selectivity of 26.7 along with the H<sub>2</sub> permeability of 6.13 Barrer (Kang et al., 2015). Ashtiani et al. demonstrated defect-free CO<sub>2</sub> selective MMMs by dispersing UiO-66-NH<sub>2</sub> (MOF) into a polyethyleneimine (PEI) (Ashtiani et al., 2021). Interestingly polymer-filler interfacial interaction enhanced by covalently bounding polyvinylpyrrolidone (PVP) with polymer and filler, exhibit CO<sub>2</sub> permeability of 394 Barrer along with a 12.7 separation factor. Ma et al. demonstrated ZIF-7@PI MMMs as a superior H<sub>2</sub> performance of  $3.0 \times 10^{-7} \text{ molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$  with 128.4 of separation factor for H<sub>2</sub>/CO<sub>2</sub> and 91.5 for H<sub>2</sub>/CH<sub>4</sub> due to the high channelling effects of ZIF-7 (Ma, X. et al., 2019). Mei et al. modified the ZIF-8/Polysulfone MMMs with polydopamine, which enhanced the performance of MMMs showing H<sub>2</sub> permeability of 23.3 along with the selectivity of 9.3 for H<sub>2</sub>/CO<sub>2</sub> (Mei et al., 2020). MMMs can thus be considered as a next-generation membrane for pre-combustion and post-combustion CO<sub>2</sub> capture due to their potential for industrial application. The novel design of inorganic fillers, such as MOFs, COFs, GOs, ZIFs, etc., makes this area more attractive.

#### 4.2.2 Mixed matrix membranes (MMMs) for post-combustion carbon capture

MMMs containing dispersed inorganic fillers in continuous polymer matrices have emerged as an effective and versatile platform to obtain superior CO<sub>2</sub>/N<sub>2</sub> separation properties for post-combustion carbon capture (Buddin and Ahmad, 2021; Hu, L. et al., 2022b). The addition of nanofillers may also improve physical and chemical stabilities against plasticization and aging (Ahmad et al., 2020; Chi et al., 2019; Smith et al., 2020; Zhao, J. et al., 2019). More importantly, the diversity of polymers and fillers offers enormous possibilities for designing membranes with desirable properties (Budhathoki et al., 2019).

A variety of functional polymers have been used as polymer matrices to construct MMMs to achieve superior CO<sub>2</sub>/N<sub>2</sub> separation properties (Han, Y. and Ho, W. S. W., 2020; Hu, L. et al., 2022b; Hu, L. et al., 2018; Lee and Gurkan, 2021), including glassy polymers such as PIMs (Chen, W. et al., 2021; Fan et al., 2022a; Shen et al., 2019) and polyimides (Hu, C. et al., 2020; Jiang et al., 2021; Wang, Hongliang et al., 2018), and rubbery polymers such as Pebax (Nadeali et al., 2019; Sanaeepur et al., 2019; Thankamony et al., 2019), Polyactive (Rahman et al., 2018; Sabetghadam et al., 2019), and polyethers (Alebrahim et al., 2022; Hu, L. et al., 2018; Liu, J. et al., 2020). Polymers containing fixed CO<sub>2</sub> carrier sites, including poly(vinyl alcohol) (PVA) (Cao, X. et al., 2019; Gao, Y. et al., 2018; Jia et al., 2020) and poly(ionic liquid)s (PILs) (Dunn et al., 2019; Lee and Gurkan, 2021; Yang, Z. et al., 2022) were also used to realize facilitated transport for CO<sub>2</sub>, but not for N<sub>2</sub>.

Porous or non-porous fillers can be used to create MMMs, while most studies focus on porous nanofillers with well-designed pores, such as metal-organic frameworks (MOFs) (Hu, L. et al., 2018; Knebel et al., 2020), metal-organic polyhedra (MOPs) (Guo, X. et al., 2021; Liu, J. et al., 2020), porous organic frameworks (POFs) (Duan, K. et al., 2019; Zhang, Yahui et al., 2022), and two-dimensional (2D) nanosheets (Shi et al., 2021; X Li, 2019). These porous fillers have high porosities that can tremendously improve gas diffusivity and solubility or well-controlled pore sizes that exhibit precise cut-off between CO<sub>2</sub> and N<sub>2</sub>. Non-porous fillers with affinities towards CO<sub>2</sub> have also been used to improve CO<sub>2</sub> solubility and CO<sub>2</sub>/N<sub>2</sub> solubility selectivity (Matteucci et al., 2008; Zhu, L. et al., 2019). Additionally, non-porous fillers might disrupt polymer chain packing, increasing free volume and thus gas diffusivity (Hu, C. et al., 2020; Merkel et al., 2002). Typical non-porous fillers include silica (SiO<sub>2</sub>) (Aghaei et al., 2018; Hu, C. et al., 2020), metal oxide (MO<sub>x</sub>) (Qiu, H. et al., 2022; Sanaeepur et al., 2019), and polyhedral oligomeric silsesquioxane (POSS) (Kanezashi et al., 2019; Ren et al., 2019).

In addition to the rapid growth of advanced materials, various empirical models are employed to describe gas transport properties in MMMs, such as the Maxwell model, modified Maxwell model, Lewis-Nielson model, and Kang-Jones-Nair model (Hoang and Kaliaguine, 2013; Monsalve-Bravo and Bhatia, 2018). Computational simulations have also been applied to predict the structure/property relationship in MMMs, such as molecular dynamics simulation (Erucar and Keskin, 2016), Monte Carlo simulation (Harami et al.,

2019), computational fluid dynamics calculation (Kattula et al., 2015; Safaei et al., 2021), and artificial neural network model (Rezazakemi and Mohammadi, 2013; Rostamizadeh et al., 2013).

Despite tremendous progresses made in the last decades, the MMMs are faced with key challenges for practical applications, including particle agglomeration, interfacial incompatibility, brittleness, and poor thin-film formability. This section will highlight various strategies to address these challenges for the MMMs containing porous nanofillers, as well as the improvement of CO<sub>2</sub>/N<sub>2</sub> separation properties. Tables 4.4 and 4.5 record separation properties for the key materials and thin-film composite (TFC) membranes developed, respectively.

Table 4.4 CO<sub>2</sub>/N<sub>2</sub> separation performance of representative MMMs.

MMMs			T (°C)	CO <sub>2</sub> permeability (Barrer)	CO <sub>2</sub> /N <sub>2</sub> selectivity	Ref.
Polymers	Fillers	Loading (wt.%)				
PEGDA-co- PEGMEA	-	0	35	424	33	(Ma, L. et al., 2019)
	ZIF-8	49.7		910	33	
	ZIF-7	34.3		1084	38	
XLPEGDA	-	0	35	130	50	(Hu, L. et al., 2018)
	ZIF-8	50		1300	33	
6FDA-DAM	-	0	35	970	18	(Chi et al., 2019)
	HKUST-1	30		2360	16	
sPIM-1	-	0	25	5929	24	(Yu, G. et al., 2019)
	UiO-66-CN	20		12063	54	
XLPEO	UiO-66-H	30	35	70	49	(Lee, Jooyeon et al., 2020)
	UiO-66-Vinyl	30		110	47	
	UiO-66-NO <sub>2</sub>	30		115	44	
	UiO-66-Naph	30		82	47	
ODPA-DAM	-	0	35	65	17	(Wang, Hongliang et al., 2018)
	UiO-66-NH <sub>2</sub> @PI	27		142	27	
PIM-1	-	0	20	7062	10	(Lu et al., 2021)
	UiO-66-NH <sub>2</sub> @IL	10		8283	23	
XLPEGDA	-	0	35	110	55	(Liu, J. et al., 2020)
	MOP-3	50		480	42	
XLPDXLA	-	0	35	190	70	(Zhang, Yahui et al., 2022)
	MOP-3	30		580	62	
XLPEO	-	0	35	440	35	(Zhang, Yahui et al., 2022)
	COF	6-9.6		804	61	
6FDA-DAM	-	0	25	812	25	(Cheng, Y. et al., 2019)
	COF300	7		1205	33	
	COF@PEI	10		1154	49	
PIM-1	-	0	35	4500	14	(Li, Siyao et al., 2019)
	Azo-COP-2	15		10,500	12	

<b>Pebax®1657</b>	-	0	20	53	51	(Thankamony et al., 2019)
	CTPP	0.025		73	79	
<b>PTMSP</b>	-	0	-	43,000	7	(Smith et al., 2020)
	p-DCX	-		42,000	12	
<b>Pebax®1657</b>	-	0	25	94	32	(He et al., 2019)
	POP-PGO	2		233	81	
<b>Pebax®1657/ PEGMEA</b>	-	0	35	590	43	(Shin et al., 2019)
	GO	0.3		610	56	
<b>Pebax®1657</b>	-	0	25	125	65	(Shamsabadi et al., 2017)
	AS-TiO <sub>2</sub>	3		189	85	
	CMC-TiO <sub>2</sub>	3		195	82	
<b>ODPA-TFMB</b>	-	0	35	67	28	(Hu, C. et al., 2020)
	SiO <sub>2</sub> -NH <sub>2</sub>	20		210	31	
<b>XLPEO</b>	-	0	35	520	52	(Alebrahim et al., 2022)
	LiClO <sub>4</sub>	2		710	53	
<b>Pebax®1657</b>	-	0	RT	71	30	(Deng et al., 2020b)
	ZIF-C	20		387	47	
<b>Pebax®1657</b>	-	0	35	96	39	(Zhang, J. et al., 2019a)
	f-GO	0.9		934	71	

Table 4.5 CO<sub>2</sub>/N<sub>2</sub> separation performance of representative TFC membranes based on MMMs.

MMMs				Gutter layer	T (°C)	CO <sub>2</sub> permeance (GPU)	CO <sub>2</sub> /N <sub>2</sub> selectivity	Ref.
Polymers	Fillers	Loading (wt.%)	Thickness (μm)					
<b>Pebax 1657</b>	ZIF-8	30	~1.5	PTMSP	25	350	31	(Sutrisna et al., 2017; Sutrisna et al., 2018)
	ZIF-7	30	1-1.5			300	48	
	UiO66-NH <sub>2</sub>	50	1-1.5			340	57	
<b>PEGDME</b>	NH <sub>2</sub> -MIL-53	47.4	4.9	None	35	560	35	(Xie et al., 2018)
<b>PIM-1</b>	MOF-74-Ni	10	0.65	PDMS@aMOF	35	1200	30	(Liu, M. et al., 2020)
<b>PGMA-co-POEM</b>	UiO-66-NH <sub>2</sub>	28.6	<0.1	PTMSP	25	1300	31	(Kim, N. et al., 2019)
<b>PEGDMA</b>	EG3-MOP	5	~0.29	PDMS	35	300	16	(Sohail et al., 2021)
<b>Pebax 1657</b>	GO/IL	0.05	~0.1	PTMSP	25	900	45	(Huang, G. et al., 2018)
<b>Pebax 1657</b>	MXene	0.05	0.07	PTMSP	25	1360	31	(Shamsabadi et al., 2019)
<b>PSF</b>	Montmorillonite	NA <sup>c</sup>	0.1	None	50	800	125	(Qiao et al., 2016)
<b>PA</b>	MIL-101(Cr)	NA	0.2	PDMS	NA	930	220	(Wang, B. et al., 2020)
<b>PIL-IL</b>	GO	~1	0.9	None	22	3090	1180	(Lee and Gurkan, 2021)
<b>PVAm</b>	PEI-g-ZIF-8	16.7	0.33	None	30	2000	80	(Gao, Y. et al., 2018)
<b>PVAm</b>	HMP(F)	NA	~0.3	PDMS/PVA	25	1800	65	(Wang, B. et al., 2020)

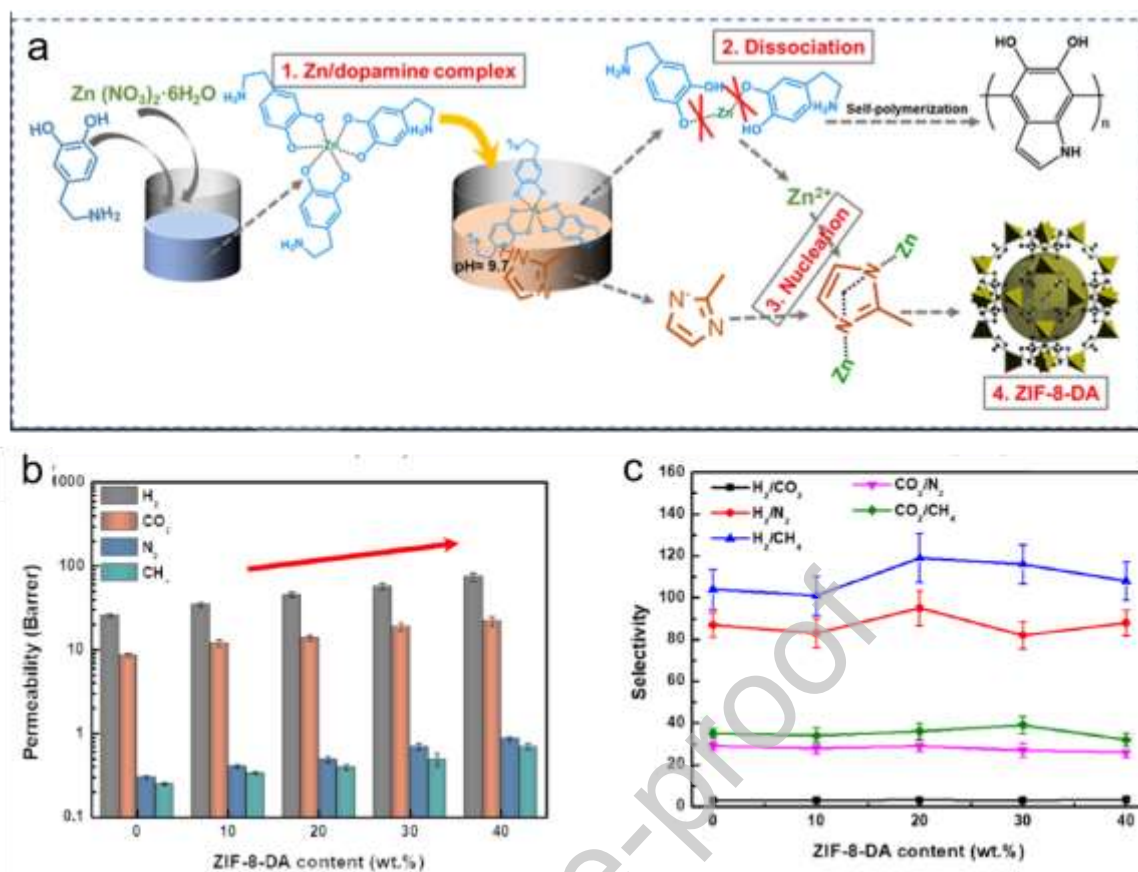
#### 4.2.2.1 MOF-based MMMs

MOFs have well-controlled apertures with sizes similar to gas molecules, such as ZIF-8 (3.4 Å) (Hu, L. et al., 2018) and ZIF-90 (3.5 Å) (Huang et al., 2010). However, MOFs have flexible structures and show “gate-opening” behavior, leading to lower intrinsic CO<sub>2</sub>/N<sub>2</sub> selectivity than most polymers (Bondorf et al., 2022; Ryder et al., 2014). Consequently, the MOF-based MMMs confine to the trade-off between CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity, though their separation properties can still be described by empirical models such as the Maxwell model. Additionally, polymers (particularly glass polymers) do not have affinities towards MOFs, generating interfacial defects that can degrade separation performance and mechanical properties.

Compared to the blending of polymers and MOFs to form MMMs, *in-situ* growth of MOF nanoparticles (NPs) in polymers or *in-situ* polymerization of polymers provides an effective approach to improve interfacial compatibility by wetting the NPs with the polymers or precursors (Hu, L. et al., 2022a; Park et al., 2020). Moreover, *in-situ* growth of the NPs can effectively control the NP sizes and avoid their aggregation (Ma, L. et al., 2019). The NP sizes and shapes (or dimensions) can also be optimized to improve gas separation performance. Interestingly, low loadings of the NPs with optimized morphologies were reported to unexpectedly increase gas permeability because of the percolation networks formed by the highly porous NPs (Ashtiani et al., 2021; Chi et al., 2019).

Creating strong interactions between MOFs and polymers can efficiently enhance interfacial compatibility (Hu, L. et al., 2022b). Specifically, the surface of the MOF NPs can be modified to exert affinities towards the polymer phase (Guo, X.Y. et al., 2019; Jiang et al., 2021; Lee, Jooyeon et al., 2020). For example, **Figure 4.1a** showed that the ZIF-8 was modified using dopamine (a bio-inspired adhesive) before mixing. The addition of ZIF-8-DA substantially increased gas permeability without reducing selectivity (**Figure 4.1b,c**), breaking the permeability/selectivity trade-off.





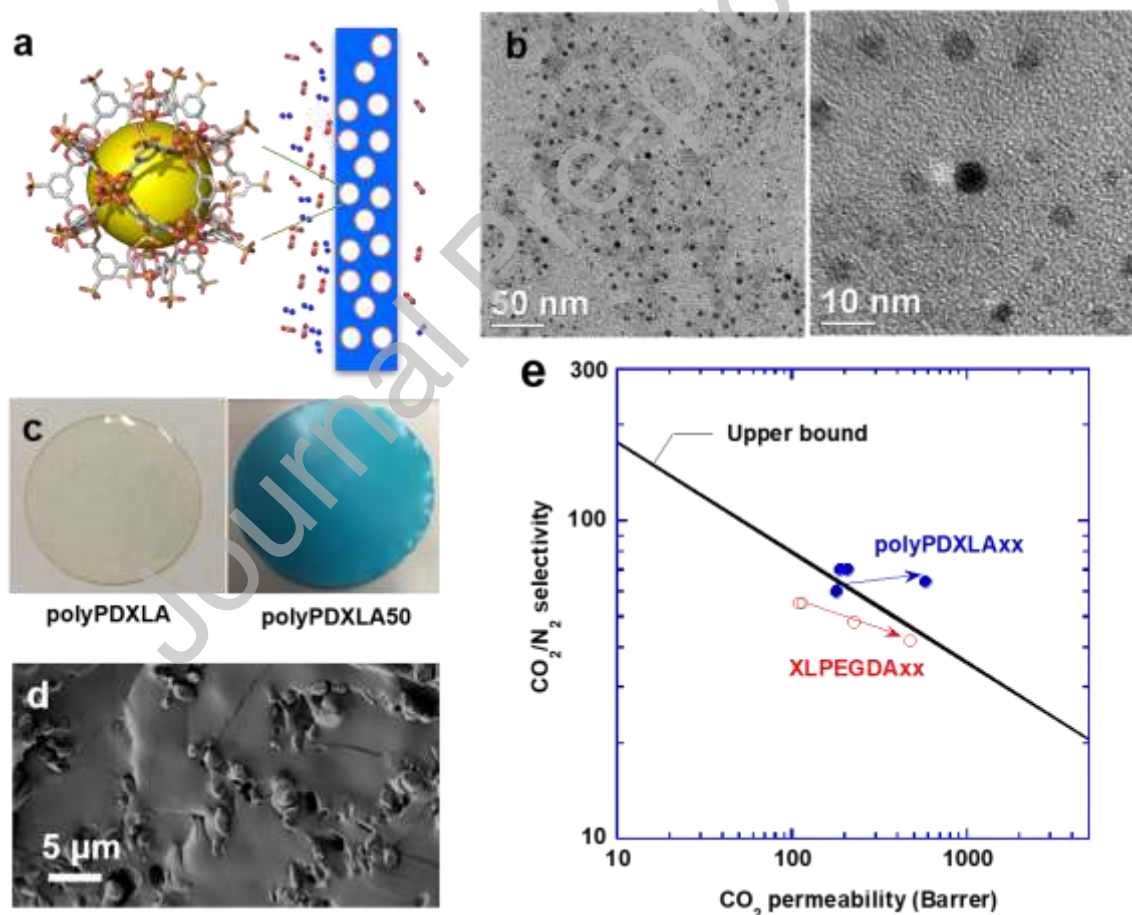
**Figure 4.1.** (a) Illustration of the dopamine-modulated synthesis process of ZIF-8-DA. Effect of the ZIF-8-DA loading in Matrimid on (b) gas permeability and (c) selectivity (Jiang et al., 2021).

The surface of the ZIF-67 NPs was functionalized with N-heterocyclic carbene ligands to achieve excellent mechanical and separation properties (Knebel et al., 2020). Polymer chains can also be grafted onto the MOF surface, acting as brushes and generating favorable interactions with the polymer (Wang, Hongliang et al., 2018). Compatibilizers like ionic liquids (ILs) were also used to modify the MOF surface (Lu et al., 2021). Additionally, the MOF was even used to cross-link polymers to improve both interfacial compatibility and size-sieving ability. For example, UiO-66 NPs were functionalized with nitrile groups and then covalently bonded to PIM-1 by thermal treatment (Yu, G. et al., 2019). The cross-linking with 20 wt% UiO-66 increased  $CO_2$  permeability by 4 times to 12,000 Barrer and  $CO_2/N_2$  selectivity by 2 times to 54 at 25 °C.

2D MOF nanosheets (NSs), especially ZIF, have been widely used to form MMMs (Bi et al., 2020; Feng et al., 2020). For instance, metal-tetrakis(4-carboxyphenyl) porphyrin (M-TCPP) NSs have open metal sites and affinities towards polymer chains and  $CO_2$ , increasing  $CO_2$  solubility and interfacial compatibility (Wang, C. et al., 2019; X Li, 2019; Zhao, M. et al., 2017; Zhao, Y. et al., 2018). In addition, the M-TCPP NSs have intrinsic micropores and interlayer spacing near 1 nm, which can be utilized to enhance gas separation properties (Lee et al., 2021a; X Li, 2019).

## 4.2.2.2 MOP- and POF-based MMMs

MOPs are highly porous molecular cages formed via the self-assembly of metal ions and organic ligands, similar to MOFs. However, MOPs are discrete cages of 1–5 nm, which can be dissolved in solvents and easily processed into TFC membranes, as shown in Fig. 2a (Fulong et al., 2018). MOPs were incorporated in glassy or rubbery polymers to improve CO<sub>2</sub>/N<sub>2</sub> separation properties (Fulong et al., 2018; Liu, J. et al., 2020; Liu et al., 2018). In particular, the metal ions on the MOPs can have favorable interactions with polymers such as polyethers, enhancing interfacial compatibility. For instance, MOP-3 NPs have a uniform size of  $\approx 5$  nm (**Figure 4.2b**) with aperture sizes of 1.1 and 0.89 nm. Fig. 2c shows a photo of a freestanding film containing 50% MOP-3, and the SEM photo confirmed the well-dispersed NPs in the polymer (**Figure 4.2d**). The introduction of 50% MOPs in the polyether increased CO<sub>2</sub> permeability from 190 to 580 Barrer while retaining high CO<sub>2</sub>/N<sub>2</sub> selectivity of 62 (**Figure 4.2e**). Interestingly, low loadings of MOPs can also significantly increase CO<sub>2</sub> permeability and retain CO<sub>2</sub>/N<sub>2</sub> selectivity because of the percolation networks derived from the MOP NPs (Hosono et al., 2019).



**Figure 4.2.** (a) Schematic of the MOP-based MMMs for CO<sub>2</sub>/N<sub>2</sub> separation. (b) TEM images of MOP-3 NPs. (c) Photos of polyPDXLA and polyPDXLA50 (containing 50 mass% MOP-3). (d) Cross-sectional SEM image of the XLPEGDA30. (e) CO<sub>2</sub>/N<sub>2</sub> separation performance of XLPEGDAxx and polyPDXLAxx in 2008 upper bound (Liu, J. et al., 2020).

Unlike MOFs and MOPs containing metal atoms, POFs are assembled by pure organic compounds and can be categorized as covalent organic frameworks (COFs), covalent organic polymers (COPs), and porous aromatic frameworks (PAFs). Due to their high crystallinity and well-defined porous structures, COFs have been intensively investigated for gas separations. However, most COFs have pore sizes far larger than gas molecules, increasing gas permeability but decreasing selectivity (Zhang, Yahui et al., 2022). Several approaches have been adopted to reduce COF pore sizes to increase the size-sieving ability (Fan et al., 2018; Yang, H. et al., 2019). For instance, 3D COF-300 NPs were constructed from 2D COF layers to attain pore sizes 4 Å, and the incorporation of the NPs in Pebax increased both CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity (Cheng, Y. et al., 2019). One of the challenges in using COFs for MMMs is their hydrophobicity, leading to poor interactions with polymers. To mitigate this problem, the COFs are often functionalized with ions or hydrophilic groups to enhance interfacial compatibility (Cheng et al., 2018; Liu, Y. et al., 2021). Additionally, the hydrophilic groups, such as PEO and polyethylenimine (PEI), can have affinities towards CO<sub>2</sub>, further improving CO<sub>2</sub>/N<sub>2</sub> separation properties (Liu, Y. et al., 2021).

POFs can also be further functionalized with N<sub>2</sub>-phobic groups, such as azo groups (–N=N–), decreasing N<sub>2</sub> solubility and increasing CO<sub>2</sub>/N<sub>2</sub> solubility selectivity (Patel et al., 2013). For example, the addition of 15% azo-COP-2 in polysulfone increased CO<sub>2</sub>/N<sub>2</sub> solubility selectivity by ~ 90% (Li, Siyao et al., 2019). Other POFs have also been developed and used in MMMs to improve CO<sub>2</sub>/N<sub>2</sub> separation properties, such as PAFs (Smith et al., 2020; Smith et al., 2019) and covalent triazine piperazine polymer (CTPP) (Thankamony et al., 2019; Zhang, Yahui et al., 2022).

#### 4.2.2.3 MMMs containing 2D nanomaterials

2D nanomaterials with tunable channels are another popular type of porous fillers used to construct MMMs, such as 2D COF and MOFs, graphene-based NSs, and MXene NSs (Shi et al., 2021). For instance, porous graphene was demonstrated with the potential to achieve CO<sub>2</sub> permeance of 100,000 GPU and CO<sub>2</sub>/N<sub>2</sub> selectivity of ~ 300 (Liu, H. et al., 2013). Graphene oxide (GO) NSs have high aspect ratios and can be stacked to form sub-nm channels for gas molecular sieving. Furthermore, GO NSs can be chemically modified by grafting or blending to enhance interfacial compatibility with polymers and affinity toward CO<sub>2</sub> (He et al., 2019; Li, X. et al., 2015). For example, the addition of 0.3 wt% GO NSs in Pebax/PEGMEA increased CO<sub>2</sub>/N<sub>2</sub> selectivity from 42 to 56 with enhanced stability against physical aging (Shin et al., 2019).

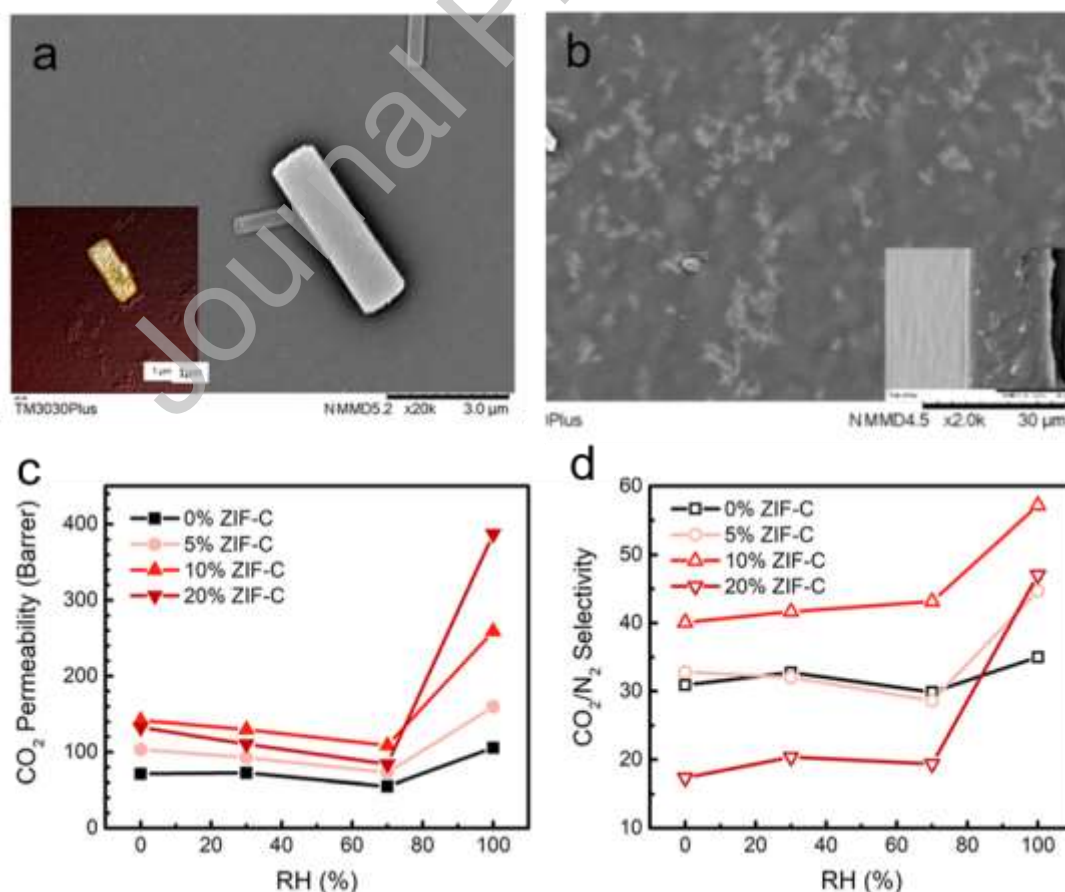
MXenes contain metal carbides and carbonitrides and have a large surface area and hydrophilicity (Huang et al., 2021). MXene nanosheets can be stacked to attain interlayer spacings near gas molecule sizes, thus achieving a strong size-sieving ability for CO<sub>2</sub>/N<sub>2</sub> separation. For example, Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> NSs

showed an interlayer spacing of 3.5 Å, larger than CO<sub>2</sub> but smaller than N<sub>2</sub> (Shamsabadi et al., 2019), and the addition of 0.1 wt% Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> in Pebax increased CO<sub>2</sub>/N<sub>2</sub> selectivity by 41% to 43 and CO<sub>2</sub> permeability by 83% to 1810 Barrer because of the disrupted polymer chain packing and increased free volume.

#### 4.2.2.4 Facilitated transport MMMs

MMMs with facilitated CO<sub>2</sub> transport have also been investigated to obtain superior CO<sub>2</sub>/N<sub>2</sub> separation properties, and typical polymers can be poly(vinyl amine) (PVAm) and PolyILs (Cao, X. et al., 2019; Lee and Gurkan, 2021). For example, MMMs were prepared by self-assembly of PVAm and modified MIL-101(Cr) (MKP) (Wang, B. et al., 2020), and a TFC membrane with 200-nm MKP/PVAm exhibited CO<sub>2</sub> permeance of 823 GPU and CO<sub>2</sub>/N<sub>2</sub> selectivity of 242 in the presence of water vapor.

Nanofillers can also be functionalized with CO<sub>2</sub> carrier groups to achieve facilitated CO<sub>2</sub> transport (Deng et al., 2020b; Zhang, J. et al., 2019a). **Figure 4.3** presents the structure and properties of the MMMs containing ZIF NSs in Pebax (Deng et al., 2020b). The ZIF NSs showed good dispersion in MMMs (**Figure 4.3b**). Increasing the relative humidity (RH) generally improves the CO<sub>2</sub>/N<sub>2</sub> separation properties due to the facilitated CO<sub>2</sub> transport. An MMM film containing 20 wt% NSs exhibited high CO<sub>2</sub> permeability of 390 Barrer and CO<sub>2</sub>/N<sub>2</sub> selectivity of 47 in the presence of saturated water vapor (**Figure 4.3c,d**).



**Figure 4.3.** Morphology of (a) ZIF-C 85–124 NS and (b) MMM with 10 wt% ZIF-C 85–124 NS. (c) CO<sub>2</sub> permeability and (d) CO<sub>2</sub>/N<sub>2</sub> selectivity of MMMs as a function of relative humidity (Deng et al., 2020b).

### 4.3. Inorganic Membranes for CO<sub>2</sub> Capture

Polymeric inorganic membranes (PIMs) are still at the initial stage of research; they display prospective characteristics for pre- and post-combustion CO<sub>2</sub> capture. These membranes offer high permeabilities, thus reducing the total investment as compared to polymeric membranes. Moreover, PIMs can be operated in a continuous operation and can withstand high flow rates.

The market of inorganic membranes is very small and is expected to rise in the near future. Inorganic membranes like zeolites, porous glass, microporous beryllium oxide, silicon nitride, carbon, and silica are quite popular because of their characteristic of high permeability and selectivity (Ogieglo, Wojciech et al., 2019; Sazali et al., 2021; Shi, Y. et al., 2020). The phenomenon of high permeability and selectivity is known as the upper bound trade-off curve, first introduced by Robeson et al. (Robeson, 1991) in 1991 and later updated in 2008 (Robeson, Lloyd M, 2008). The phenomenon describes an inverse dependency of selectivity and permeability for gas separation of membranes. For example, as the gas selectivity decreases, the permeability decreases, and vice versa. For this reason, inorganic membranes have superior performance as compared to glassy membranes. J.W. McBain introduced the first ever inorganic polymeric membrane in 1930s. This membrane was initially utilized as a molecular sieve material and surprisingly displayed excellent selectivity (McBain, 2002). Apart from the processes of permeability and selectivity, membrane properties play another important role in carbon capture and separation. Primarily, the support material for any membrane is selected based on the requirements of mechanical strength, chemical resistance, and durability (Lee et al., 2016). In most cases, the support material is porous in nature to experience minimal gas/water transport resistance. Porous inorganic membranes contain either contain porous metal or ceramic support structures, with additional porous layers on top with different structures and morphologies. Inorganic membranes have different pore shapes like (i) straight pores of equal diameter extending from end to end of the membrane, and (ii) conical pores smaller at the bottom and a larger diameter at the surface of the membrane.

In addition to the general advantages of the PIM, new generation hybrid materials of zeolites, silica, and organometallic frameworks (MOFs) offer an abundance of opportunities to produce new membranes with selective functional groups for carbon recovery (Ding et al., 2019; Shi, Y. et al., 2020). Recent reviews of CO<sub>2</sub> capture on hybrid membranes have provided only brief insights into membrane design for CO<sub>2</sub> and H<sub>2</sub> separation.

### 4.3.1 Zeolite based inorganic membrane

Zeolites, also known as semi-stable silicates or alumina silicates, with a uniform topology, giving an intracrystalline network of voids and channels. They also have an abundant surface chemistry that varies with the Si/Al ratio, amount, and type of exchangeable cations. Cations in zeolites sometimes act as Lewis acids, while the framework oxide ions nearby cations may act as Bronsted/Lewis bases. Furthermore, the silanol groups might act as Brönsted acids. The CO<sub>2</sub> adsorption capacity of zeolites are highly affected by their topology, modelling the energy interactions, segregating, and clustering effects. The dependence of zeolites on topology is not always precise as most of the zeolites are very complex to prepare in pure silica form or in proper Si/Al ratios. Noteworthy exceptions to this statement are silicalite-1 (Tawalbeh et al., 2021; Zhu, W. et al., 2006), clathrasil DD3R (Himeno et al., 2007; Van Den Bergh et al., 2010), CHA (Debost et al., 2020; Miyamoto et al., 2012), and ITQ-29 (Palomino et al., 2010). Silicalite-1 composite membranes with thin zeolite layers, prepared by Wirawan et al. (Wirawan et al., 2011) provided a simulated results of 9.8 and 4.0 mol/(m<sup>2</sup>s) for CO<sub>2</sub>/H<sub>2</sub> separation factor and CO<sub>2</sub> flux, respectively. Faujasite (FAU)-type zeolites with low Si/Al ratio often provide the highest adsorption selectivity for CO<sub>2</sub>. Study by Krishna et al. (Krishna and van Baten, 2010). proposed that FAU-type membrane can achieve a selectivity of 500 and permeability of 10000 Barrer for CO<sub>2</sub>/N<sub>2</sub> separation. The presence of aluminum in the silicon-aluminum framework creates a negative charge that must be neutralized by the metal cations in the pores. The most observed configurations involve the presence of Na<sup>+</sup> ions as counterions, termed NaX and NaY. Compared to N<sub>2</sub>, CO<sub>2</sub> exhibits a stronger interaction with the electric field of the micropores, influenced by the number and type of cations present. NaX, which has a lower Si/Al ratio than NaY and contains more cations, exhibits higher selectivity for CO<sub>2</sub> over N<sub>2</sub>, despite having a smaller pore volume than NaY (Maurin et al., 2005). White et al. (White et al., 2010) developed a zeolite Y membrane on alumina, which gave CO<sub>2</sub> permeance of 300 GPU and more than 500 selectivity factors for CO<sub>2</sub>/N<sub>2</sub>.

#### 4.3.1.1 Surface chemistry

The Si/Al ratio in zeolite surface is highly responsible for influencing its ability to adsorb CO<sub>2</sub> by pitching the number and setting of exchangeable cations, including the acid-base character of zeolite topology. Among the most famous zeolite structures, faujasites provide the highest CO<sub>2</sub> uptake capacity of 5-10 mmol CO<sub>2</sub>/g at 101 kPa and 303 K. The CO<sub>2</sub> affinity follows the order of NaA > NaX > NaY. This trend can be explained by decreasing pore size and the presence of a high number of type III cations at the starting of super-cage structure, leading to preferential interaction with CO<sub>2</sub> (Li and Pidko, 2019). The CO<sub>2</sub> uptake in ITQ-29 dramatically increase with Si/Al ratio (Figure 4.4). This property is exceptional for membrane design as it enables preferential separation of CO<sub>2</sub> by precisely modulating the polarity and surface science of LTA scaffold in specific separations. In the case of Aluminosilicate-



based zeolites, CO<sub>2</sub> adsorption Henry's coefficients are 1-2 orders greater than corresponding N<sub>2</sub> and CH<sub>4</sub>. This difference is attributed to the high heat of adsorption of CO<sub>2</sub> as compared to N<sub>2</sub> and CH<sub>4</sub>.

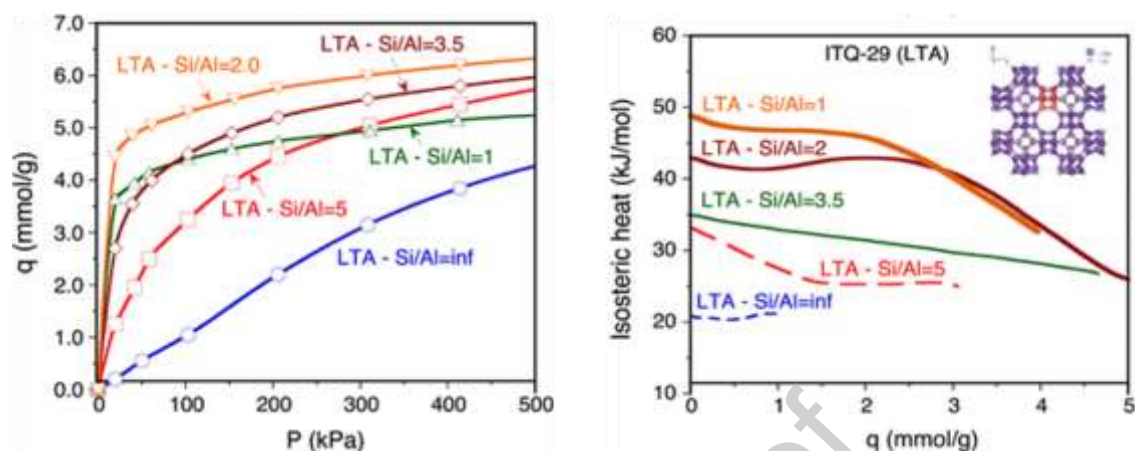


Figure 4.4 Effect of the Si/Al ratio on the isosteric heat of CO<sub>2</sub> adsorption for a series of ITQ-29 zeolites displaying the LTA (Pera-Titus, 2014).

The zeolite basicity increases with Al content and cation electro-positivity (Barthomeuf, 2003; Verdoliva et al., 2019). Ward and Habgood (Ward and Habgood, 1966) supported the hypothesis of chemical interactions among adsorbed CO<sub>2</sub> and alkaline cations. They reported the characteristic IR bands of carbonates for CO<sub>2</sub> adsorption in KX, NaX, and LiX zeolites. Heavy cations (Rb and Cs) compensate for the strong basicity with electrostatic interactions of cation and quadrupole (Walton et al., 2006). The basicity of zeolite structure can further be devised by incorporating amine groups, resulting in phase alteration of zeolite, and the formation of Si-N-Si moieties (Han et al., 2005).

#### 4.3.1.2 Effect of water on CO<sub>2</sub> adsorption

Water is studied as a simple molecule to increase the CO<sub>2</sub> adsorption of zeolites. The CO<sub>2</sub> uptake can be highly influenced by high water partial pressure as CO<sub>2</sub> and H<sub>2</sub>O molecules compete for the sorbent sites (Kolle, Joel M et al., 2021). H<sub>2</sub>O favourably adsorb on exchangeable cations, lessening the electrical field on zeolite cavities. For instance, as reported by Brandani and Ruthven (Brandani and Ruthven, 2004), the CO<sub>2</sub> uptake in CaX-zeolite at 0.06 bar and 323 K decreases between 2.5 and 0.1 mmol/g on increasing H<sub>2</sub>O concentration from 0.8 wt% to 0.1 wt% (Figure 4.5). Meanwhile, in case of CO<sub>2</sub> concentration less than 300 ppm, H<sub>2</sub>O pre-adsorption may promote CO<sub>2</sub> adsorption capacity by forming surface bicarbonate species. This improvement automatically normalises CO<sub>2</sub> uptake as the CO<sub>2</sub> concentration reaches 1000 ppm, stating that CO<sub>2</sub> loadings are higher for dry adsorption.

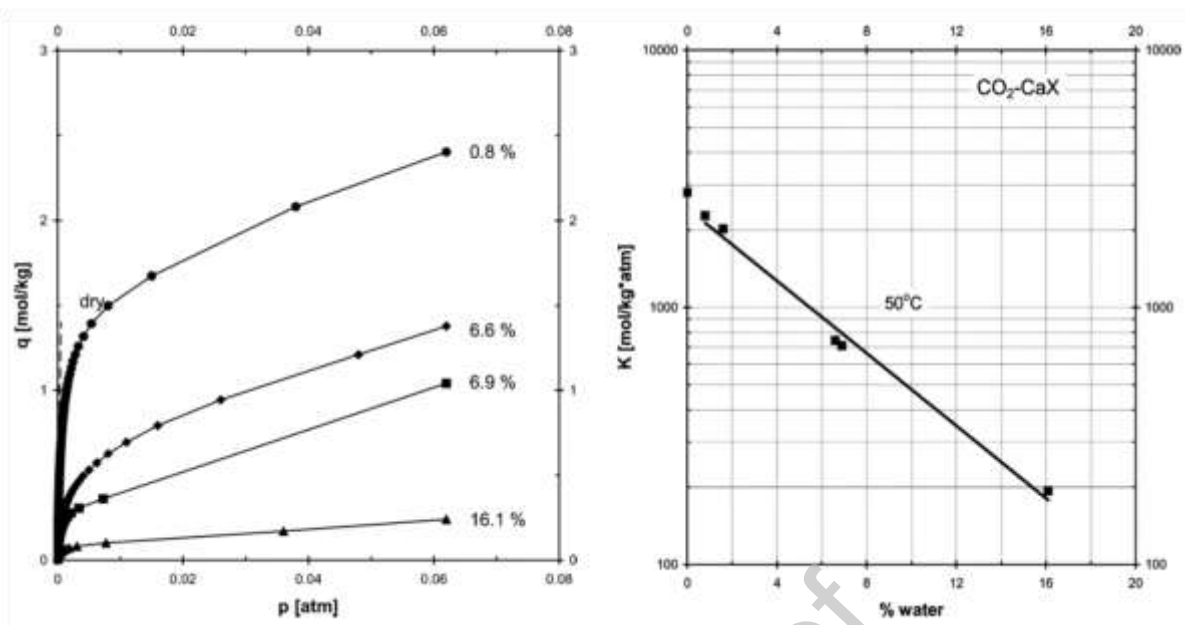


Figure 4.5 CO<sub>2</sub> adsorption isotherms (left) and Henry's constants (right) on CaX at 323 K for different pre-adsorbed water loadings (Brandani and Ruthven, 2004).

In zeolites with high Si/Al ratios, the H<sub>2</sub>O isotherm deviates from the characteristic type-I trend (i.e., Langmuir type), as noticed in LTA and FAU zeolites. The H<sub>2</sub>O adsorption proceeds through the formation of clusters in MFI channels, resulting in the reduction of CO<sub>2</sub> uptake capacity (Ahunbay, 2011; Cailliez et al., 2008; Trzpit et al., 2007). The deviation from Langmuir-type is generally known as type-II behaviour. Introducing germanium in the MFI structure also improves hydrophobic properties. Figure 4.6 represents water adsorption on MFI zeolite improved with Al, B, and Ge species.

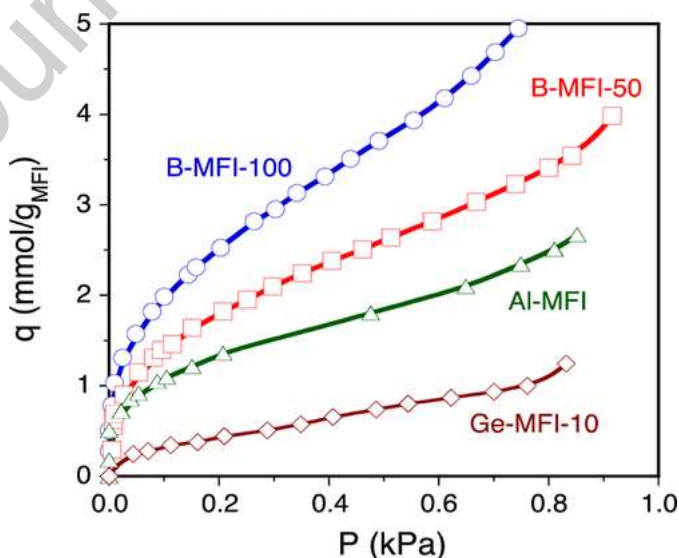


Figure 4.6 Water adsorption at 303 K on crushed Al-MFI (Si/Al = 30), B-MFI-100 (Si/B = 100), B-MFI-50 (Si/B = 50), and Ge-MFI-10 (Si/Ge = 10) (Nicolas and Pera-Titus, 2012).



MFI membranes have yielded comparatively low amounts of CO<sub>2</sub>/N<sub>2</sub> separation factors. However, their use for the separation of CO<sub>2</sub>/N<sub>2</sub> mixtures is still being investigated because of their low Al content. This gives the membranes better reproducibility and chemical stability. Ando et al. (Ando et al., 1998) reported a separation factor of 25.5 at a CO<sub>2</sub> permeance of  $6.6 \times 10^{-7}$  mol/(m<sup>2</sup>·s·Pa). The MFI membranes synthesized by Guo et al. (Guo et al., 2006) show CO<sub>2</sub>/N<sub>2</sub> separation of about  $65 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$  at room temperature with equimolar CO<sub>2</sub>/N<sub>2</sub> mixtures under Wicke–Lallenbach conditions. In addition, the CO<sub>2</sub> molecules were seen to pass at the rate of  $0.7 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$  through the membrane. These factors were better than the pre-recorded values for silicate-1, BaZSM-5, B-NaZSM-5, and BHZSM-5. The isomorphous substitution of Si(IV) in place of B(III) results in materials with comparable CO<sub>2</sub> permeation, but with better stability. Sublet et al. (Sublet et al., 2012) reported the post-combustion separation of CO<sub>2</sub>/N<sub>2</sub> using  $\alpha$ -supported MFI zeolite membrane. At higher water concentrations, MFI membranes show static reduction of gas permeance of 40% for water concentration. The insertion of water improves CO<sub>2</sub>/N<sub>2</sub> separation due to the development of (bi)carbonate stable intermediates. In addition, the MFI membranes like HZSM-5 (Guo et al., 2006) and NaZSM-5 (Shin et al., 2005) show a good perspective for CO<sub>2</sub>/N<sub>2</sub> separation in the presence of water. These two membranes compete with the best reported NaY membranes in terms of CO<sub>2</sub>/N<sub>2</sub> separation, CO<sub>2</sub> permeances, and permeabilities. Shin et al. (Shin et al., 2005) proposed an increased membrane selectivity of ZSM-5 for the separation of an equimolar CO<sub>2</sub>/N<sub>2</sub> mixture saturated with moisture. At room temperature, the separation factor for the dry mixture was 50, while it was 60 for the wet mixture. Due to the higher ration of Si/Al in ZSM-5, these membranes can be a potential candidate for future membranes in CO<sub>2</sub> separation technologies.

## 4.4 Carbon molecular sieve membranes for post-combustion carbon capture

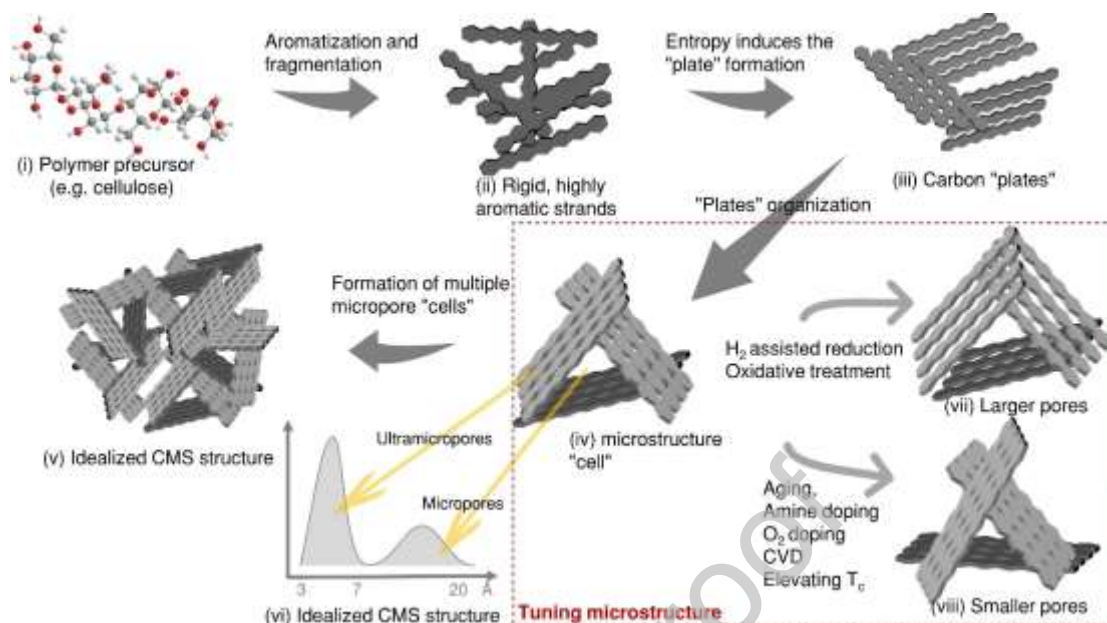
### 4.4.1 Introduction for carbon molecular sieve membranes

The rapid increase of greenhouse gas emissions causes global climate change (Hoegh-Guldberg et al., 2019; Malhi et al., 2021), and CO<sub>2</sub> capture, utilization and storage (CCUS) is becoming one of the most attractive solutions for the reduction of CO<sub>2</sub> emissions (Figuerola, José D. et al., 2008; Hassanlouei et al., 2013). Different technologies such as chemical absorption, adsorption, membranes, and cryogenic distillation, have been developed for CO<sub>2</sub> capture (Araújo et al., 2022; Shah et al., 2020). Among them, membrane-based gas separation technology is one of the most promising strategies due to its high adaptability and reliability, energy-saving, and being environmentally friendly (Agaton and Karl, 2018; Araújo et al., 2022; He et al., 2022; Kunalan and Palanivelu, 2022; Rodrigues et al., 2019). Various membrane materials have been investigated for CO<sub>2</sub> capture (Kunalan and Palanivelu, 2022; Lei et al., 2020; Liu, M. et al., 2022; Shah et al., 2020), such as polymer membranes (Meixia Shan 1 and Freek Kapteijn 1 2018; Zhu, L. et al., 2018), mixed matrix membranes (MMMs) (Guo, F. et al., 2022; Voon et al., 2022; Zhang, Q. et al., 2021a), fixed-site-carrier (FSC) membranes (Hägg et al., 2017; He et al., 2017b), two-dimensional (2D) nanosheets (Achari et al., 2016; Cacho-Bailo et al., 2017; Ding et al., 2018; Ying et al., 2018; Yu et al., 2011) and carbon molecular sieve membranes (CMSMs) (Araujo et al., 2020; Cao, Y. et al., 2019; Karousos et al., 2020; Lei et al., 2021; Sazali et al., 2021; Tseng et al., 2016). Among them, CMSMs are considered the next-generation gas separation membranes due to their high separation performance, and thermal and chemical stability, which shows great potential for pre- and post-combustion carbon capture (Koros and Zhang, 2017; Lei et al., 2020). Importantly, the development of flexible carbon hollow fiber membranes (CHFMs) is expected to produce practical membrane modules with a low cost and a high packing density (Liu, L. et al., 2016). In this section, a systematic review of CMSMs for CO<sub>2</sub> capture or removal related to both material and process performances will be conducted.

### 4.4.2 Carbon membrane structure and gas transport mechanisms

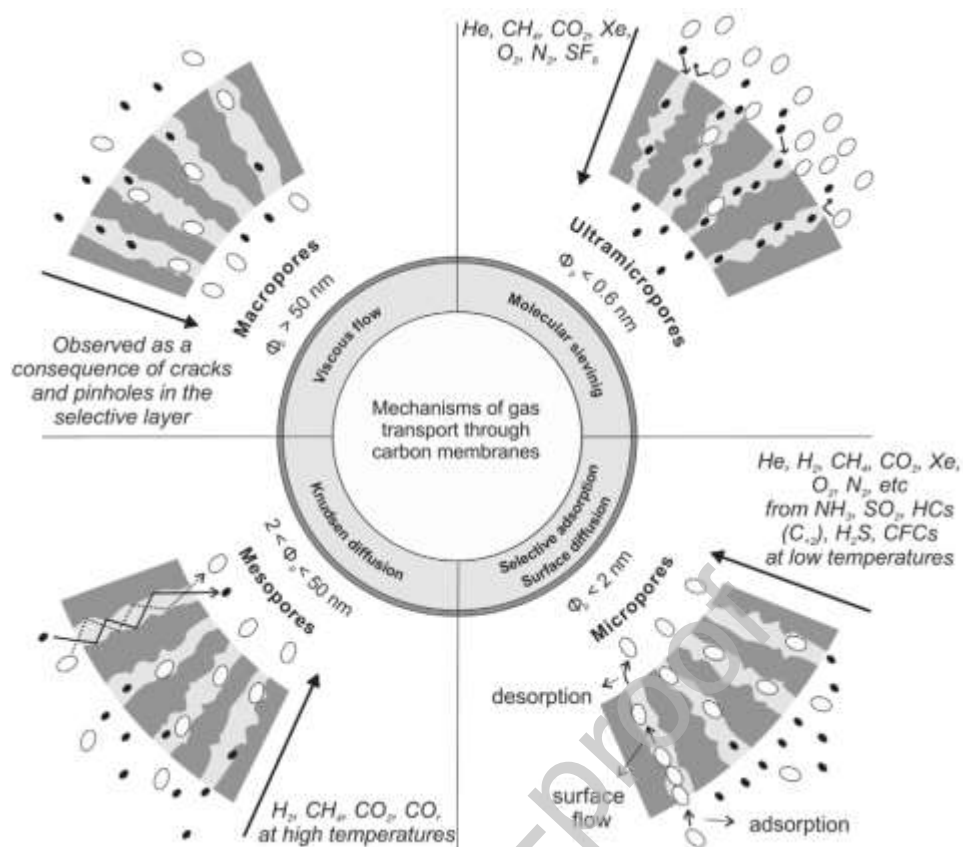
Under inert purge gas or vacuum conditions, CMSMs are prepared by pyrolysis of precursors at high temperatures. During the pyrolysis process, the polymeric precursors are transformed to ordered carbon plates, which usually results in a bimodal structure with ultramicropores (3-7Å) and micropores (7-20Å) (Ma, Y. et al., 2019; Qiu et al., 2019; Rungta et al., 2017; Zhang and Koros, 2017). Fig. 1 illustrates the proposed pyrolysis mechanism from a cellulosic precursor to CMSMs (Lei et al., 2020). The polymeric precursors start aromatization and fragmentation with temperature ramping and afterwards transform into rigidly aromatic carbon strands (**Figure 4.7** (i) & (ii)). Next, the rigid carbon strands align and form carbon “plates” due to higher entropy to the system (Fig. 1(iii)). The final CMSMs usually result in a microstructure with imperfectly packed plates due to the kinetic restrictions (limited time at high

temperature) (**Figure 4.7** (iv)). In the end cooling stage, the micropore “cells” are stacked to form a cellular structure (**Figure 4.7** (v)) in which the ultra-micropores share the “walls” between micropores.



**Figure 4.7.** Illustration of pyrolysis mechanism from a cellulosic precursor to CMSMs (Lei et al., 2020).

There are four different mechanisms related to mass transfer of gas through a porous carbon membrane: Poiseuille flow; Knudsen diffusion; partial condensation/capillary diffusion/selective adsorption and molecular sieving, as it is shown in **Figure 4.8** (Hamm et al., 2017). The dominating mechanism will be dependent on the membrane properties, the permeated gases and the operating conditions such as feed temperature and pressure (Anne Julbe \* 2001), and quite often more than one mechanism will contribute to the gas separation performance together. Carbon membranes with a selective surface flow mechanism (with micropores of  $< 20 \text{ \AA}$ ) may be applied to the separation of heavy hydrocarbons (HHCs) in the petroleum industry, while carbon molecular sieve membranes with ultramicropores ( $3\text{-}7 \text{ \AA}$ ) can potentially be used for the separation of small gas molecules that are alike in size such as  $\text{CO}_2\text{-N}_2$ , and  $\text{CO}_2\text{-O}_2$  (i.e., post-combustion carbon capture) (Kumakiri, 2020).



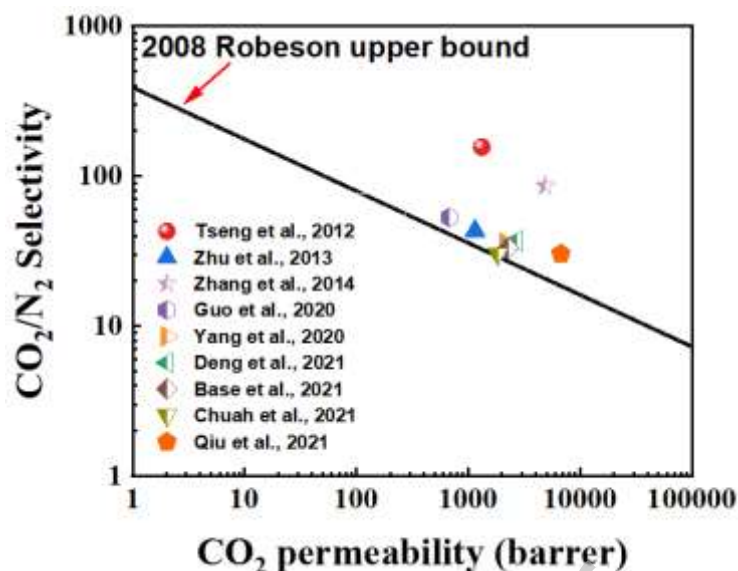
**Figure 4.8** Different mechanisms of gas transport through carbon membranes (Hamm et al., 2017).

#### 4.4.3 Carbon membranes for CO<sub>2</sub>/N<sub>2</sub> separation

Carbon membranes for pre-combustion carbon capture and CO<sub>2</sub> removal from biogas and natural gas have been critically reviewed in the previous work (Lei et al., 2020). Therefore, the main focus in this section is to discuss the status and challenges of applying carbon membranes for post-combustion carbon capture. The low feed pressure (~1 bar), the low CO<sub>2</sub> concentration and similar sizes like CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> in the flue gas are the main challenges for post-combustion CO<sub>2</sub> capture. Development of high performance CMSMs with high CO<sub>2</sub>/N<sub>2</sub> selectivity is of emerging interest in this application. **Figure 4.9** summarizes the gas separation performances of CMSMs for CO<sub>2</sub>/N<sub>2</sub>, which clearly surpass the Robeson upper bound. To improve the separation performance of CMSMs, the pore size and distribution of CMSMs can be finely tuned by the chemical deposition method. Tseng et al. (Tseng and Itta, 2012) selected poly(propylene oxide) (PPO) polymers as the segment-forming agent, and applied the self-deposition method to adjust the pore structure of CMSMs, The modified PPO/polyimide(PI)-derived CMSMs presented CO<sub>2</sub> permeability of 1318.2±37.6 Barrer and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 156.4, respectively. The porous N-doped carbon as an advanced adsorbent has been investigated for CO<sub>2</sub> separation as the polar N-doped sites within the carbonaceous framework provide a strong and selective dipole-quadrupole interaction with CO<sub>2</sub> molecules. Zhu et al. (Zhu et al., 2013) prepared polymeric membranes through superacid-based method using the trimerization of aromatic nitriles with a superacid catalyst (trifluoromethanesulfonic acid, CF<sub>3</sub>SO<sub>3</sub>H), and the obtained precursors were further

used to synthesize the N-doped CMSMs. The final carbon membranes showed a CO<sub>2</sub> permeability of 1149.3 Barrer and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 43.2, respectively. Moreover, the resorcinol–formaldehyde (RF) with high char yield and thermal stability, can be applied as nanoporous carbon membranes (NCMs). Zhang et al. prepared NCMs through pyrolysis of thermosetting RF resin blending with thermally labile F-127 in the presence of a basic catalyst. The RF resin/F-127-based NCMs have CO<sub>2</sub> permeabilities of 4862±350.8 Barrer and CO<sub>2</sub>/N<sub>2</sub> selectivity of 85.9, respectively (Zhang, B. et al., 2014). To enhance gas separation performance of CO<sub>2</sub>/N<sub>2</sub>, the introduction of functional materials to the pore of CMSMs has been proven to be a versatile strategy (Hou, 2016). Ionic liquids (ILs) are promising candidates for CO<sub>2</sub> capture and separation due to their low vapor pressure, high thermal stability, good mechanical stability, non-toxic nature, non-flammable, designability and high CO<sub>2</sub> affinity (Patil et al., 2022; Tome and Marrucho, 2016). Guo et al. prepared the IL/ CMS hybrid membrane spin-coating IL dissolved in ethanol at different concentrations on Matrimid®-derived CMSMs with CO<sub>2</sub> permeability of 675 Barrer and CO<sub>2</sub>/N<sub>2</sub> selectivity of 53, respectively (Guo et al., 2020). Interestingly, the covalent triazine frameworks (CTFs)-derived materials with fluorine functional groups have been proved to significantly enhance the CO<sub>2</sub> sorption properties. Yang et al. reported fluorinated CMS hybrid membrane has CO<sub>2</sub> permeability of 2140 Barrer and CO<sub>2</sub>/N<sub>2</sub> selectivity of 36, respectively (Yang et al., 2020).

Although some previous work reported the evolution mechanism of polyimide-based precursors to carbon membranes, the design and synthesis of novel polyimide precursors are still required to fabricate high-performance carbon membranes for gas separation due to the complicated rearrangement of the pyrolytic aromatic fragments of the decomposed precursors (Hazazi et al., 2019; Ngamou et al., 2019; Ogieglo, W. et al., 2019; Pérez-Francisco et al., 2020). Deng et al. synthesized new binaphthol-6FDA polyimide precursors and pyrolyzed into the CMS membranes. The binaphthol-6FDA polyimide-derived CMSMs have CO<sub>2</sub> permeability of 2674 Barrer and CO<sub>2</sub>/N<sub>2</sub> selectivity of 37.1, respectively (Deng, G. et al., 2021). It is well-known that the gas separation performance of CMSMs is highly dependent on the intrinsic property of polymer precursors, so the pyrolysis of polymeric precursors comprising thermally-stable microporous fillers has been promising as a sample approach to improve gas separation performance of CMSMs (Li, W. et al., 2019). Chuah et al. fabricated mixed matrix carbon membranes (MMCMs) including SAPO-34 zeolites have CO<sub>2</sub> permeabilities of 2248±4 Barrer and CO<sub>2</sub>/N<sub>2</sub> selectivity of 33.2 ± 0.7, respectively (Chuah, Chong Yang et al., 2021). Moreover, the MMCMs with activated carbon (YP-50F) presented a high CO<sub>2</sub> permeability of 1833 Barrer and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 30.4, respectively (Chuah, C. Y. et al., 2021). Yang et al. prepared polyimide/sepiolite derived MMCMs have CO<sub>2</sub> permeability of 6711.5 Barrer and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 30.4, respectively (Yang, C. et al., 2021). Overall, it can be found that CMS membranes have been proven attractive for post-combustion carbon capture due to their rigid, typical tunable and bimodal pore structure, which could effectively transport CO<sub>2</sub> molecules.



**Figure 4.9** The CO<sub>2</sub>/N<sub>2</sub> separation performances of different CMSMs.

#### 4.4.4 Techno-economic feasibility of CMSMs for post-combustion carbon capture

The current and fairly established technology (such as chemical absorption) allows for effective CO<sub>2</sub> capture from flue gas with a low concentration at low temperatures, but it is expensive owing to the large size of columns and equipment installation. Additionally, thermal efficiency is also reduced. Utilizing membrane separation units could be a different approach. A carbon membrane separation unit was designed to be integrated into typical post-combustion power plants, as it was previously described (He et al., 2009). To ensure a significant reduction in emissions and to reduce the future costs for compression and transport, the criteria of purity and recovery of CO<sub>2</sub> from flue gas are highly required, generally higher than 90 % (Yang et al., 2009). The CO<sub>2</sub> content in flue gas is low (10–20 %), rendering it difficult to accomplish through a single-stage membrane technique. Consequently, implementing a multi-stage membrane arrangement becomes necessary, and two-stage membrane systems have been reported to be the effective configuration to achieve the separation target (Xu, J. et al., 2019; Yang et al., 2009). For the purpose of creating a driving force for CO<sub>2</sub> diffusion, several studies on the techno-economic feasibility analysis of a process by combining the feed compression with the vacuum suction on the permeate side (Merkel, Tim C. et al., 2010; Yang et al., 2009). The operating conditions (e.g., feed temperature, feed and permeate pressures), membrane properties (CO<sub>2</sub> permeance, selectivity, membrane lifetime), and corresponding costs were typically reported along with representative parameters such as specific area [m<sup>2</sup>/(kgCO<sub>2</sub>/s)], specific energy [MJ/kgCO<sub>2</sub>], and CO<sub>2</sub> capture cost [\$/tonCO<sub>2</sub>] (energy cost and capital cost for membranes, pumps, compressors, etc.).

Favre et al. outlined the major difficulties in applying membranes for post-combustion capture and indicated the ranges of operating conditions within which the membrane process can compete with

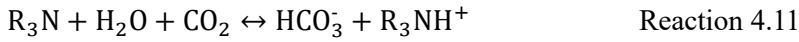
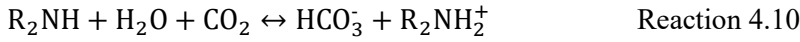
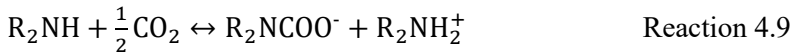
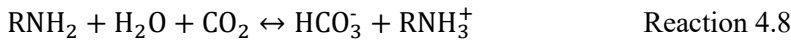
cutting-edge absorption technology (Favre, 2007). Due to the significant energy consumption of the compression step, it has been claimed that the membrane process with feed compression can only be competitive when the inlet CO<sub>2</sub> content is more than 20 %. Benchmarking was performed by Roussanaly et al. to determine the required CO<sub>2</sub> permeance and membrane selectivity to ensure the membrane process is competitive with absorption technology (Roussanaly et al., 2016). It was revealed that simple membrane process configurations and more sophisticated configurations, including recycling or sweep could be economically competitive with the absorption technology. He et al. explored the techno-economic feasibility of hollow fiber carbon membranes which is based on the carbonization of deacetylated cellulose acetate (He and Hägg, 2011). It was reported that the CO<sub>2</sub> recovery of 67 % and the CO<sub>2</sub> purity of 88 % could be achieved with a total required membrane area of  $1.62 \times 10^7$  m<sup>2</sup> and a total compressor duty of  $1.37 \times 10^5$  kW [1]. In addition, He et al. also contrasted the feasibility of single-stage membrane process and two-stage cascade membrane process. It was indicated that the single stage membrane process cannot achieve high CO<sub>2</sub> purity and CO<sub>2</sub> recovery simultaneously employing such hollow fiber carbon membrane whereas the two-stage cascade membrane technology can be economically competitive with the chemical absorption method (He and Hägg, 2011).

#### 4.4.5. Future perspectives

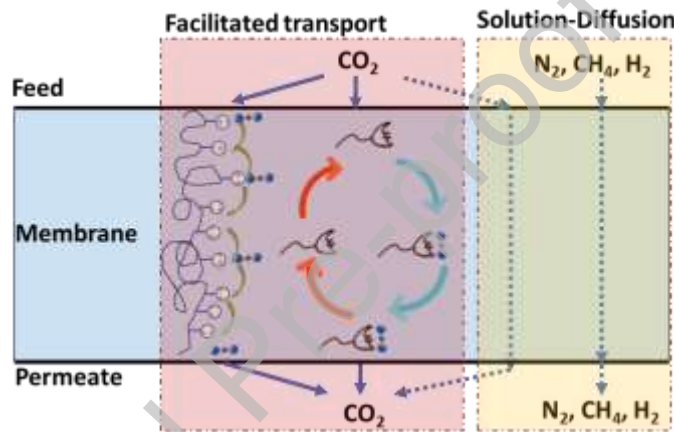
Although carbon membrane technology is considered one of the energy-efficient processes for CO<sub>2</sub> separation, the application of CMSMs for post-combustion CO<sub>2</sub> capture is still challenging: (1) the relatively low CO<sub>2</sub> permeance compared to polymeric membranes, which requires a large carbon membrane area and thus increases the membrane unit cost significantly; (2) many CMSMs are sensitive to water vapor existing in flue gas, which may reduce the membrane durability and lifetime; (3) difficult in the flat-sheet carbon membrane upscaling and production cost as well as the brittleness of carbon structure. To address these challenges, the development of hydrophilic, ultra-thin supported carbon membranes or flexible asymmetric CHFMs should be pursued in future work. It should be noted the advantage of its strong mechanical strength may direct the operation of carbon membranes for CO<sub>2</sub> capture at a relatively higher feed pressure, but the optimal operating conditions should be identified based on cost minimization by balancing capital expenditure and operation cost.

### 4.5 Facilitated transport membranes

In facilitated transport (FT) membranes, the transport of CO<sub>2</sub> molecules can be enhanced through specific reversible reactions (Li, Y. et al., 2015). Many studies have shown that the transport of CO<sub>2</sub> occurs in the form of carbamate and bicarbonate in FT membranes (Caplow, M., 1968). In most cases, water is required in FT processes (Chiwaye et al., 2021). The reaction equations for primary amine, secondary amine, and tertiary amine with CO<sub>2</sub> are given in Reaction 4.7-4.11 below.



The scheme of FT processes is illustrated in **Figure 4.10**. In comparison to conventional polymeric membranes, where gas is transported through the membrane via a solution-diffusion model, gas transport in FT membranes involves a reversible reaction, which is depicted in eq.4.4 (Kim, T.-J. et al., 2013).

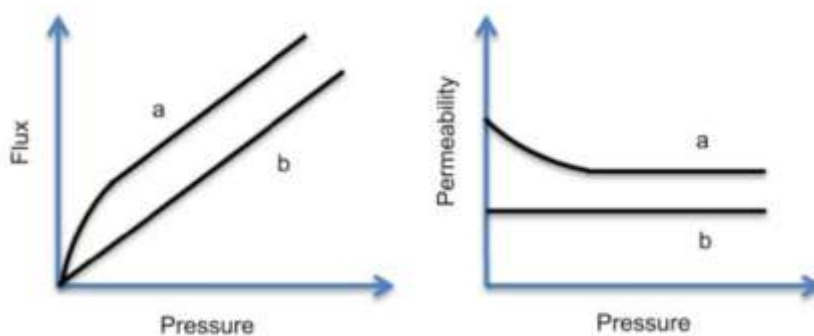


**Figure 4.10.** Gas transport through the facilitated transport membrane

$$J_A = \frac{D_A}{l} (c_{A,0} - c_{A,l}) + \frac{D_{A,B}}{l} (c_{AB,0} - c_{AB,l}) \quad \text{eq. 4.4}$$

Compared to solution-diffusion based membranes, FT membranes can achieve much higher CO<sub>2</sub> fluxes at relatively low CO<sub>2</sub> concentration conditions by utilizing reversible reactions between CO<sub>2</sub> and carriers, as shown in **Figure 4.11 (a)**. This property makes FT membranes ideal for flue gas CO<sub>2</sub> capture, as flue gas is usually present in large amounts and at low pressures (Chao et al., 2021; Kárászová et al., 2020). However, the phenomenon of ‘carrier saturation’ (Han and Ho, 2022; Li, Y. et al., 2015) causes a gradual reduction in CO<sub>2</sub> permeance as the CO<sub>2</sub> partial pressure increases in the feed. As a result, the CO<sub>2</sub> separation performance of FT membranes is sensitive to the CO<sub>2</sub> partial pressure.





**Figure 4.11.** FT membrane presents higher CO<sub>2</sub> flux at lower CO<sub>2</sub> partial pressure conditions but the CO<sub>2</sub> permeance gradually reduces due to carrier saturation.

#### 4.5.1 Mobile carrier

Mobile carriers have been intensively studied for CO<sub>2</sub> separation purposes, with representative examples including alkaline solutions (e.g., KOH) (Ansaloni et al., 2015), amino acid salts (e.g., GlyK, ProK) (Dai et al., 2019a; Dai et al., 2019b), small amine molecules (e.g., MEA, DEA) (Teramoto et al., 1996), and ionic liquids (ILs) (Klemm et al., 2020) (**Figure 4.12**). In the early stage of FT membrane research, these mobile carriers were incorporated into supported liquid membranes (SLMs) (Bao and Trachtenberg, 2006; Peng et al., 2022; Teramoto et al., 1997), which exhibited rather high intrinsic CO<sub>2</sub> separation performance for CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, and CO<sub>2</sub>/H<sub>2</sub> separations. However, the stability of SLMs is always a serious issue, especially under high operational pressure conditions. Additionally, reducing the thickness of an SLM to ensure a feasible CO<sub>2</sub> flux across the membrane is difficult. As a result, mobile carrier-based SLMs are less competitive in practical CO<sub>2</sub> separation applications.

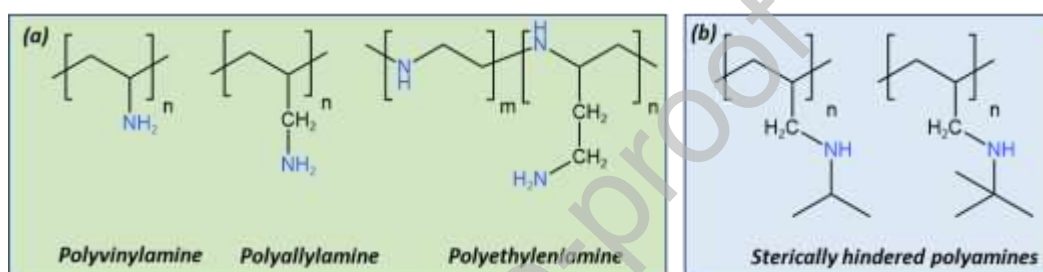
On the other hand, mobile carriers are also widely used in TFC membranes for CO<sub>2</sub> separation applications (Tong, Z. and Ho, W.S.W., 2017a). Exceptional separation performances have been obtained for many of these materials. However, similar to SLMs, long-term stability is always an issue, as the small molecules may easily leach out of the membrane, especially if there is water vapor condensation on the surface of the membranes.



**Figure 4.12.** Typical mobile carrier used in FT membranes, reproduced from (Zhang, Z. et al., 2021)

#### 4.5.2 Fixed site carrier

Fixed site carrier (FSC) membranes are a group of polymers with functional groups that can undergo reversible reactions with CO<sub>2</sub> to facilitate its transport (Deng et al., 2009; He et al., 2017a). Normally these materials contain different kinds of amine groups, including primary amine, secondary amine, and tertiary amine (**Figure 4.13**). In some cases, -COOH group can also function as an effective carrier for CO<sub>2</sub> transport (Zhao et al., 2006). Compared to mobile carrier FT membranes, FSC membranes typically exhibit better stability. On the other hand, since many FSC membranes contain a large amount of amine groups, they can be rather brittle in the dry state due to strong hydrogen bonding, and their mechanical strength is not good. Therefore, in many cases, a second polymer is blended with the FSC polymer to improve its mechanical strength and sometimes to promote water uptake as well (Han, Yang and Ho, W. S. Winston, 2020; Han and Ho, 2021a; Han et al., 2018).



**Figure 4.13.** (a) Typical fixed site carrier materials used in FT membranes, (b) sterically hindered membranes exhibited higher CO<sub>2</sub> separation performances, reproduced from (Han, Yang and Ho, W. S. Winston, 2020).

**Figure 4.13** presents a few representative FSC polymers. In principle, for primary and secondary amines, with the help of water vapor, one mole of amine could react with more than one mole of CO<sub>2</sub>, thus making it a very promising option for CO<sub>2</sub> separation. However, it has been found that tertiary amines only react with one mole of CO<sub>2</sub>, even with one mole of tertiary amine. In some cases, if the amine is sterically hindered, it can be more effective than primary and secondary amines (Tong, Z. and Ho, W.S.W., 2017b). There have been several reviews discussing this topic (He, 2021; Rafiq et al., 2016; Tong, Z. and Ho, W.S.W., 2017a).

#### 4.5.3 Hybrid membranes

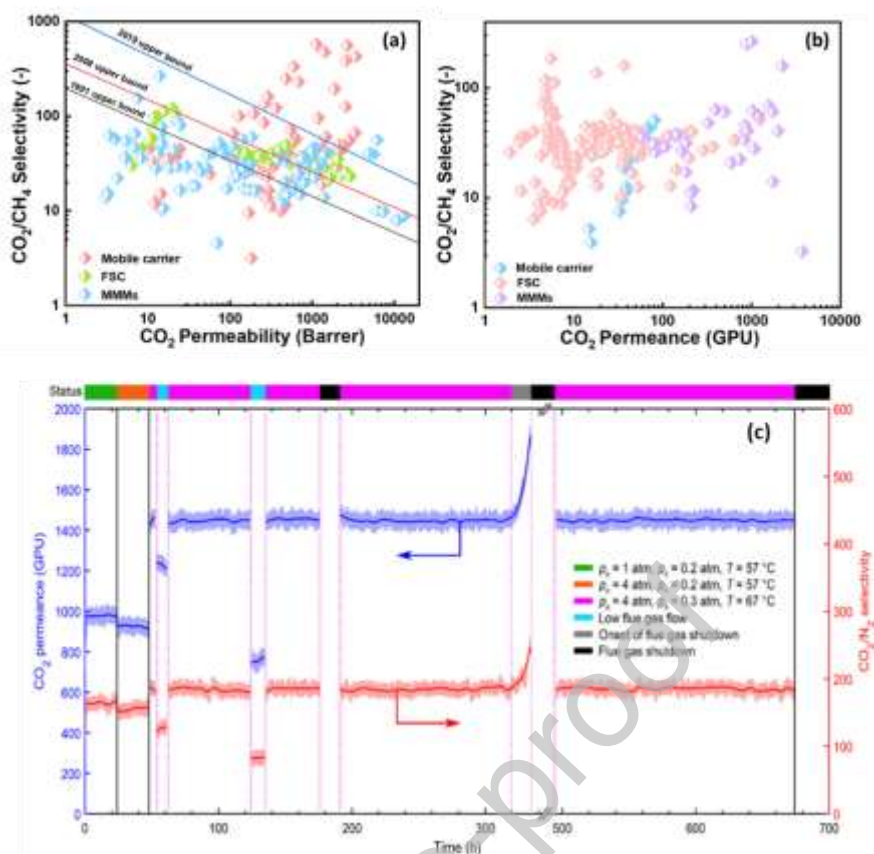
Compared to the pure mobile carrier or fixed site FT membranes, in many cases, both mobile carrier and fixed site carrier can be employed in FT membranes. The polymeric phase works as a hosting matrix for mobile carriers (Han and Ho, 2021b). In addition, to improve the mechanical strength of the membrane, the hosting matrix is sometimes crosslinked (Deng and Hägg, 2015; Han et al., 2019b). Another category of facilitated transport hybrid membranes includes those membranes containing functionalized nanoadditives (Nithin Mithra and Ahankari, 2022). Compared to conventional mixed matrix membranes (MMMs), which are fabricated by blending nanoadditives and polymer phases

together, facilitated transport membranes contain nanoparticles with amine-functionalized groups. Representative nanofillers include MOFs (Kim, Jiyoung et al., 2016; Wu et al., 2014), GO (Dong et al., 2016), and CNT (Ansaloni et al., 2015; Saeed et al., 2017). Additionally, hybrid membranes containing three different components are also being studied (Guo, X. et al., 2019), which typically consist of a liquid phase, a polymer phase, and a solid phase. The liquid phase works as both facilitated transport carriers and fillers for the non-selective voids between the polymer phase and solid additives (Kalantari et al., 2020).

Many facilitated transport membranes are made using thick films with a thickness in the range of dozens of micrometers, while others have been fabricated as thin-film-composite (TFC) membranes with feasible CO<sub>2</sub> permeances. Dip-coating is the most commonly used method to fabricate FT TFC membranes, with both flat-sheet and hollow fiber geometries (Dai et al., 2016). Other methods, such as interfacial polymerization (Zhao et al., 2006), knife casting (Pate et al., 2022), and spin-coating (Zhang, H. et al., 2018) have also been reported. The thickness of TFC membranes varies a lot. In principle, the thickness of the selective layer should be as thin as possible to ensure a high CO<sub>2</sub> flux across the membrane. Interestingly, for facilitated transport membranes, as there is a need for a proper carrier in the selective layer, it is sometimes found that membranes with thinner selective layers present lower CO<sub>2</sub> permeances (Kim et al., 2004), which is different from conventional membranes based on solution-diffusion model.

The CO<sub>2</sub>/CH<sub>4</sub> separation performances of FT membranes developed in the past few years are listed in **Figure 4.14**. As can be seen from the figure, many FT membranes showed very promising CO<sub>2</sub> separation performances, which are far above the Upper Bound. Meanwhile, for FT TFC membranes, both high CO<sub>2</sub> permeance and high CO<sub>2</sub>/CH<sub>4</sub> selectivity have also been documented, indicating that FT membranes are very competitive materials in CO<sub>2</sub> capture.

The long-term stability of the FT membrane has also been investigated. Unlike conventional glassy polymeric membranes, which suffer from physical aging problems (Brunetti et al., 2017; Merrick et al., 2020; Xu et al., 2014), there are few reports about physical aging of FT membranes. In addition, though the presence of impurities in the feed (e.g., SO<sub>x</sub> and NO<sub>x</sub>) may negatively affect the CO<sub>2</sub> separation performances of FT membranes, as long as the impurities are removed from the feed, the CO<sub>2</sub> separation performances will gradually recover to the original value (Liao et al., 2014). Ho et.al. also investigated the separation performances of FT membranes under industrial conditions and concluded that the FT membrane demonstrated excellent stability over the testing period (Han et al., 2019a).



**Figure 4.14.** Comparison of CO<sub>2</sub> separation performances of the thick film (a) and TFC FT membranes (b). Data obtained from ref (Aframehr et al., 2022; Alkhouzaam et al., 2016; Chen, X.Y. et al., 2012; Guo et al., 2015; Hanioka et al., 2008; Iarikov et al., 2011; Isanejad and Mohammadi, 2018; Li et al., 2010; Li, X. et al., 2020; Liu, B. et al., 2021; Liu et al., 2014; Mashhadikhan et al., 2020; Mubashir et al., 2018; Murugiah et al., 2018; Park et al., 2009; Peng et al., 2017; Pu et al., 2022; Qu et al., 2020; Regmi et al., 2022; Sasikumar et al., 2021; Shahkaramipour et al., 2014; Shamair et al., 2020; Swati, Imran Khan et al., 2021; Tu et al., 2021a; Tu et al., 2021b; Wang, C. et al., 2020; Wang, Y. et al., 2021; Wu et al., 2014; Yu et al., 2020; Zhang, B. et al., 2021; Zhang, H. et al., 2018; Zhang, X.-M. et al., 2017b; Zhang, Yahui et al., 2022). (c) long-term stability performances of FT membranes tested under industrial conditions. Reproduced from ref (Han et al., 2019a)

Overall, FT membranes are promising CO<sub>2</sub> capture membrane materials showing exceptionally high CO<sub>2</sub> separation performances. Future research can be carried out to develop more efficient carriers for CO<sub>2</sub> transport, which could work under high CO<sub>2</sub> partial conditions. On the other hand, developing novel FT membranes with good RH variation tolerance can also be useful for practical CO<sub>2</sub> capture applications.

## 5. Other CO<sub>2</sub> capture technologies

### 5.1 Oxy-fuel combustion

#### 5.1.1 Oxygen production technologies (OPTs)

This section aims to analyse oxygen production Technologies (OPTs) that are most widely utilized for oxygen production. Figure 5.1 shows the technologies that are discussed in this work and divided into conventional OPTs: Cryogenic Distillation and Pressure Swing Adsorption, and novel OPTs: Membranes, Chemical Looping Air Separation and electrochemical water splitting technologies.

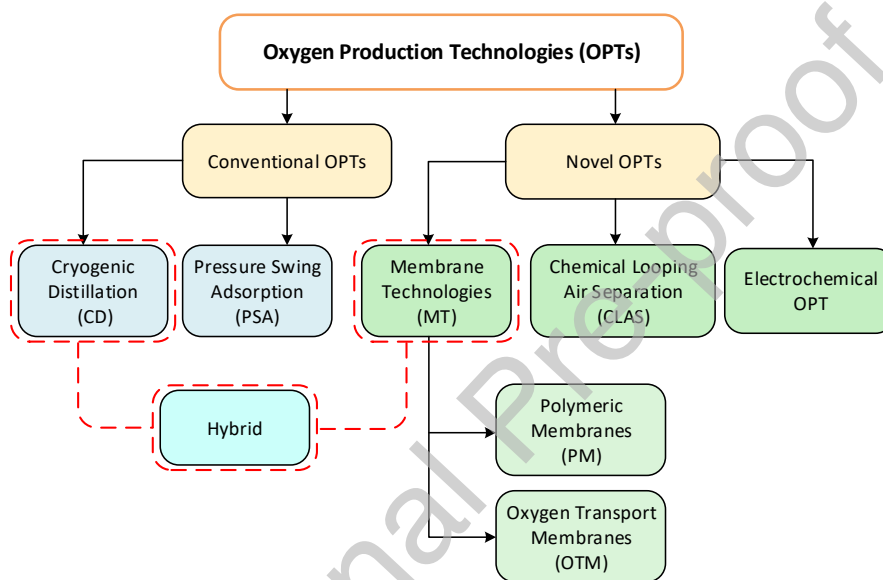


Figure 5.1 Main oxygen production technologies for oxyfuel combustion process

##### 5.1.1.1 Cryogenic distillation

The cryogenic air separation (ASU) is a traditional process for producing large quantities of oxygen, nitrogen, and argon as gaseous or liquid. The technology is considered one of the most developed (Wu et al., 2018) and feasible methods for high-volume oxygen production that is required for the oxyfuel combustion process (Yadav and Mondal, 2022). The idea behind the technology is to use fractional distillation at low pressure and temperature to separate oxygen (with a purity of 99.5%) from air elements based on their different boiling temperatures. The most important design parameters of the distillation column are the number of stages, feed stage, and reflux ratio. These parameters are selected based on distillation requirements. Table 5.1 shows the main advantages and disadvantages of the cryogenic air separation method. One added benefit is that cryogenic air separation is specifically

suitable for oxyfuel technology due to the high O<sub>2</sub> volume production. Oxy-combustion requires high O<sub>2</sub> production capacity; for example, a 500 MWe coal-fired oxy-combustion power plant requires 9000 - 10,000 tO<sub>2</sub>/d (Chorowski and Gizicki, 2015; Higginbotham et al., 2011). On the other hand, one of the main drawbacks of the cryogenic air separation unit is high energy intensity, as mentioned earlier. The energy demand for the system oxygen production is about 240 kWh/tO<sub>2</sub> resulting in an overall efficiency drop of a power plant of around 8–10% (Davison, 2007). CD ASU at lower oxygen product purities, the separation of oxygen and nitrogen is only required, which is relatively easier than the separation of oxygen and argon. Figure 5.2 illustrates that the rapid decrease in separation energy required takes place as the product oxygen purity is decreased from 99.5% to 97.5%, corresponding to the change from oxygen–argon separation to an oxygen–nitrogen separation and the switch to an improved low purity oxygen process (Shash).

Cryogenic technology has greatly contributed to scientific research, specifically for oxyfuel combustion (Scaccabarozzi et al., 2016; Xiong et al., 2011, 2012; Ziółkowski et al., 2013). Beysel G. found that the energy consumption to produce O<sub>2</sub> with a purity of 95% instead of 99%, can reduce the energy consumption from 245 to 175 kWh/ton (Beysel). Tranier J. et al. reported that if the oxygen purity up to 95% is acceptable, then the auxiliary power consumption of oxygen production can be reduced from 350 to 200 kWh/ton of oxygen (Tranier et al., 2011). R. Šulc (Šulc and Ditl, 2021) obtained a relation between energy consumption per ton of oxygen and cryogenic plant capacity and reported that the specific energy consumption per ton of oxygen remains constant up to a value of 200 kWh/t of oxygen. Overall, the power consumption of the cryogenic air separation unit to produce O<sub>2</sub> of 95% purity varies between 184 and 260 kWh/tO<sub>2</sub> (Chorowski and Gizicki, 2015; Skorek-Osikowska et al., 2015; Ströhle et al., 2009).

Despite the widespread of cryogenic air separation units in industrial use and their major benefits, the high energy demands of cryogenic distillation commonly contribute to over 50% of plant operating costs reported by G. Li (Li and Bai, 2012a). And S. García-Luna reported that cryogenic distillation is responsible for 54.42% of the total power consumption of plant net electric power of 242.24 MWe to provide the required amount of oxygen with 95% purity (García-Luna et al., 2022). However, R. López, based on techno-economic analysis, found that the use of cryogenic ASU makes oxy-coal fired plants unattractive for inversion due to its high total equipment plant cost (López et al., 2016).

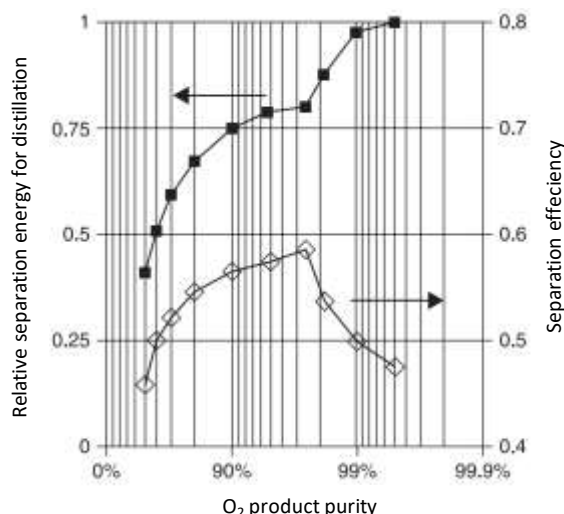


Figure 5.2 Effect of oxygen purity on ASU separation energy (Prosser and Shah, 2011)

Table 5.1 Main advantages and disadvantages of CD (Agrawal and Herron, 2000; Cao et al., 2016; Chen and Yu, 2021; Smith and Klosek, 2001; Zhu, Y. et al., 2006)

Advantages	Disadvantages
<b>Mature and reliable technology suitable for large-scale air separation with high O<sub>2</sub> volume production</b>	The air compression and fractional distillation of its constituents are very energy-intensive, accounting for around 85% of the total energy consumption in the ASU (Zhu, Y. et al., 2006)
<b>Cryogenic air separation units produce oxygen with a purity of 99.5% by volume at an oxygen recovery rate of 97.85% (Agrawal and Herron, 2000)</b>	The technique results in a 3–4% energy penalty and the capital investment for the CAS technique contributes to around 14% of the overall oxy-fuel plant cost (Cao et al., 2016)
<b>Cryogenic technology can also produce high-purity nitrogen as a useful byproduct stream at a relatively low incremental cost (Smith and Klosek, 2001)</b>	Inappropriate for processes requiring fast startup and shutdowns
<b>Established technology</b>	large units with a large physical footprint
	Not profitable for processes that consume small amounts of oxygen (Chen and Yu, 2021)
	Requires moisture pre-removal

### 5.1.1.2 Pressure swing adsorption (PSA)

Pressure swing adsorption (PSA) is a separation method that is much newer as compared to cryogenic ASU. The first PSA technology for oxygen enrichment using nitrogen-selective zeolite was designed by Skarstrom (Skarstrom and Attorney, 1958). PSA devices take atmospheric air into a pressurized tank, a sorbent that is filled inside the tank. Zeolites are typically used and can selectively adsorb nitrogen

while allowing oxygen gas to pass depending on the chosen sorbent dipole that has been created under high pressure (Ruthven and Farooq, 1990). After a certain volume of air has been separated, the adsorption sorbent will become saturated and eventually require regeneration. The adsorbent is regenerated by blowdown and a low-pressure purge using a part of the oxygen that was produced. The PSA has found use in medium and small-scale productions including industrial and health care. The performance of the adsorption system depends highly on the properties of adsorbents including: sorbent selectivity, adsorption capacities, sorption and desorption kinetics, and regeneration method (Yang et al., 2002).

One of the main drawbacks of PSA is the low oxygen purity, as shown in Figure 5.3. Whereas PSA devices are best suited for processes that do not require extremely high purities of oxygen. Since the output of oxygen is largely controlled by the bed size, costs will rise drastically when higher volumes of oxygen are required. In addition, the installation of multiple volume PSA plants is generally required for higher capacities, as shown in Figure 5.3. However, due to economies of scale, there is a practical limit above which cryogenic supply becomes more economically attractive.

Another disadvantage of this method is that it has limited adsorbent capacity for large-scale applications (Prosser and Shah, 2011). The rest main advantages and disadvantages of PSA ASU are summarized in Table 5.2. The reported literature shows that from an energy consumption perspective, the oxygen production for a small unit using the vacuum-pressure-temperature swing adsorption technology is between 500-888 kWh/ton of oxygen (Banaszkiewicz and Chorowski, 2018; Chorowski and Gizicki).

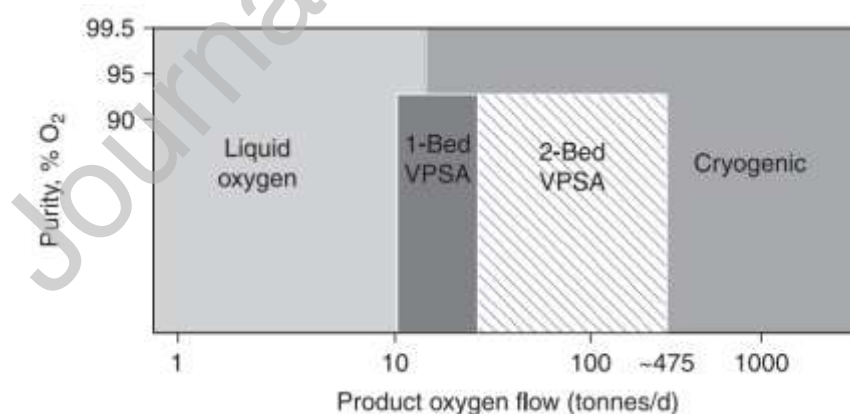


Figure 5.3 PSA Oxygen supply system typical economic ranges (Prosser and Shah, 2011)

Table 5.2 Main advantages and disadvantages of PSA (Banaszkiewicz et al., 2014; Cao et al., 2016; Smith and Klosek, 2001; Zhao et al., 2015)

Advantages	Disadvantages
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Oxygen production, typically approximately 300 ton/day (Banaszkiewicz et al., 2014)	Limited scalability
Quick installation and start-up (minutes)	Not profitable for processes that consume small amounts of oxygen (Chen and Yu, 2021)
Low capital investment	Low Oxygen purity is typically 93–95 vol.% (Smith and Klosek, 2001) Energy penalty for large-scale applications is considerably high (Zhao et al., 2015)
Established technology	Pretreatment is required to maintain the performance of the major adsorbents in the system, which makes process design more complicated
Low waste generation, due to adsorbent recycling	It is not possible to obtain other separation products (nitrogen, argon)

### 5.1.1.3 Membrane technology for oxygen production

Membrane separation is simpler than the cryogenic separation method. One such alternative approach is to use polymeric membranes or ion transport membranes (ITM). The difference between these two techniques is that polymer membranes are used for applications at ambient temperature, while for high-temperature applications, inorganic solid-oxide ceramic materials are mainly used [23]. The differences between the two approaches are shown in Table 5.3. Membrane technology has quick start-up times and operates at near ambient conditions. In contrast, capital costs with membrane systems increase linearly with the output volume desired. However, compared to cryogenic distillation and PSA, they are less complicated since they do not require regenerative steps (Murali et al., 2013).

Table 5.3 Main advantages and disadvantages of MT (Bai et al., 2021b; Hofs et al., 2011; Hosseini et al., 2015; Sidhikku Kandath Valappil et al., 2021)

Membrane separation technology	Advantages	Disadvantages
Polymeric	lowest capital costs among the different membranes (Hosseini et al., 2015)	less competitive in improving oxygen purity in large-scale production compared with other conventional technologies
	Low environmental impact	Low oxygen purity ~ 40 % (Sidhikku Kandath Valappil et al., 2021)
	They can easily be modified and fabricated according to the specified requirements (Hofs et al., 2011)	
	have competitive selectivity and permeability with ceramic and metallic counterparts	

OTM	High chemical, mechanical and thermal stabilities	Very Brittle
	can obtain 99.99% high purity oxygen (Bai et al., 2021b)	More expensive than organic polymer materials (Sidhikku Kandath Valappil et al., 2021)

A general polymeric membrane-based air separation is the feed gas that is passed across the membrane surface under a pressure driving force. The permeate is the gas that penetrates through the membrane and comes out as the low-pressure stream. The retentate is the remaining gas that exits as the high-pressure stream (Wijmans and Baker, 1995). Both permeate and retentate can be used if they meet the desired product purities (Murali et al., 2013). Polymeric membranes have received the most attention due to their advantages: high selectivity between gases, good mechanical properties, and economical processing capability. Polymeric membranes are often preferred to inorganic or ceramic membranes as they have a low environmental impact, are easy to incorporate into large-scale modules, and have the lowest capital costs among the different membranes [35]

Polymeric membranes are characterised by two factors: permeability and selectivity. The higher the permeability, the lower the selectivity, and vice versa (tradeoff) (Freeman, 1999). Consequently, the tradeoff between permeability and selectivity limits the use of polymeric membranes in large-scale applications (Robeson et al., 2015). A purity of 90% with one stage polymer membrane system is not practically achievable currently. A purity of 90% O<sub>2</sub> can be achieved by using two and three stages, depending on the type of membrane that is used (Adhikari et al., 2021). Up-to-date large-scale oxy-fuel combustion process, the feed stream is composed of an oxygen concentration higher than 21% but lesser than 40% in the best cases (Kianfar and Cao, 2021; Sidhikku Kandath Valappil et al., 2021).

Oxygen Transport membrane OTM or ion transport membrane (ITM) is an inorganic oxide ceramic material that is solid at the molecular level and acts as a membrane by allowing oxygen ions to pass through the ceramic crystalline structure. To conduct oxygen, the temperature of the OTM must be maintained above 800 °C and an oxygen partial pressure gradient must be applied across the membrane (Boot-Handford et al., 2014). The significant advantage of this approach is the potential reduction of capital cost and energy demand (Rastogi and Nayak, 2011).

Several studies (Engels et al., 2010; Stadler et al., 2011) have been conducted to reduce the energy consumption of the ASU by investigating the use of high-temperature OTM technology for oxygen production as an alternative to conventional cryogenic distillation methods. Reported literature shows that the OTM approach can be integrated into the front-end of combustion equipment, which results in the effective energy demand reduction to 147 kWh/ton of oxygen (Bai et al., 2021b). Normally, the conventional process has an associated consumption of 201.38 kWh/ton O (Dillon et al., 2005), whereas literature estimated a decrease in power consumption ranging between 85-362 kWh/ton of oxygen (Dillon et al., 2005; Shin and Kang, 2018). While some researchers maintain that OTM technology may

replace cryogenic ASU in the long term because this alternative achieves energy and economic savings of 0.5–9 and 10.5–17.5% (Portillo et al., 2019). Compared to cryogenic ASUs, a small-scale OTM unit consumes 60% less energy and costs 35% less to produce 500 kg O<sub>2</sub>/day (Bernardo et al., 2009).

Integration of membrane and cryogenic technologies has recently attracted attention (Chen and Yu, 2021; Janusz-Szymańska and Dryjańska, 2015), as many researchers tried to evaluate the feasibility of oxy-combustion-based plants utilizing air separation units (ASUs) via cryogenic or membrane technology (Castillo, 2011; Pfaff and Kather, 2009; Skorek-Osikowska et al., 2015). Considering the implementation of a hybrid membrane-cryogenic ASU for further power reduction, Szymanska et al. (Janusz-Szymańska and Dryjańska, 2015) Demonstrated that the cryogenic ASU's reduced power usage for 99.8% oxygen purity was 179 kWh/tO<sub>2</sub>. In addition, Osikow et al. (Skorek-Osikowska et al., 2015) reported that the hybrid membrane cryogenic oxygen separation method has a 1.1% higher net efficiency than the conventional cryogenic ASU.

#### 5.1.1.4 Chemical looping

Chemical Looping Air Separation (CLAS) is based on the oxidative and reductive reactions of two interconnected reactors: air reactor and fuel reactor, which are oxidized to CO<sub>2</sub> and water vapor. The reduced oxygen carrier (typically metal oxide) is then transported to the air reactor where it reacts with the oxygen to reform the original metal oxide for recirculation back to the fluidized reactor (Mattisson, 2013). CLAS has been developed from chemical looping combustion (CLC), which has several challenges including the used material, mechanical stability and oxygen transfer rates, the temperature at which the oxygen carrier is active, reactor capacity, and solid handling (Shah et al., 2015; Wu et al., 2018). Yet, on the other hand, CLAS is considered a promising approach capable of reducing the cost of oxygen production required for oxyfuel combustion technology (Cormos, 2020; Zhou et al., 2015b).

Shah et al. (Shah et al., 2013) studied the integrated chemical looping air separation (ICLAS) modes with oxy-fuel coal-fired power plants. The results show that the specific energy required to produce oxygen in an ICLAS using flue gas (ICLAS[FG]) is 71 kWh/ton (CH integration) and 69 kWh/ton (solar integration) and in an ICLAS using steam (ICLAS[S]) and solar integration of 64 kWh/ton (without NSC) and 43 kWh/ton (with NSC). While in a conventional cryogenic ASU of 415 kWh/ton (99% purity) and 330 kWh/ton (95% purity), in an advanced cryogenic-based ASU (CASU) of 250 kWh/ton (99% purity) and 200 (95% purity). Zhou et al. (Zhou et al., 2015a) reported that by replacing a CASU with an ICLAS unit, the average reduction in the ASU power demand was up to 47% and 76%, respectively, for ICLAS[S] and ICLAS[FG]. Similarly, the average thermal efficiency penalty associated with the CASU, the ICLAS[S] and ICLAS[FG] units was found to be about 9.5%, 7.5%, and 5%, respectively, indicating that the ICLAS[FG] unit is the most energy-efficient option for oxy-fuel plants. The levelized cost of electricity associated with the cryogenic and the ICLAS[S] and ICLAS[FG]

units for the NSW fleet of coal-fired power plants were found to be about 118, 105, and 95 \$/MWh, respectively.

Cai et al. (Cai, R. et al., 2022) developed a one-dimensional packed bed model using perovskite sorbent to investigate the CLAS operation. The power consumption was 115 kWh/ton and 161 kWh/ton at 90% and 95% oxygen purities, respectively, while for a 5-step cycle configuration, the power consumption was 118 kWh/ton at 95%. Cromos (Cormos, 2020) demonstrated that by using manganese-based CLAS, the energy efficiency was higher than the cryogenic process by 2–3.5 net percentage points. However, it was approved that the utilization of the CLAS system in coal and lignite-based oxy-combustion and gasification power plants significantly reduce the capital investment by about 12-18% (Cormos, 2018), and the ICLAS offers between 40-70% lower operational expenses as compared to conventional O<sub>2</sub> production technologies (Zhou, C. et al., 2016).

### 5.1.1.5 Electrochemical water splitting

Electrochemical separation of hydrogen and oxygen using the electrolysis process dissociate water molecule by means of oxidation-reduction reactions taking place in two electrodes: cathode and anode, and separated by a medium (electrolyte) through which the ionic species transfers from one electrode to another (Bailera et al., 2020). Lately, the interest in the promotion of hydrogen energy to decarbonize the current energy system has strongly increased and is based on the Renewable Energy Roadmap (REmap) analysis. Hydrogen share will be increased by 6% of total final energy consumption by 2050 (Gielen et al., 2019). Figure 5.4 shows a schematic structure of the four types of electrolysis available in the market based on the difference in the operating temperature range and the ions exchange. These types include high temperature operation as; (a) solid-oxide steam electrolyzer (SOEC) and low temperature operation as; (b) Alkaline water electrolyzer (AWE), (c) Proton exchange membrane water electrolyzer (PEMWE) and (d) Anion exchange membrane water electrolyzer (AEMWE).

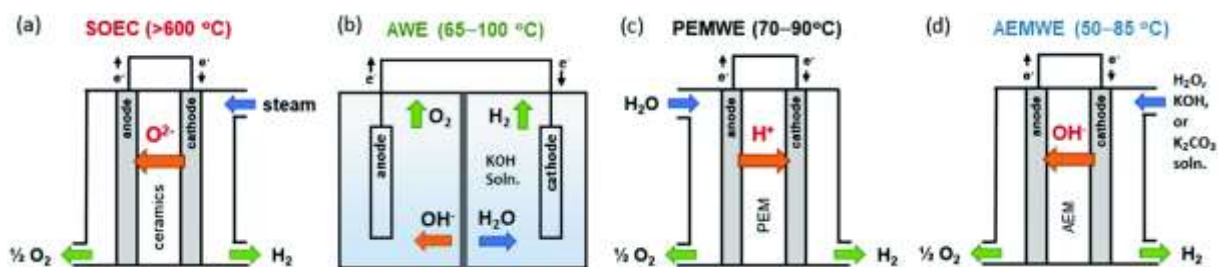


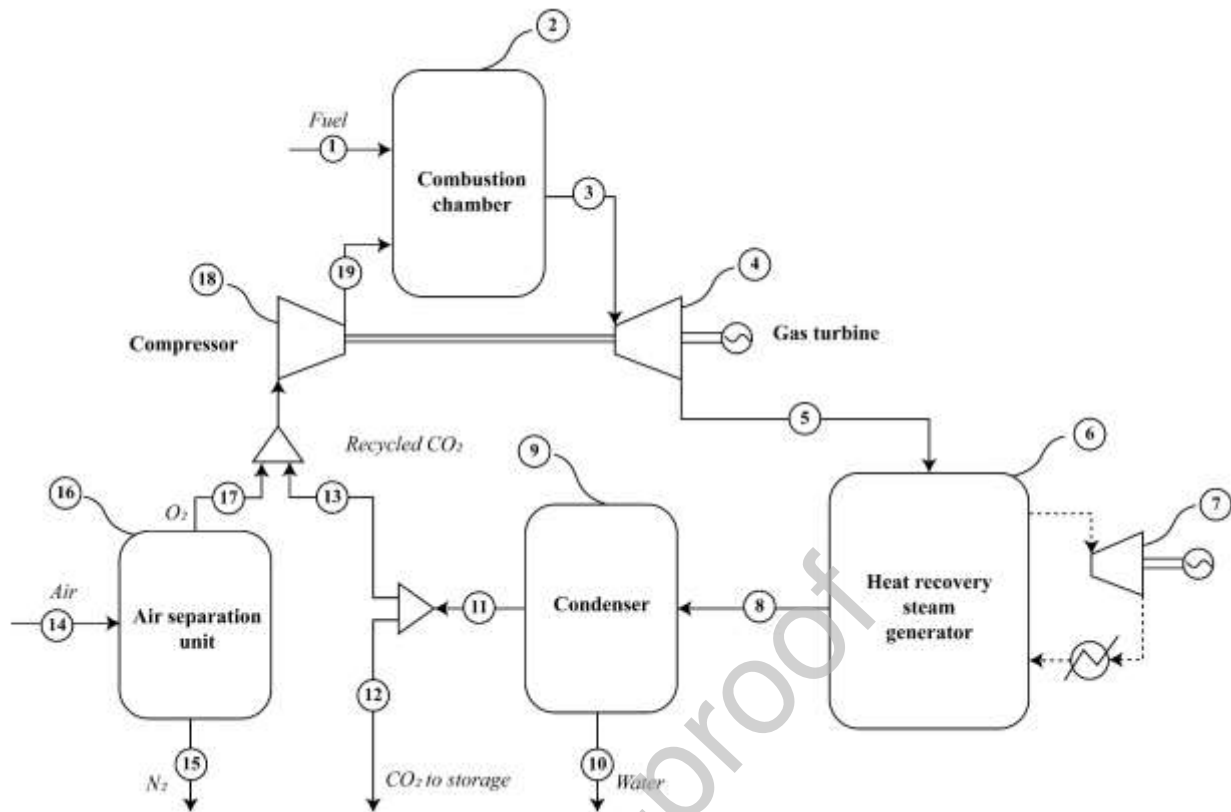
Figure 5.4 Types of electrolysis technologies (Li, D. et al., 2021)

Very limited publications regarding considering the potential of co-production of the energy free oxygen supplied from renewable base electrolysis for oxy-fuel combustion plants. As a reason, the high-power demand of such a process makes this option less competitive with other oxygen production methods. Yet, the efficiency of this process can be improved by using the co-product hydrogen to generate the power required for electrolysis (Iora and Chiesa, 2009).

Bailera et al. reported in different studies on hybrid power-to-gas oxy-combustion power plants where the co-product of oxygen in the water electrolysis for hydrogen production was used for the combustion (Bailera et al., 2015; Bailera et al., 2016; Bailera et al., 2021). The simulation of an electrolyser using Aspen Plus software that consumed 4.3-4.9 kWh/Nm<sup>3</sup> to produce hydrogen with integration with methanation results in an increase in the overall efficiency from 55.9 % to 67.5% since the OPT is avoided in the oxy-coal combustion. Kezibri et al. (Kezibri and Bouallou, 2017) demonstrated a conceptual model of a 200 MW power supply to the electrolysis process that leads to a corresponding 155 MW of Synthetic Natural Gas (SNG) produced in a thermally integrated methanation process with an efficiency of 83.1%. And found that by producing and storing enough amount of SNG and oxygen, an oxy-combustion power plant can be subsequently used to recover up to 480 MW of electric power as well as to produce CO<sub>2</sub> rich gas with an overall efficiency of 51.8%.

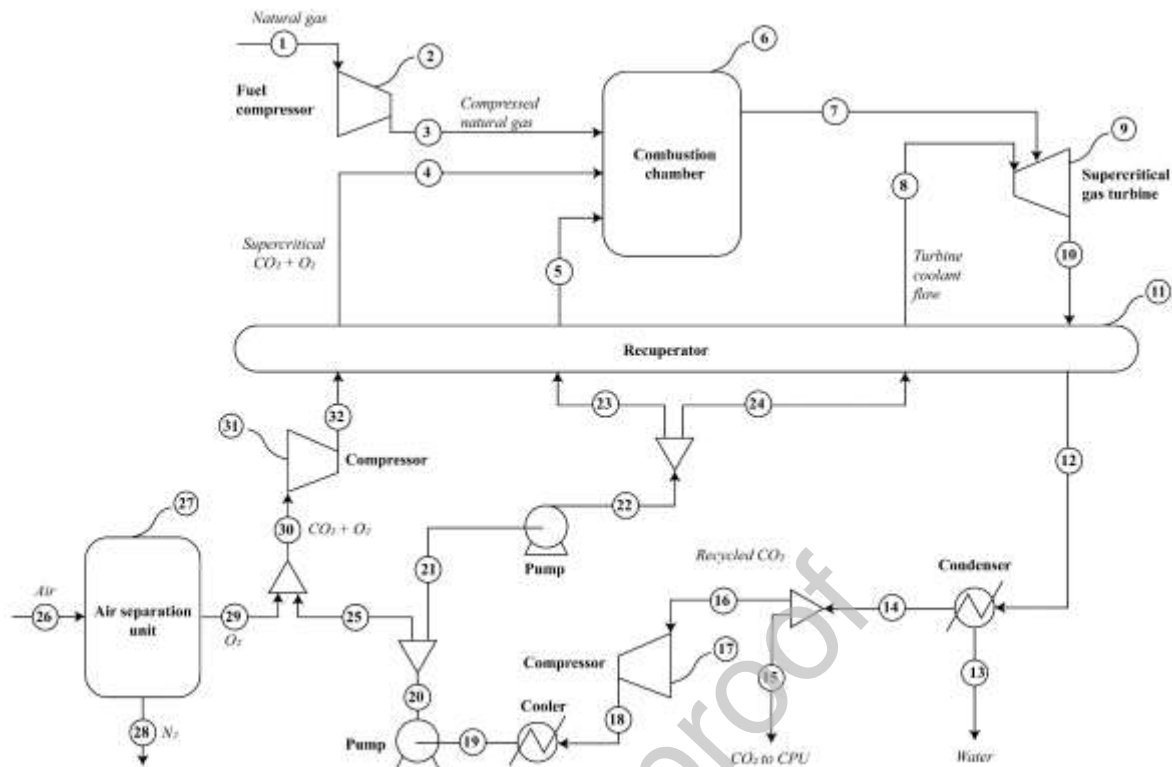
### 5.1.2 Allam Cycle

Oxy fuel combustion utilizes a pure stream of oxygen (generally > 95%) as the oxidant for fuel combustion to achieve a product stream consisting solely of CO<sub>2</sub> and water vapor. The N<sub>2</sub> from air functions as a temperature regulator in conventional combustion; an oxidant stream devoid of N<sub>2</sub> can result in high flame temperatures, and this is controlled by recycling a part of the CO<sub>2</sub> flue gas back to the combustor. The difference in the two diluting gases (CO<sub>2</sub> and N<sub>2</sub>) causes significant differences such as the density of the flue gas, heat capacity, diffusivity of oxygen and radiative properties of the furnace gases (Wall et al., 2009b). A process flow diagram of a general oxy-fuel combustion plant is shown in Figure 5.5.



**Figure 5.5:** Schematic of the general combined cycle oxy-fuel combustion process

The Allam cycle, also known as the NET Power cycle or Allam-Fetvedt cycle, is an oxy-fuel based cycle which uses trans-critical  $\text{CO}_2$  used as the thermal fluid (Allam et al., 2013a). The schematic of the cycle, as proposed by the original inventors, is shown in Figure . The combustion chamber (6) operating at 300 bar is fed with pressurized gaseous fuel (3) and an oxidant mixture (4) of recycled supercritical  $\text{CO}_2$  and pure  $\text{O}_2$  from an Air Separation Unit (ASU) (27). The products (7) consisting of  $\text{CO}_2$  and water vapor are expanded at an approximate pressure ratio of 10 in a gas turbine (9), co-fed with a bypassed coolant flow (8) of recycled supercritical  $\text{CO}_2$  to avoid critical damage to the turbomachinery blades due to the high turbine inlet temperature. The gases (10) exiting the turbine are recuperated in a multi-stream heat exchanger (11) where the extracted heat is transferred to the incoming supercritical streams (32, 23 & 24). The cooled flue gas (12) is sent through a condenser where water (13) is eliminated, and a portion of the remaining pure  $\text{CO}_2$  (15) stream is exported to a  $\text{CO}_2$  processing unit (CPU) for capture, sequestration, or utilization. The rest (~95%) is recycled (16) by compressing, cooling, and pumping to supercritical conditions. A split stream (25) is drawn to be mixed with the pure oxygen (29) from the ASU (27), forming the oxidant feed (30) to the combustion zone. The second split stream (21) is further divided (23 & 24) to form the cooling media (5 & 8) to the combustion chamber and the gas turbine, respectively.



**Figure 5.6:** Schematic of the natural gas fueled Allam power cycle (Allam et al., 2013b)

The cycle developers evaluated the process efficiency (LHV basis) to be 58.9% for natural gas (simulated using pure methane) and 51.4% for coal (Allam et al., 2017). The extremely high efficiency was attributed to the difference in the thermodynamic properties of the working fluid, i.e., supercritical CO<sub>2</sub>, which enables more energy recovery by eliminating losses typically encountered in Rankine cycles due to the phase changes (Allam et al., 2013b). While the cycle was initially developed for natural gas, it was adopted for solid fuel such as coal with some minor changes to the layout, such as the addition of a gasifier and ash filtration system upstream of the combustion chamber and flue gas desulphurization, deNO<sub>x</sub>, and particulate removal units downstream. In addition to the high target efficiencies, the cycle claims a small plant footprint owing to the use of only a single turbine. For a power supply of 25 MW, the sCO<sub>2</sub> turbine is 90% smaller than an equivalent steam turbine (Service, 2017). The Allam cycle offers 100% carbon capture with the resulting CO<sub>2</sub> gas pressurized at pipeline conditions for sequestration, EOR and storage. The capital costs are expected to be lower than conventional plants without carbon capture due to the simplicity of operation (Allam et al., 2017).

The inventors have partnered with Toshiba Corporation to design the sCO<sub>2</sub> turbine and the oxyfuel combustor for use in the 50 MW demo plant at La Porte facility in Texas, USA, where the first run was conducted in May 2018. Planned commercialization in collaboration with multiple industrial partners has resulted in NET Power, the business venture of 8 Rivers, the inventors of the Allam cycle,

announcing multiple 280+ MW scale plants at various locations across the United States and United Kingdom. With a goal of net zero emissions by 2050, each plant is capable of avoiding 1 million tons of CO<sub>2</sub> emissions annually.

There are, however, many challenges associated with the design components of this cycle. One such part is the heat recuperator section which handles multiple hot and cold streams. There is a large pressure gradient between the various streams, the required heat transfer area is large and the hot side may corrode the equipment as it contains CO<sub>2</sub> and condensing water (Scaccabarozzi et al., 2016). It is also noted that there is a significant imbalance between the heat requirement by the high pressure recycle streams and the heat supplied by the low pressure turbine exhaust, which can be corrected by adding external heat either from the ASU air compressors or the CO<sub>2</sub> recycle compressors into the recuperator (Allam et al., 2017). This adds to the complexity of the whole process and reduces the novelty of flexible operation. While there are several ways to provide pure oxygen to the process, the most mature technology is the cryogenic distillation of air. This is integrated into the Allam cycle as a standalone unit operation. However, the compression and air separation units impose an energy penalty on the Allam cycle; when combined, they account for one-third of the gross turbine power production. Several potential modifications have been proposed in the literature to reduce this power consumption and further increase the performance of the Allam cycle.

Scaccabarozzi et al. (2016) performed a thorough thermodynamic analysis and optimization of the Allam cycle. Their study indicates the existence of an optimal range where the cycle efficiency is maximum for the turbine inlet pressure between 260 and 300 bar and turbine inlet temperature between 1100 and 1200 °C. The turbine backpressure of the cycle was increased by Zhu, Z. et al. (2019a) to keep the turbine outlet gases at near supercritical value so that all gas compressors can be eliminated and replaced by pumps, thus increasing the performance by 2.15% at a turbine inlet temperature (TIT) of 700 °C and 2.96% at a TIT of 900 °C. This modified process, also known as the Allam-Z cycle, also introduced the utilization of cold energy of liquefied natural gas (LNG) and liquid O<sub>2</sub> into the cycle, but the performance enhancement was subject to the TIT not being higher than 900 °C. While the substitution of multi-stage adiabatic compression with centrifugal pumps does decrease power consumption, it also requires extreme cooling and liquefaction of the flue gas. Chan et al. (2021) proposed to do this by utilising the cold energy of LNG through a series of condensers and chillers. This, however, leads to the demand for an excessive amount of LNG (87.5 kg/s), far beyond the actual amount required for combustion (2 kg/s). Accordingly, the authors propose to send the regasified natural gas (85.5 kg/s) to other potential end users. A secondary source of power output was included as a natural gas expander, which could raise the overall efficiency to 65.7%, much higher than the efficiency of the basic Allam cycle design, with the assumption that the cold energy associated with LNG regasification is freely available and does not constitute energy usage. A similar LNG heat sink concept, with a dual pressure Allam cycle for the cascade utilization of LNG cold energy, was proposed by Li,



B. et al. (2021); they suggested that their process could achieve 70.56% electricity efficiency at its optimal operation point. On the other hand, an optimization study to determine the best configuration to utilize the LNG cold energy suggests that it may be difficult to justify the additional capital cost associated with employing a standalone organic Rankine cycle to recover additional energy, because the performance of the modified Allam cycle only marginally increases (Yu et al., 2021).

Some design changes have been proposed by Allam and co-workers, e.g. the introduction of a low-pressure reheat loop with a two-turbine system, which was found to afford a 57.5% net efficiency (Allam et al., 2014). The authors also suggested that, in comparison to a single loop system, the net power output could increase by 2.5 times. Recently, Chan et al. (2020) described a reheating configuration for the Allam cycle. They added a low-pressure turbine and decoupled the ASU from the heat exchange network of the power island, at the expense of an increase the capital cost owing to the extra turbomachinery, a potentially more hazardous operation associated with the reheating of fuel and oxygen mixture and a decline in net efficiency.

The concept of Allam cycle is not limited to the combustion of natural gas, as its original designers also considered the efficient utilization of gasified coal. In fact, studies of coal-fired Allam cycle have also been conducted as part of the effort to develop clean-coal technologies. An analysis of the type of gasifiers and coal feedstock was conducted to determine the optimal performance by the Allam cycle using solid fuels (Lu et al., 2016). The key finding of the study validated the original hypothesis that a coal-fired Allam cycle could perform at higher efficiencies than the state-of-the-art integrated gasification combined cycle (IGCC) processes without carbon capture. While it was found that the different feedstock quality does not have a significant impact on cycle performance, emphasis is given to the future development of DeSNO<sub>x</sub> (de-sulphurisation and nitrogen oxide removal) processes, heavy metal removal, fouling prevention and corrosion prevention, all of which are important considerations for developing truly clean coal technologies, which are less commonly studied in the context of Allam cycle. A detailed exergy analysis of a coal-fueled Allam cycle, by Luo, J. et al. (2021) revealed that 50% of the exergy destruction comes from just three components, the gasifier, the turbine and the combustion chamber. These insights are important for determining the focus of further R&D efforts to improve the performance of the Allam cycle systems.

Zhu et al., who proposed the Allam-Z cycle (Zhu, Z. et al., 2019a), also proposed a similar scheme for coal-fired Allam cycle, denoted as the Allam-ZC cycle (Zhu, Z. et al., 2019b). In the Allam-ZC cycle, supercritical water coal gasification technology was employed to produce a syngas which can be directly sent to the Allam cycle with a higher turbine backpressure. As such, there is no need to add costly syngas cleaning procedures as supercritical water gasification ensures the complete conversion of contaminating elements such as N, S, P and Hg to inorganic salts and deposits. Even though a lower net efficiency of 47.3% was reported (c.f. the original Allam coal cycle efficiency of 51.4%), the authors

argued that the Allam-ZC is still superior over the state-of-the-art to IGCC and other coal-fired plants without carbon capture.

An economic evaluation of the Allam cycle found it has a levelized cost of electricity of 91.7 €/MWh, which is higher than that of a typical natural gas CCGT (62.5 €/MWh) (Rodríguez Hervás and Petrakopoulou, 2019). Indeed, Allam cycle remains a relative new power generation technology with relatively few dedicated studies and analyses. The economic viability of the Allam cycle would also depend heavily on the CAPEX of highly specialized equipment, such as a supercritical CO<sub>2</sub> turbine, the cost of which may be far from being commercially competitive at its current state of development. The shortage of comprehensive experimental data in the open domain also imposes great uncertainties in validating the performance and cost-effectiveness of the Allam cycle and its various process variations (Haseli, 2021). In addition, the energy efficiency of the ASU units and their integration with the thermal power cycle would further impact the net efficiency of the Allam cycle. Optimistically, future near-commercial scale demonstration projects will provide the research community with more data validating the practical performance of the Allam cycle, highlighting the needs for further R&D and encouraging more research efforts to improve its competitiveness, e.g. by exploring integrating and hybridizing Allam cycles with other cryogenic, thermal and/or chemicals processes, under a variety of operating scenarios, including the use of gasified solid fuels.

### 5.1.3 O<sub>2</sub>/CO<sub>2</sub> and O<sub>2</sub>/H<sub>2</sub>O Oxy-fuel combustion

Oxy-fuel combustion is considered one of the technologies applied to capture and sequester CO<sub>2</sub> in coal-fired power plants, and three generations of combustion technology have been developed so far. The circulating flue gas in the first-generation oxy-fuel combustion technology is about 70%, and flue gas recirculation (FGR) results in exergy losses and additional auxiliary loads (Gopan et al., 2020). The air separation unit (ASU) and the CO<sub>2</sub> purification unit (CPU) will cause about 8% carbon capture efficiency loss. The second-generation and third-generation combustion technologies are the main development targets. According to the combustion atmosphere, they are divided into O<sub>2</sub>/CO<sub>2</sub> and O<sub>2</sub>/H<sub>2</sub>O combustion. Combustion pressure develops towards higher, making the entire technology economically competitive.

#### 5.1.3.1 Characteristics of O<sub>2</sub>/CO<sub>2</sub> combustion

The reactive gases in O<sub>2</sub>/CO<sub>2</sub> combustion are O<sub>2</sub> and recycled flue gas. Pure oxygen and partially recovered flue gas produced in the ASU control the flame temperature and supplement the missing N<sub>2</sub> volume to transfer heat to the boiler (Stanger et al., 2015). Compared with air combustion, replacing N<sub>2</sub> with CO<sub>2</sub> will significantly reduce the combustion gas temperature (Khatami et al., 2012), but the

combustion temperature of  $O_2/CO_2$  can match the air combustion temperature curve when the  $O_2$  concentration exceeds 30%(Scheffknecht et al., 2011).

The comparison of the characteristics between the second-generation oxy-fuel combustion technology and air combustion and its technical schematic diagram is shown in Figure 5.7.  $O_2/CO_2$  combustion has advantages in combustion characteristics and is conducive to  $CO_2$  capture compared with air combustion. However, the flue gas circulation will enhance the coupling of the boiler, making it difficult to start and stop(Toftegaard et al., 2010), and cause pollutant accumulation and air leakage, which will increase the cost of  $CO_2$  capture(Croiset and Thambimuthu, 2001). Chen et al.(Chen, L. et al., 2012)systematically reviewed the research on combustion thermodynamics, ignition, kinetics, pollutant emissions, combustion stability, and CFD simulation design of  $O_2/CO_2$  before 2011. However, the research on pressurized oxy-fuel combustion has not been thoroughly analyzed.

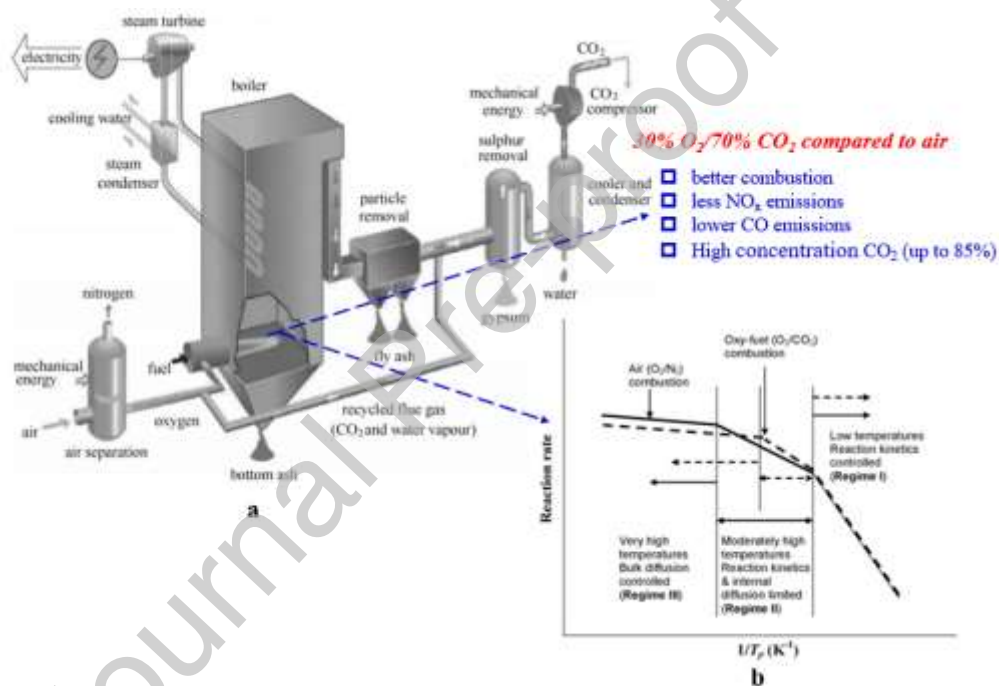


Figure 5.7. a: technical route of oxy-fuel combustion (Horn and Steinberg, 1982), b: schematic diagram of control stage in air and  $O_2/CO_2$  atmosphere (Wall et al., 2009a), comparison of char combustion characteristics in 30%  $O_2/70%$   $CO_2$  and air combustion (Stanger et al., 2015; Toftegaard et al., 2010)

### 5.1.3.2 Pressurized $O_2/CO_2$ combustion

The ASU and CPU in the traditional oxy-fuel combustion system are carried out under high pressure, but the working pressure of the fuel combustion unit (pulverized coal boiler or fluidized bed) is normal. The pressure conversion process in the system results in a reduction in power generation efficiency of around 10%(Tranier et al., 2011). Therefore, the concept of pressurized oxy-fuel combustion (POFC) was proposed to overcome the energy loss by increasing the pressure of the combustion unit. In addition, pressurized oxy-fuel combustion has the following advantages:

- 1) The size of boiler equipment is reduced, and the cost of infrastructure is reduced;
- 2) More latent heat of steam in flue gas can be recovered;
- 3) Avoid system air leakage and reduce CPU energy consumption;
- 4) Convective heat transfer is improved at the same speed.

Current research shows that the optimal working pressure of pressurized fluidized bed combustion is around 1MPa(Shi et al., 2019; Ying et al., 2016). Studies on pressurized oxy-fuel combustion systems have shown that the elevated pressure of the combustion unit can improve the power plant system's net power efficiency (LHV), reduce pollutant emissions, and obtain high concentrations of CO<sub>2</sub>(Soundararajan and Gundersen, 2013). Chen et al.(Chen, S. et al., 2019) analyzed the 600MW pressurized fluidized bed oxy-fuel combustion power plant and found that more phase change heat in the flue gas can be recovered under pressurized conditions, which can increase the net power efficiency by 36.83%. Hong et al.(Hong et al., 2009; Hong et al., 2010)and Gopan et al.(Gopan et al., 2014)reported that the net power plant cycle efficiency increased by 3%–6% when the pressure was increased beyond 1 MPa. Shi et al.(Shi et al., 2019)showed that circulating compression work on pressurized circulating fluidized bed (PCFB) systems are negligible at a lower pressure than PC boilers. The higher combustion pressure is beneficial to the oxy-fuel circulating fluidized bed combustion, the net efficiency is increased from 27.2% to 30.5%, and the mole fraction of CO<sub>2</sub> can reach 92%.

The research on a laboratory-scale oxy-fuel-PFBC platform found that elevated pressure can improve pulverized coal combustion performance, thereby reducing CO, NO<sub>x</sub>, and SO<sub>2</sub> emissions(Duan, Y. et al., 2019; Lasek et al., 2013; Wu et al., 2011). Zhang et al.(Zhang, W.D. et al., 2020)studied the O<sub>2</sub>/CO<sub>2</sub> thermal conversion characteristics of bituminous coal at 1273 K using a pressurized drop tube furnace (PDTF) and found that the char yield decreased from 59.18% to 44.47% when the CO<sub>2</sub> partial pressure was increased from 0 to 0.45 MPa. Axelbaum et al. proposed a staged pressurized oxy-combustion (SPOC) process and successfully operated it at 1.5 MPa and ~100 kW of pilot scale. The results show that the system can capture more than 90% of CO<sub>2</sub> with high efficiency and affordable cost, and the efficiency is at least 3.5% higher than that of traditional oxy-fuel combustion devices(Yang, Z. et al., 2021).

The oxy-fuel combustion of pulverized coal mixed with biomass for power generation to reduce carbon emissions has also attracted widespread interest. Long et al.(Spiegel et al., 2021) performed a series of works on the oxy-fuel combustion of pulverized coal mixed with biomass using a laboratory-scale fluidized bed reactor, demonstrating the feasibility of mixed fuel blending. Zhong et al.(Liu, Q. et al., 2022) used a pressurized fluidized bed to achieve stable combustion of the mixed fuel, but the working pressure was only 0.1-0.3MPa and found that the increased pressure can increase the combustion efficiency and facilitate CO<sub>2</sub> enrichment.

### 5.1.3.3 Characteristics of O<sub>2</sub>/H<sub>2</sub>O combustion

The O<sub>2</sub>/H<sub>2</sub>O combustion technique was originally proposed by Carlos et al.(Salvador, 2007), Seepana, and Jayanti et al.(Seepana and Jayanti, 2010), which was called steam-moderated oxy-fuel combustion (SMOC). The CANMET Energy Technology Center in Canada proposed a zero-emission power generation system based on O<sub>2</sub>/H<sub>2</sub>O combustion. The system uses steam to adjust the flame temperature, reducing the size of the power generation system by 2/5, and the energy consumption is greatly reduced compared with the second-generation oxy-fuel combustion technology(Zou et al., 2014b).

The O<sub>2</sub>/H<sub>2</sub>O combustion system eliminates the flue gas circulation system. And the flue gas condensed water is heated by the residual heat of the flue gas into steam, which is injected into the furnace to adjust the temperature. This series of processes improves the heat utilization rate of the system and removes the impurity gas in the water through the condensation and vaporization of steam, which is beneficial to the later CO<sub>2</sub> purification [30](Cai et al., 2015). Deng et al.(Deng et al., 2022)compared the characteristics of air combustion, O<sub>2</sub>/CO<sub>2</sub>, and O<sub>2</sub>/H<sub>2</sub>O combustion in the review of O<sub>2</sub>/H<sub>2</sub>O combustion of pulverized coal, as shown in Table 5.4.

Table 5.4.Comparison of air combustion, O<sub>2</sub>/CO<sub>2</sub> and O<sub>2</sub>/H<sub>2</sub>O combustion technologies (Deng et al., 2022)

	Air combustion	O <sub>2</sub> /CO <sub>2</sub> combustion	O <sub>2</sub> /H <sub>2</sub> O combustion
Flame temperature	low	high	low
Combustion rate	low	high	high
Smoke volume	high	low	
System layout		complex	simplify
Pollutant emissions		low	low
CO <sub>2</sub> capture	low	high(<90%)	high (>95%)
Cost		higher	high

### 5.1.3.4 Atmospheric pressure O<sub>2</sub>/H<sub>2</sub>O combustion

The H<sub>2</sub>O concentration in O<sub>2</sub>/H<sub>2</sub>O atmosphere under oxygen-enriched conditions is between 25% and 35%(Hecht et al., 2012), which affects the ignition mode of char. Zou et al.(Zou et al., 2015b) studied the ignition behavior of pulverized coal particles in an O<sub>2</sub>/H<sub>2</sub>O atmosphere (reaction temperature of 1373K, H<sub>2</sub>O concentration of 50%-79%) and found that the addition of steam promoted the formation of a large amount of CO and H<sub>2</sub> on the char surface. Under the same oxygen concentration, pulverized coal ignites earlier in O<sub>2</sub>/H<sub>2</sub>O atmosphere than in O<sub>2</sub>/N<sub>2</sub> atmosphere(Zou et al., 2014a). The high concentration of steam strengthens the reactions of C+H<sub>2</sub>O→CO+H<sub>2</sub> and CO+H<sub>2</sub>O→CO<sub>2</sub>+H<sub>2</sub>. A large amount of H<sub>2</sub> and CO in the char particle boundary layer will affect the heterogeneous reaction of char, making the char combustion mode change to joint ignition(Moors, 1999; Zou et al., 2015a). Blackwood

et al.(Blackwood et al., 1958)found that the  $\text{CO}_2$  generated around the particles in  $\text{O}_2/\text{H}_2\text{O}$  atmosphere was mainly attributed to the homogeneous reaction ( $\text{CO}+\text{H}_2\text{O}\rightarrow\text{CO}_2+\text{H}_2$ ).

A high concentration of  $\text{H}_2\text{O}$  affects the combustion mode of char. The enhanced gasification reaction and the thermal effect significantly affect the combustion process of char. Therefore, many scholars quantitatively analyze the consumption of char in the  $\text{H}_2\text{O}$  gasification reaction to study the effect of  $\text{H}_2\text{O}$  concentration on the combustion characteristics of char. Hecht et al.(Hecht et al., 2012)found that the  $\text{H}_2\text{O}$  gasification reaction of char in the wet flue gas cycle of oxy-fuel combustion contributed 8.7% to the overall char consumption. The gasification reaction accounted for about 20% of the carbon consumption under low oxygen conditions. Zhang et al.(Pratono et al., 2015) studied the char gasification-combustion model and found that under 31%  $\text{O}_2/\text{CO}_2$ -18%  $\text{H}_2\text{O}$  atmosphere (reaction temperature is 1373K), the char-  $\text{H}_2\text{O}$  gasification reaction contributed 26.2% to the char consumption. Chen et al.(Chen, K. et al., 2022) found that the contribution of gasification reaction to carbon consumption in the  $\text{O}_2/\text{H}_2\text{O}$  atmosphere increased with the increase in temperature and  $\text{H}_2\text{O}$  concentration. Increasing the  $\text{H}_2\text{O}$  concentration from 5% to 15% increased the gasification reaction's contribution to carbon consumption by 1.96 at 1373 K.

#### 5.1.3.5 Pressurized $\text{O}_2/\text{H}_2\text{O}$ combustion

The research on  $\text{O}_2/\text{H}_2\text{O}$  combustion technology is still at the laboratory scale. Due to the complexity and high requirements of the experimental equipment, the understanding of the combustion characteristics of pulverized coal pressurized  $\text{O}_2/\text{H}_2\text{O}$  is still in its infancy. As shown in Figure 5.8, Sun et al.(Zhao, Y. et al., 2019) proposed the concept of an oxy-coal combustion steam system of near-zero emissions (OCCSS).

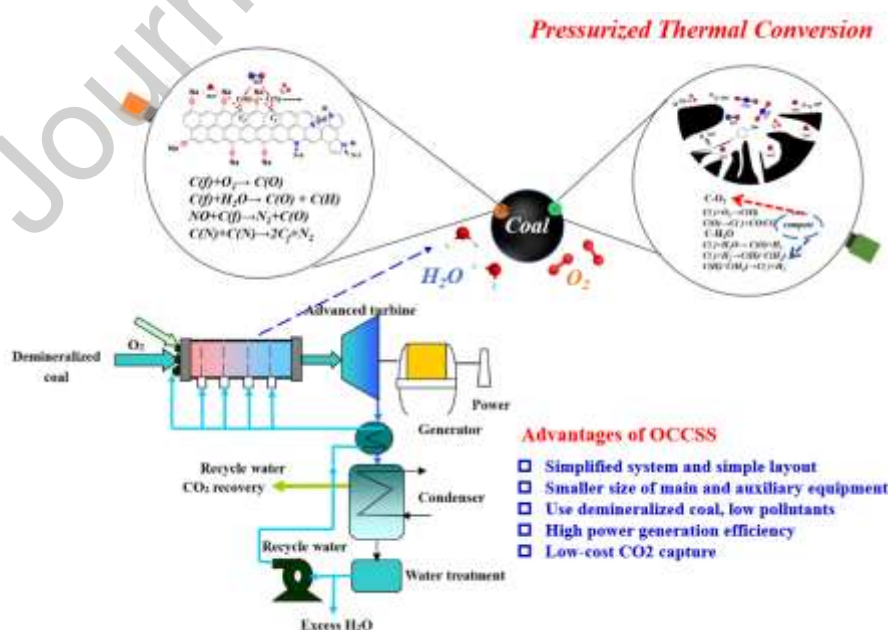


Figure 5.8. OCCSS system diagram and technical advantages (Deng, L. et al., 2021a, b; Zhao, Y. et al., 2019)

The fuel of the system in the O<sub>2</sub>/H<sub>2</sub>O atmosphere is demineralized coal, and the high temperature and pressure mixed gas (the final steam concentration is about 90%, and the rest is mainly CO<sub>2</sub>) drives the advanced turbine to work. Then the exhaust gas is condensed to obtain high concentrations of CO<sub>2</sub>. The economic comparison between this system and other different CO<sub>2</sub> emission reduction systems is shown in Table 5.5. The CES (based on coal gasification technology) and OCCSS show absolute advantages over IGCC and USC (ultra-supercritical) oxy-fuel combustion power generation systems.

Table 5.5 Economic comparison of different CO<sub>2</sub> emission reduction system technologies

Power generation method	CES	Hydroxy-fuel	OCCSS	IGCC wCO <sub>2</sub>	USC Oxy-fuel
Thermal Efficiency	50.7	35	53.4	39	35.4
CO <sub>2</sub> emissions (Kg/MWh)	0	0	0	83	83.7
Equipment cost (US\$/kW)	1210	--	--	1642	1857
Electricity price (\$/kWh)	0.054	--	--	0.069	0.062

MacNeil et al. (Macneil and Basu, 1998) found that when the oxygen concentration was constant, the combustion rate of char first increased and then decreased with the elevated pressure. The experimental work on pressurized O<sub>2</sub>/H<sub>2</sub>O combustion of pulverized coal is currently being carried out by Harbin Institute of Technology (Bai, C. et al., 2022; Deng, L. et al., 2021a, b) and Southeast University (Zan et al., 2020). Figure 5.9 (Deng, L. et al., 2021a, b) summarizes the char thermal conversion process of demineralized coal in the context of OCCSS under different pressure conditions, H<sub>2</sub>O concentration, and temperature. The increase of pyrolysis pressure helps increase the yield of pyrolysis char, and the increase of pressure and H<sub>2</sub>O concentration can both promote the combustion of char. Under pressurized conditions, the temperature exceeds 1173K, and the thermal transformation of char is significantly promoted. At equal intervals of the reaction time, the char is transformed linearly.

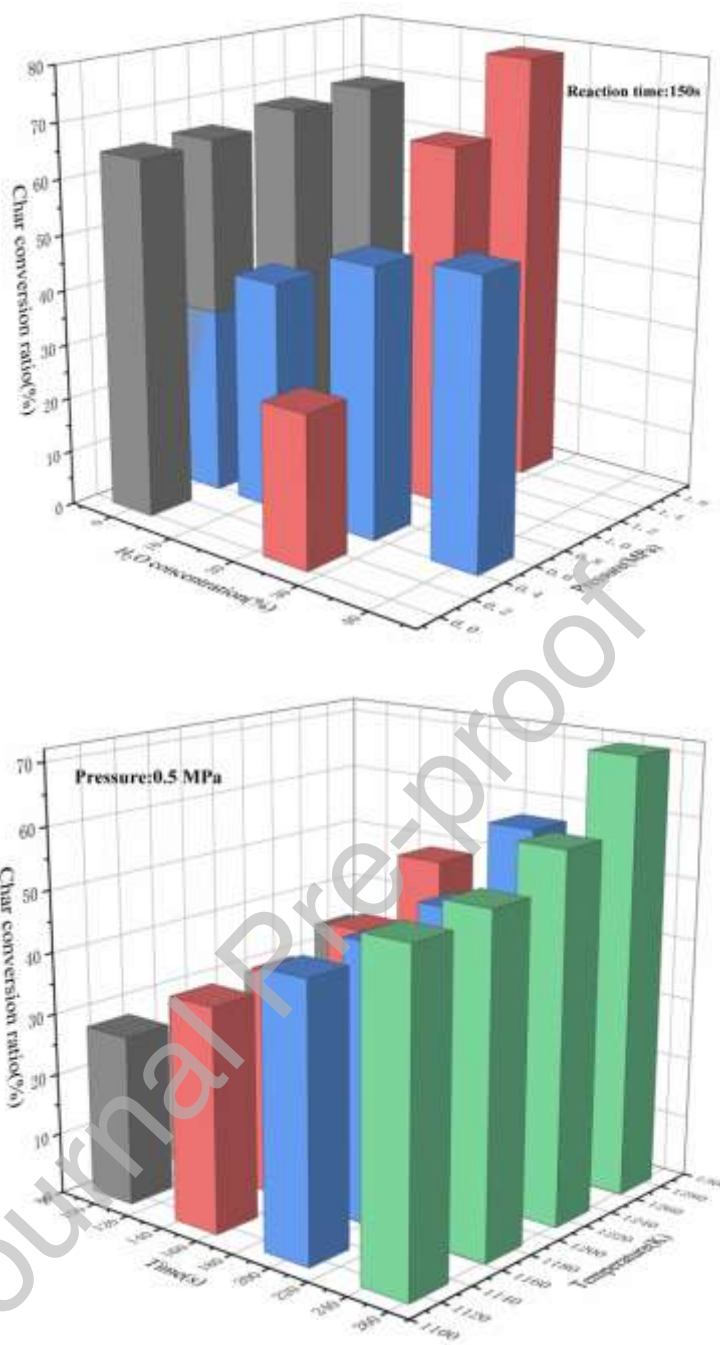


Figure 5.9. Char conversion rate of demineralized char under different pressure, H<sub>2</sub>O concentration and temperature, data adapted from (Deng, L. et al., 2021a, b)

The chemical kinetics in the pressurization stage is the rate-limiting reaction, and the pore diffusion becomes the rate-limiting reaction at high pressure (Turnbull et al., 1984). The char-H<sub>2</sub>O reaction fully develops the micropore surface area, and pore development is achieved by consuming 5–10% of the char (Jasieńko-Hałat and Kędzior, 2005). Therefore, under pressurized O<sub>2</sub>/H<sub>2</sub>O conditions, the change of char pore structure strongly affects its combustion process. Deng et al. (Deng, L. et al., 2021a, b) studied the effect of H<sub>2</sub>O concentration and pressure on char pores and found that the development of



char pore structure increases first and then decreases with the increase of H<sub>2</sub>O and pressure. When the H<sub>2</sub>O concentration is 25%, and the pressure is 1MPa, the specific surface area of the char is the largest. Therefore, pressure can inhibit NO production is consistent, but the optimal pressure is not unified. Zan et al.(Zan et al., 2020) found that increased system pressure significantly suppressed NO emissions, and H<sub>2</sub>O suppressed the formation of NO and N<sub>2</sub>O. Bai et al.(Bai, C. et al., 2022) found that pressure affects NO emission, and the lowest relative migration of char-N to NO is 0.4 MPa. In summary, the application of pressurized oxy-fuel combustion technology to coal-fired power plants has great potential to achieve CO<sub>2</sub> emission reduction, especially to improve the combustion efficiency of pulverized coal and reduce pollutant emissions.

#### **5.1.4 Oxygen transport membranes for oxy-fuel combustion**

##### **5.1.4.1 Status**

To meet expanding global energy demand, the power generation sectors have integrated carbon capture and sequestration technology (CCS) into their current infrastructures in order to reduce combustion emissions while maximizing process efficiency (Li, T. et al., 2022; Shaw and Mukherjee, 2022). Directly capturing CO<sub>2</sub> emissions from power plants is a potential route and oxyfuel combustion technology using pure oxygen for fuel combustion has gained increasing interest from many researchers and governments since it is easy to be integrated into current power generation facilities. The massive amounts of oxygen can be obtained by incorporating oxygen transport membrane (OTMs) reactors that filter pure oxygen directly from air (Figure 5.10 (a)), with the required heat for the oxygen permeation reaction provided by the combustion process itself. The oxygen transport membrane reactors can also be used in many other industrial sectors, such as iron and glass factories, to capture enormous quantities of CO<sub>2</sub> emissions. Academic and industrial communities are becoming increasingly interested in OTMs. In theory, these oxygen permeable membranes can separate oxygen with 100% permeation selectivity and provide a cost-effective and simplified method for producing O<sub>2</sub>. In comparison to current cryogenic technology, the revolutionary method based on OTMs can save 60% of energy consumption and reduce production costs by 35% (Chen, G. et al., 2022; Chen, W. et al., 2015; Kiebach et al., 2022). Another appealing advantage of OTMs is the ability to directly implement oxygen separation units into high-temperature processes such as oxy-fuel combustion. Recently, OTMs are also becoming increasingly appealing for use in membrane reactors for chemical and fuel production, in addition to O<sub>2</sub> separation (Chen, G. et al., 2022; Plazaola et al., 2019).

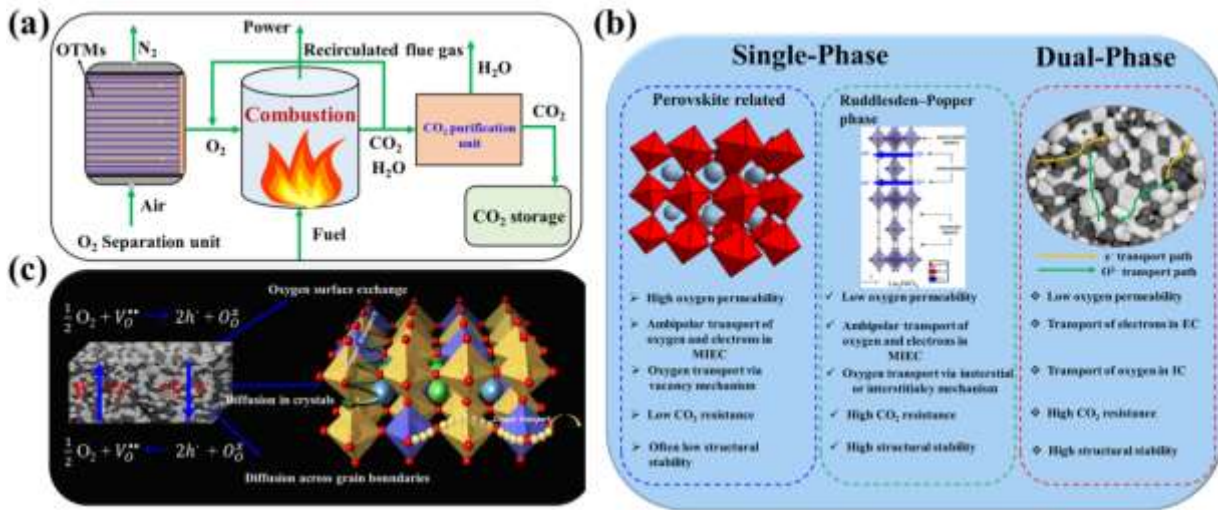
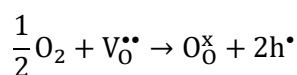


Figure 5.10. (a) Schematic representation of using OTMs reactors for oxy-fuel combustion (b) the most common types of OTMs used for oxygen permeation and (c) a diagram of the oxygen transport mechanism (Chen, G. et al., 2022).

#### 5.1.4.2 Transport mechanism of OTMs

OTMs for oxygen separation have been extensively researched in recent decades and are broadly classified into two types, as shown in Figure 5.10 (b): single-phase and dual-phase. The selective permeability of oxygen from the high oxygen partial pressure side to the low oxygen partial pressure side can be realized based on a driving force created by oxygen partial pressure difference on the two sides of the dense OTMs. The oxygen ionic transfer in one direction and the simultaneous electronic transfer in the opposite direction allow oxygen to permeate through dense OTMs membranes at high temperatures (Figure 1 (c)). The oxygen transport process is generally comprised of the following steps (Bai et al., 2021a; Garcia-Fayos et al., 2020; Kiebach et al., 2022):

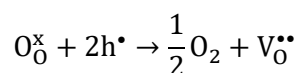
- 1) Diffusion of oxygen from the feed stream to the OTMs surface
- 2) Adsorption of O<sub>2</sub> on the surface of the OTMs
- 3) The adsorbed oxygen on the OTMs surface undergoes dissociation surface exchange reaction:



where  $V_O^{\bullet\bullet}$  represents oxygen vacancies,  $O_O^x$  represents lattice oxygen and  $h^\bullet$  represents electron holes.

- 4) Oxygen ion incorporation into membrane crystal lattice to form lattice oxygen.
- 5) Lattice oxygen diffusion and electrons diffusion via electron bands inside OTMs.
- 6) Lattice oxygen undergoes charge transfer on the OTMs surface to create chemisorbed oxygen.

7) Recombination surface exchange reaction:



8) O<sub>2</sub> molecule desorption from the OTMs surface

The oxygen permeation process involves a number of physical and chemical processes that are primarily controlled jointly by surface exchange and bulk diffusion in most cases. It is important to note that the rate-limiting steps are determined by several parameters, including membrane material, operating conditions, and membrane geometry. To obtain accurate prediction of the oxygen permeation fluxes for various limiting cases, intensive efforts have been devoted to developing empirical equations or models that integrate surface exchange and bulk diffusion reactions. More detailed descriptions of the existing oxygen permeation flux models on the basic assumptions and transport mechanism of OTMs can be found in the previous excellent reviews (Li, C. et al., 2018; Sunarso et al., 2008).

#### 5.1.4.3 Performance overview of different types of OTMs

Single-phase perovskite-type OTMs materials with a general formula of A'<sub>x</sub>A''<sub>1-x</sub>B'<sub>y</sub>B''<sub>1-y</sub>O<sub>3-δ</sub> are among the most studied and promising candidates for oxygen separation since they exhibit high mixed ionic and electronic conductivity, which allow transporting the oxygen ions sustainably. An ion is typically an alkaline-earth metal like Ba<sup>2+</sup> or/and Sr<sup>2+</sup>, whereas B ion is generally a transition metal like Fe<sup>3+</sup> or/and Co<sup>3+</sup>. Based on the literature (Chen, G. et al., 2022; Han, N. et al., 2022; Widenmeyer et al., 2020), the chemical compound combinations Ba<sub>x</sub>Sr<sub>1-x</sub>Co<sub>y</sub>Fe<sub>1-y</sub>O<sub>3-δ</sub> (BSCF) appear to be the best candidates with the highest oxygen permeation flux, which is generally more than 1 mL min<sup>-1</sup> cm<sup>-2</sup> for a 1 mm-thick membrane at 950 °C and can even reach to more than 10 mL min<sup>-1</sup> cm<sup>-2</sup> for an ultra-thin BSCF membrane at 1000 °C (Zhang, C. et al., 2017). Despite exhibiting good performances for oxygen separation, the low chemical stability of BSCF membranes in CO<sub>2</sub>-containing atmospheres resulted in oxygen permeation flux deterioration because of the formation of strontium or barium carbonates, which limits their applicability for oxy-fuel combustion. In addition, the high thermal expansion arising from the phase transition in the OTMs operating temperature range will lead to mechanical instability. Based on the reported studies, several major approaches have been taken to improve the chemical stability of perovskite-based OTMs towards CO<sub>2</sub> (Chen, G. et al., 2022; Chen, G. et al., 2019; Zhang, C. et al., 2017):

- (a) Partially substituting the transition metal components in the B-site with more stable or acidic metal components.
- (b) Reducing the Co content in the B-site;
- (c) Using a rare earth metal cation as the A-site cation (e.g. La or Pr);

Although the proposed approaches (partial substitution of A- and B-site cations) can enhance the CO<sub>2</sub> resistance of perovskite-type OTMs, performance degradation is unavoidable due to the formation of an alkaline-earth carbonate layer over time when exposed to CO<sub>2</sub>-containing atmospheres.

An attractive alternative to perovskite is the Ruddlesden–Popper single-phase membrane material with a general formula A<sub>n+1</sub>B<sub>n</sub>O<sub>3n+1</sub> (A is an alkaline earth or lanthanide and B is a transition metal; n = 1, 2, 3, 4...). One of the most studied examples is Ln<sub>2</sub>NiO<sub>4+d</sub> (Ln is referred to rare earth metals such as Nd, Pr or La), which has been proved to be totally CO<sub>2</sub> tolerant during long-term oxygen permeation test in a CO<sub>2</sub> atmosphere (Chen, G. et al., 2019; Xue et al., 2015). However, when compared to perovskite-type OTMs, the oxygen permeability of Ruddlesden–Popper single-phase membrane is significantly lower. Furthermore, it is reported that the presence of a small amount of SO<sub>2</sub> was sufficient to damage the Ruddlesden–Popper phase membranes because of the formation of sulphur containing products (Kiebach et al., 2022), which instantaneously blocks the active sites of the membranes for oxygen transport.

Dual-phase membranes, which are composed of an electronic phase and an ionic phase, have a high potential for oxygen separation and can address the issues of low chemical stability of single-phase OTMs (Bai et al., 2021a; Chen, G. et al., 2021; Fang et al., 2015; Garcia-Fayos et al., 2020). Ideally, they combine the best properties of the electronic and ionic conductors to achieve both good oxygen permeation fluxes and satisfied chemical and mechanical stability in harsh operating conditions (for example, CO<sub>2</sub> and SO<sub>2</sub>) at high temperatures. The successful materials for dual-phase membranes should meet the basic requirements: (a) no reactions between these two phases at working temperature; (b) the creation of good percolation paths for the diffusion of electrons and ions; (c) a proper ratio between these two phases; (d) high electrical conductivities of both electronic and ionic conductors. Noble metals such as Ag or Pd were used as electronic conductors in early approaches. More recently, conductive oxide phases were selected as the electronic conductor. It is well accepted that the incorporation and release of oxygen are restricted to triple-phase boundaries (gas phase / electronic conductor / ionic conductor). The concept of combining two mixed ionic-electronic conductors in the dual phase OTMs is a promising route to overcome this limitation, where one shows superior electronic conductivity while the other has excellent ionic conductivity. Although dual-phase membranes also exhibit high CO<sub>2</sub> resistance after long-term CO<sub>2</sub> exposure, their oxygen permeability is lower than that of perovskite-type single-phase OTMs, similar to ruddlesden–popper single-phase membranes. To sum up, there is a trade-off between oxygen permeability and CO<sub>2</sub> tolerance. It is difficult to achieve high oxygen permeation flux while maintaining excellent chemical stability for the designed OTMs. Often, improving one property comes at the expense of sacrificing another. Reduced membrane thickness or optimization of OTMs geometry are two alternatives that do not induce such a trade-off. Since oxygen flux and membrane thickness are inversely related, reducing membrane thickness generally increases the oxygen permeation flux of the membrane. This is true up to a certain thickness known as

characteristic thickness, after which the predominant bulk diffusion is limited by the oxygen surface exchange at gas/solid interfaces.

#### 5.1.4.4 Membrane geometry and strategies for improving CO<sub>2</sub> resistance and oxygen permeability

At present, three shaped membrane configurations of OTMs have been widely studied: disk, tubular, and hollow fiber membranes. Despite being relatively simple to fabricate, the oxygen permeation performance of disk and tubular membranes is constrained by their small surface area, thick wall, sealing, and connection issues. The hollow fiber membranes have been considered as the most promising and practical one to improve O<sub>2</sub> permeation flux, which solves the problems faced by disk and tubular membranes. It is important to note that when the thickness of the membrane is reduced in order to achieve high oxygen permeability, the mechanical strength of the membrane decreases. A promising method for simultaneously obtaining high oxygen permeability and satisfied mechanical strength was an asymmetric structure membrane supported by a porous substrate. Aside from structural and chemical modifications to improve the oxygen permeability and CO<sub>2</sub> resistance of the OTMs, engineering approaches are effective methods to be applied. Coating the membrane surface with a porous CO<sub>2</sub> resistant layer is currently used as an effective approach to protect the single-phase perovskite-type membranes from CO<sub>2</sub> poisoning. For an ideal CO<sub>2</sub> protective layer material, high ionic conductivity, good chemical and mechanical stability towards CO<sub>2</sub> at working temperatures, and compatibility with the protected membrane are required. It is possible for the protected dense membrane and the porous protective layer to be made of the same material. If oxygen surface exchange predominates the transport process, it may be possible to increase the oxygen permeation fluxes by speeding up the surface exchange reaction rate by depositing a surface decoration (catalyst) layer on the membrane surface. Some intriguing ideas for improving oxygen permeability include using external electronic short-circuit methods to enhance the electronic conductivity of the membrane and utilizing plasma-based approaches that decouple oxygen molecule splitting and oxygen incorporation from the OTMs surface (Buck et al., 2021; Zhang, C. et al., 2017; Zheng, Q. et al., 2022).

#### 5.1.4.5 Existing developments for potential industrial applications of OTMs

The design of modules is a critical step in enabling OTM technology for large-scale purity oxygen production. Significant efforts are being made to improve the performance and stability of OTMs materials, and significant steps are also being taken in the design and integration of OTMs with oxy-fuel combustion systems. There are several developed OTMs membrane modules (Figure 5.11.) with different design configurations targeted at small and medium scale oxygen production, as recently summarized by Kiebach et al. (Kiebach et al., 2022). A number of companies and academic research institutions have been working to scale up OTM concepts, developing membrane modules and successfully integrating them into industrial environments. Praxair, Inc. (now Linde plc) has made significant progress towards applications of dual-phase OTMs containing multipanel tubular reactor

systems to improve the syngas produced by coal-gasification (Gupta et al., 2016). Currently, the pilot scale infrastructure is being reconfigured to connect OTM technology with steam methane reforming for blue hydrogen production by Linde. In terms of technology readiness levels and O<sub>2</sub> production rates, Air Products and Chemicals Inc. has made the most advanced developments. A membrane vessel with a total capacity of 2000 ton-per-day (TPD) O<sub>2</sub> production was developed, consisting of several 1 TPD OTM modules. However, no new information about OTM development activities was revealed, which was most likely due to a significant company restructuring in 2015 (Garcia-Fayos et al., 2020). It's also important to mention the OTM pilot module research conducted by the two Germany academic research organizations - RWTH Aachen University and Fraunhofer Institute for Ceramics Technologies and Systems (IKTS), both of which used Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (BSCF) as the membrane material. With regard to the pilot module developed by RWTH Aachen University, a membrane module with a total of 596 tubular BSCF membranes was created and tested in a variety of environments (Nauels et al., 2019). It was possible to operate continuously for a maximum of 1800 h with an operating pressure of 10 bars and a temperature of 880 °C. The testing results demonstrated their concept is generally feasible. However, significant improvement is still needed to address the problems of breakages of membrane tubes. Since 2009, Fraunhofer IKTS has developed various OTM pilot plants with a growing oxygen production rate and a decreasing energy demand. A 18,000 h long-term oxygen permeation measurement was carried out using 93 capillaries, and the results showed the O<sub>2</sub> permeation flux dropped only by approximately 6% during the last 14,000 h continuous operation (Chen, G. et al., 2022). The pilot plant design is still being refined, and more information can be found in (Chen, G. et al., 2022). Similarly, a perovskite membrane module made up of 889 La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> hollow fiber membranes has also been developed and could be operated continuously for 1067 h at about 960 °C (Tan et al., 2010).

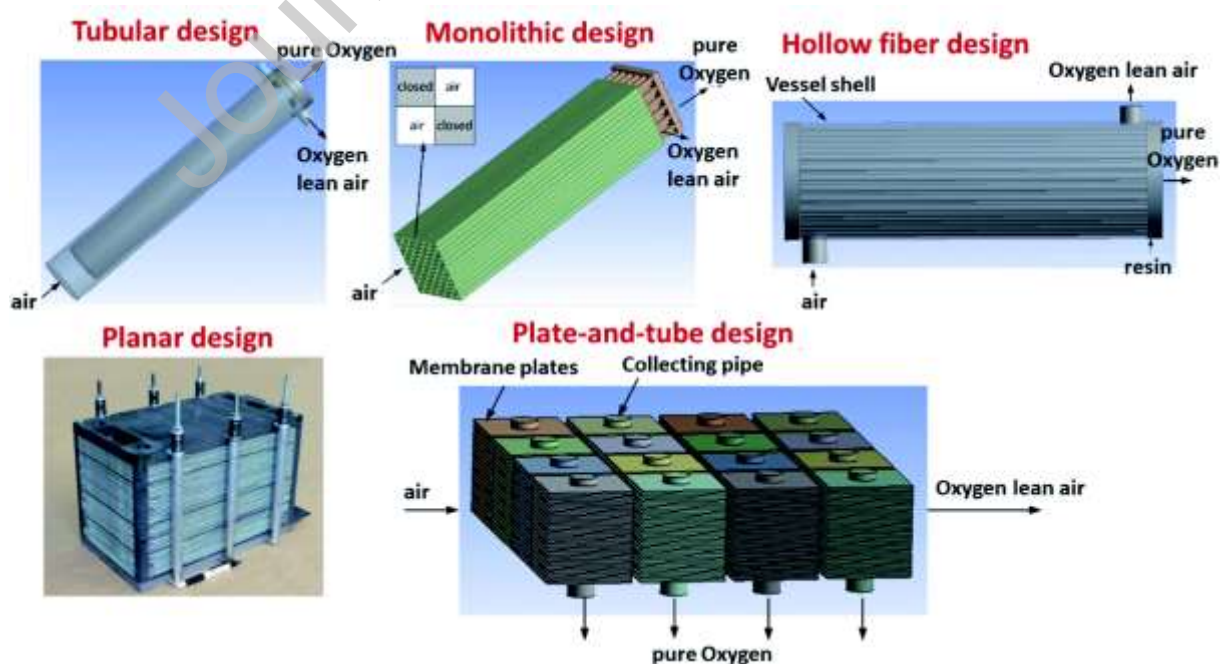


Figure 5.11. Different design configurations for OTM modules for large-scale oxygen production.

Reprinted with permission from (Kiebach et al., 2022).

It is worth noting that the majority of the above results were obtained in the absence of CO<sub>2</sub>. Considered the harsh operation environments of the oxy-fuel combustion process, the membranes should deliver high stability while maintaining satisfied performance. In this context, special attention should be given to the development of dual-phase OTMs by optimizing the preparation approaches and microstructures, which have shown high resistance towards CO<sub>2</sub> and acceptable oxygen permeation flux. Engineering approaches such as depositing a surface decoration (catalyst) layer and designing an appropriate module should also be considered. Despite many advancements, there are still many research and technological challenges to overcome before OTMs for oxy-fuel combustion in power plants can be commercialized.

## 5.2 Chemical looping related carbon capture

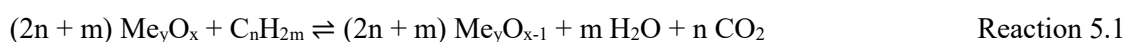
In a fuel-based power generation unit, the combustion of fuels is the route for energy generation, and carbon capture and storage (CCS) technology is necessarily employed to minimize CO<sub>2</sub> emissions combustion reactions (Gao et al., 2022b; Song et al., 2018b). CO<sub>2</sub> capture can be implemented in post-, oxy- or pre-combustion, wherein post-combustion is the conventional fuel oxidation method of combining fuel and air in a single heated reactor to give power (Alalwan and Alminshid, 2021). The flue gas containing CO<sub>2</sub> emitted has a low CO<sub>2</sub> partial pressure (i.e., < 0.15 atm), which makes current CO<sub>2</sub> technology challenging due to difficulties in separation and absorption. Progressing toward more efficient carbon capture, oxy-combustion, as described in Section 5.1, is the alternative to improve energy efficiency for the separation of CO<sub>2</sub> due to using pure oxygen from separation for fuel combustion to give only CO<sub>2</sub> and water vapor (Figuerola, José D et al., 2008). More importantly, the CO<sub>2</sub>-rich stream could be obtained by condensing water vapor, which is favorable for more-energy efficient carbon capture. Similar to oxy-combustion, pre-combustion primarily aims to form synthesis gas or syngas, a mixture of H<sub>2</sub> and CO, from gasification or reforming. Thereafter, CO<sub>2</sub> is produced from CO via a water-gas shift reaction to produce more H<sub>2</sub> for combustion to give energy (Alalwan and Alminshid, 2021). Hence CO<sub>2</sub> before the combustion stage is captured (i.e., pre-combustion).

In any case, combustion technologies that require either CO<sub>2</sub> separation or O<sub>2</sub> separation from the air will incur high economic and energy costs. With the desire to avail of more energy-efficient process technologies for energy and material conversions, chemical looping processes, whereby a reaction or separation is divided into at least two sub-reactions that take place in a decoupled manner, have emerged as a competitive alternative in terms of the facile intrinsic CO<sub>2</sub> capture ability (Zeng, L. et al., 2018). Typically, the chemical looping process involves circulating a chemical intermediate or looping material, such as metal oxides (MeO), that oxidizes feedstocks and reduces MeO. The reduced MeO (i.e., metals;

M) would be re-oxidized, typically with air, in another unit. Such process is known as Chemical Looping Full Oxidation (CLFO), or conventionally also known as Chemical Looping Combustion (CLC). Some researchers labeled CLC as a pre-combustion CO<sub>2</sub> capture technology or a standalone fourth technique after post-, oxy- and pre-combustion CO<sub>2</sub> capture (Mukherjee et al., 2015). Importantly, CLC differentiates itself from pre-combustion CO<sub>2</sub> capture due to much higher concentrations of CO<sub>2</sub> in an effluent stream (i.e., up to 100 %) compared to only 50 % in that of pre-combustion. While many carbon capture technologies are being developed (e.g., solvent scrubbing, integrated gasification combined cycle), chemical looping is the most competitive technology by means of carbon capture cost (Bhave et al., 2017; Fan et al., 2012). Presently, most of the chemical-looping technologies for carbon capture in the power generating sector are still under laboratory research development stage, with several pilot-scale setups in operation for at least 11 000h in 46 chemical looping combustors (Lyngfelt et al., 2019).

### 5.2.1 Chemical looping techniques

Chemical looping concept dates back to the 19<sup>th</sup> century by Quentin and Arthur Brin for air separation, with BaO as the looping material (i.e.,  $\text{BaO} + 1/2\text{O}_2 \rightleftharpoons \text{BaO}_2$ ) (Hepworth, 1892). CLC, the most widely adopted concept for chemical looping, was first introduced and patented by Lewis and Gilliland for the production of pure CO<sub>2</sub> using a solid oxygen carrier or any oxidizable carbon-based materials in two interconnected fluidized bed reactors. (Lewis and Gilliland, 1954) More scholars began to explore a deeper understanding of the process design (Mattisson et al., 2018; Mattisson et al., 2009), looping material selection (Tian, M. et al., 2021; Zeng, L. et al., 2018; Zhang, Z. et al., 2022), and the energetics of CLC, (Mukherjee et al., 2015) and expanded to a broad range of applications, depending on the nature of the recyclable reaction or looping reaction (Hu, J. et al., 2018; Zeng, L. et al., 2018). CLC consists of two mutually exclusive reaction steps that are performed sequentially and in a cycle with two interconnected fluidized bed reactors (i.e., fuel combustion reactor; reducer and air reactor; oxidizer) and solid oxygen carriers like metal oxides (Figure 5.12 A1). In the first reaction step within the fuel combustion reactor, fossil fuel feedstock such as natural gas is oxidized by lattice oxygen found in MeO. Complete combustion with oxygen resulted in the formation of CO<sub>2</sub> and H<sub>2</sub>O (Reaction 5.1), for which pure CO<sub>2</sub> can be obtained by condensation, thus doing away with costly CO<sub>2</sub> separation. Sequentially, in the second reactor (i.e., air reactor; oxidizer), the reduced oxygen carrier is subjected to airflow for re-oxidation (Reaction 5.2). The oxidized MeO is then circulated back to the first reactor for complete feedstock combustion.



The reduction reaction (equation 1) is, in general, an endothermic reaction for most oxygen-carrier metal oxides, while the re-oxidation of MeO is exothermic. (Peltola et al., 2013) The heat released from



equation (2) is of the same magnitude as if for complete conventional combustion of fossil fuel in the air, thus making CLC intrinsically advantageous.(Lyngfelt et al., 2001)

Chemical looping processes can be broadly classified into two groups depending on the type of looping material carriers, oxygen-carrier or non-oxygen carriers (e.g., CO<sub>2</sub>-carrier).(Fan et al., 2012) Others may classify the different chemical looping processes as either CO<sub>2</sub>-producing or separation is involved or not. CLC or CLFO process is one of the processes that only use oxygen carriers for energy generation (Figure 5.12 A1), and others include partial oxidation or selective oxidation for syngas or hydrocarbons production, respectively, thus going beyond energy generation efficiency (Figure 5.12 A2,3). Chemical looping can be extended to hydrogen production (i.e., chemical looping hydrogen production; CLH), and other forms of chemical looping, such as sorption enhanced reforming (SER) and sorption enhanced chemical looping reforming (SECLR).(Chisalita and Cormos, 2019) Regardless of the choice of looping materials (i.e., oxygen-carriers, non-oxygen-carriers, or both in tandem), chemical looping has been shown to effectively give better yields and product selectivity while having better CO<sub>2</sub> management, either by concentrating the CO<sub>2</sub> stream for capture or efficient CO<sub>2</sub> utilization. For example, Chisalita and co-workers conducted a techno-economic analysis of CLH with iron-based oxygen carriers for natural gas reforming to hydrogen and found that the chemical looping process is expected to have a production cost of 41.84 €/MWh, lower than 42.43 €/MWh from that of a conventional natural gas reforming without carbon capture.(Chisalita and Cormos, 2019) Furthermore, CLH allows for a very high carbon capture rate of > 99%, the unexpected inherent advantage of using chemical looping. The techno-economic assessment was applied to the natural gas combined cycle using oxy-fuel and carbon capture technologies with and without chemical looping design. With CO<sub>2</sub> and H<sub>2</sub>O splitting chemical looping that permitted CO<sub>2</sub> recycling, the parasitic power load was reduced and thus resulted in an increase in net energy efficiency by 7.5% from 43.25%.(Farooqui et al., 2018) Hence, the chemical looping process can improve economic viability for chemical processes with 100% intended carbon capture. Figure 1 briefly describes possible chemical looping processes, including more advanced hybrid chemical looping processes with three reactors for desulfurization and ammonia synthesis (Laassiri et al., 2018; Xuan et al., 2018).

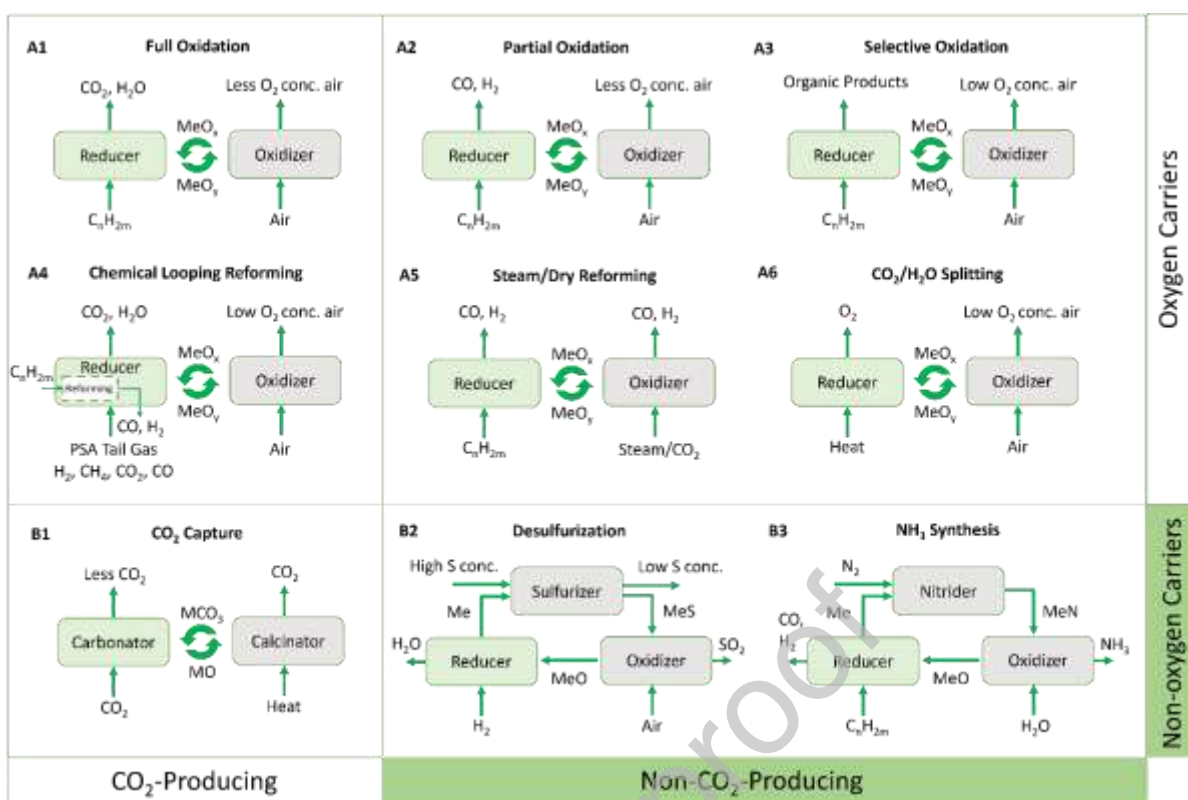


Figure 5.12. Chemical looping techniques with different looping materials, broadly classified as either oxygen carriers (A) or non-oxygen carriers (B), and with different process designs, broadly classified as either CO<sub>2</sub>-producing (A1, A4, B1) or non-CO<sub>2</sub>-producing (A2, A3, A5, A6, B1-3). A1) Conventional chemical looping full oxidation (CLFO) or chemical looping combustion (CLC) (Alalwan and Alminshid, 2021). A2) Partial oxidation of carbonaceous feed to give syngas (Zhang, Xiaorong et al., 2022). A3) Selective oxidation of carbonaceous feed affords high-value higher order hydrocarbons such as alkanes and alkenes. A4) Chemical looping reforming (CLR) with separate standalone conventional stream reforming in a reducing reactor (Luo et al., 2018). A5) Alternate chemical looping reforming (CLR) via steam or dry reforming process to convert carbonaceous feed into syngas (Hu, J. et al., 2018; Hu et al., 2021c). A6) Thermochemical splitting chemical looping reactors for CO<sub>2</sub> to give CO and H<sub>2</sub>O to give H<sub>2</sub> (Kim et al., 2022). B1) Carbon capture with carbonates to trap CO<sub>2</sub> (Zhang, Z. et al., 2022). B2) Hybrid chemical looping to carry O and S atoms for desulfurization (Xuan et al., 2018). B3) Hybrid chemical looping to carry O and N atoms for NH<sub>3</sub> synthesis (Laassiri et al., 2018).

## 5.2.2 Chemical Looping Materials

Ideal carriers, be it to carry oxygen or other atoms, require good reactivity with respective carrying atoms (e.g., oxidation in the air in oxidizers) or reduction with carbonaceous feed in the reducer reactor. Secondly, the carriers should have sufficient mechanical strength to minimize attrition and excellent resistance to carbon deposition, sintering, and agglomeration at high temperatures. Carriers also need

to be fluidizable, and their physical and chemical properties remain robust against repeated reduction and oxidation kinetics at high temperatures. Transition metals such as Co, Ni, Cu, Fe and Mn have been investigated as oxygen carriers with their corresponding oxides CoO, NiO, CuO, Fe<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>(Zhang, Z. et al., 2022) .

Among the transition metals, Ni and Co are among the costlier metals, but both have good reactivity with hydrocarbons(Dewangan et al., 2019; Hu et al., 2021a; Zhou et al., 2022), making them good candidates for the chemical looping process with carbonaceous feedstock. Close to 100% CH<sub>4</sub> conversions can be obtained over Ni-based oxygen carriers during a CLR process(Han et al., 2021; Huang, J. et al., 2018). However, Ni sintering and the loss of metallic Ni, owing to partial re-oxidation into NiO, resulted in a reduction of the overall active surface area and hence catalytic performance after repetitive chemical looping cycles. Ni-based catalyst also suffers from sulfur-poisoning with the formation of nickel sulfide, Ni<sub>3</sub>S<sub>2</sub>.(García-Labiano et al., 2009) Co possesses high oxygen transport capacity, and readily undergoes a redox process between Co and CoO at above 900 °C (Figure 5.13A). However, CoO has a strong affinity with common catalyst support materials like Al<sub>2</sub>O<sub>3</sub>, MgO, and TiO<sub>2</sub> to give thermally-stable and unreactive CoAl<sub>2</sub>O<sub>4</sub>, Mg<sub>0.4</sub>Co<sub>0.6</sub>O, and CoTiO<sub>3</sub> phases (Hu, J. et al., 2018). Cu-based catalyst has increasingly gained attention for their flexible redox ability from Cu with +2 oxidation state in CuO to +1 or 0 oxidation state in Cu<sub>2</sub>O or Cu. Moreover, Cu is less toxic and low cost, and has a sulfur-resistant ability that Ni-based oxygen carrier lacks(Forero et al., 2010). Drawbacks of Cu include severe agglomeration at high temperatures due to its low melting point (i.e., 1085 °C) (Figure B), but strategies with tuning metal-support interaction to disperse Cu can overcome the limitation to give high chemical and mechanical stability(Izquierdo et al., 2021).

Fe-based oxygen carriers also face similar agglomeration problems with the formation of magnetite(Rydén et al., 2010). But, among the metals, Fe is environmentally-friendly, low cost, and possesses high mechanical strength – suitable for fluidization. While Fe falls short in the spectrum of oxygen transport capacity and reactivity towards hydrocarbons, its flexible oxidation states (i.e., Fe, FeO, Fe<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub>) allow for use in different reaction systems (e.g., counter-flow moving bed reactor (Hu, J. et al., 2020; Luo, S. et al., 2014; Yu, Z. et al., 2019) Akin to Cu, Fe has modest resistance against H<sub>2</sub>S poisoning, with H<sub>2</sub>S being instead oxidized to SO<sub>2</sub> in the flue gas(Cabello et al., 2014), making Fe the most common versatile choice, together with Ni, for oxygen-carriers in many chemical looping processes and applications(Zhang, Xiaorong et al., 2022).

Lastly, Mn-based catalysts as oxygen carriers are beneficial in terms of toxicity and cost, comparable with Fe, except that they boast higher oxygen transport capacity. However, Mn has flaws consisting of sulfur intolerance and the ability to form unreactive phases with Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub>(Tian et al., 2009; Zafar et al., 2006). Figure C shows a broad overview of the possible metal-based oxygen carriers, contingent on a certain desirable chemical looping process (i.e., activity, sulfur-tolerance, cost etc.) To

better meet the practicality and commercial viability of chemical looping processes, strategies to improve the shortcomings in the monometallic oxygen-carriers have been reported with 1) introducing promoters (Hu et al., 2021b; Hu et al., 2021c; Machida et al., 2015), 2) mixed oxide or bimetallic catalysts (Hossain and de Lasa, 2007; Mungse et al., 2015), and 3) unique structures (e.g., perovskites(He et al., 2013), core-shell (Neal et al., 2015; Tian et al., 2017) etc.)

Conventional oxygen carriers generally function by 1) generating oxygen vacancies or ions and electron-hole pairs, 2) permitting bulk diffusion of the oxygen species and electron-hole pairs, and 3) providing surface sites for reactions (Figure 5.13D). In the reduction step of the chemical looping process, where the oxygenated oxygen carriers are subjected to a reducing gas (e.g., carbonaceous feedstock, hydrogen, etc.), oxygen anions are first generated due to the exposure and absorption of thermal energy, which would diffuse from within the bulk (i.e., higher oxygen potential) to the surface (i.e., lower oxygen potential) with a concomitant counter-current flow of electrons to ensure charge neutrality. The active oxygen anions that have diffused to the surface can react and oxidize the reacting gas. On the other side, in the oxidation reactor, the oxidation of the oxygen-deficient oxygen carriers proceeds with oxygen occupying the oxygen vacancies on the surface before moving towards the bulk down an oxygen concentration gradient.

Another variant of the chemical looping process is chemical looping with oxygen uncoupling (CLOU), wherein the oxygen carriers do not just generate oxygen anions or vacancies, but rather release oxygen gas ( $O_2$ ) to the gaseous phase in the reducer. The separated oxygen available for direct combustion overcomes the rate-limiting surface reaction with lattice oxygen on the typical oxygen carriers(Skulimowska et al., 2017). The common types of oxides capable of uncoupling oxygen are Cu and Mn-based, which allow the uncoupling of oxygen with sufficient oxygen partial pressures for combustion at elevated temperatures(Abián et al., 2017; Rydén et al., 2014). Interestingly, the majority of these carriers are Mn-based, either pure  $Mn_2O_3$  or combined with other oxides (i.e., Ni, Fe, Mg, and Si) to give mixed oxides(Abián et al., 2017; Azimi et al., 2013; Shulman et al., 2009, 2011). The mixed oxides allowed higher oxygen partial pressures than pure  $Mn_2O_3$  from between 850 to 1000 °C for combustion – a temperature range that is unsuitable for low-melting point Cu-based oxides.

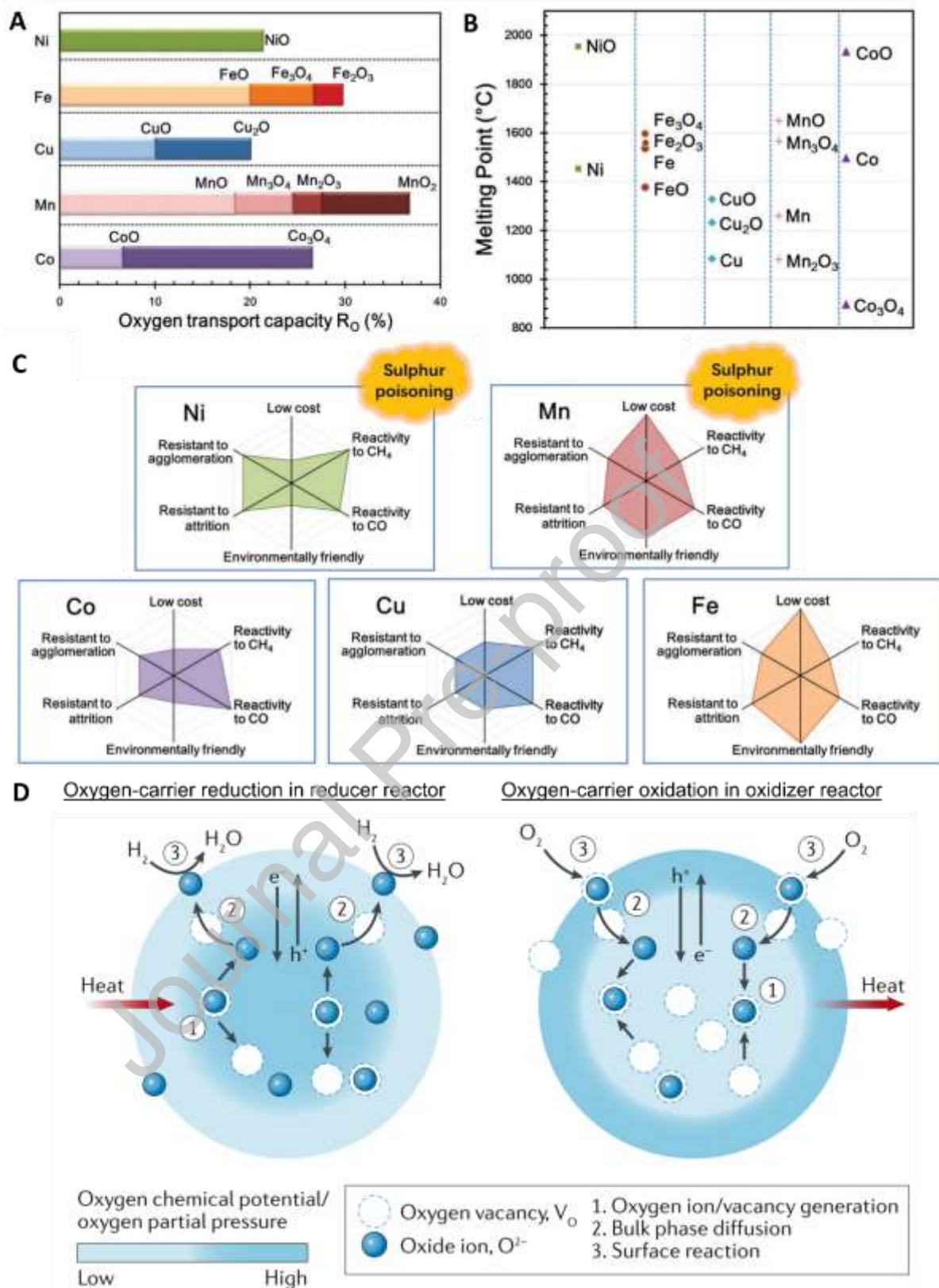


Figure 5.13. Chemical and mechanical properties of oxygen carriers. A) Oxygen transport capacities comparison among Ni, Fe Cu, Mn and Co. B) Melting points of common metal oxides as oxygen carriers. C) Catalytic performance, cost, environmental-friendliness, agglomeration, and attrition

resistance comparison (Zhao, X. *et al.*, 2017). D) Lattice oxygen generation and consumption of oxygen carriers in reducer and oxidizer segments of the chemical looping process (Zeng, L. *et al.*, 2018).

Non-oxygen-carriers such as carbonates, sulfides, and nitrides for carbon capture, desulfurization, and ammonia production deviated from conventional oxygen carriers to allow novel applications (Zeng, L. *et al.*, 2018). Super-dry reforming is one example of hybrid chemical looping with both oxygen-carrier (e.g., Fe<sub>3</sub>O<sub>4</sub>) and carbon dioxide-carrier (e.g., CaCO<sub>3</sub>), to convert CO<sub>2</sub> and CH<sub>4</sub> in a 3 by 1 molar ratio to H<sub>2</sub>O in the reducer unit (Buelens *et al.*, 2016). The work demonstrated that carriers can be used in tandem with other carriers (for a different purpose) to achieve broader applications. Also, the chemical looping concept can also be ingeniously exploited in a way without the use of an existing carrier. Hu and co-workers demonstrated that carbon deposits formed from dry reforming reaction (i.e., CO<sub>2</sub> + CH<sub>4</sub> ⇌ 2H<sub>2</sub> + 2CO) on the catalyst could serve as a transient looping material for NO reduction in a sequential step (i.e., C + xNO → CO<sub>x</sub> +  $\frac{x}{2}$  N<sub>2</sub>) (Hu *et al.*, 2021a). Henceforth, chemical looping technologies have high commercial-deployability value in the near future for efficient carbon capture, CO<sub>2</sub> utilization, or higher exergy efficiency with immediate CO<sub>2</sub> mitigation.

### 5.3. Cryogenic CO<sub>2</sub> capture

#### 5.3.1 Introduction for cryogenic CO<sub>2</sub> capture

Cryogenic CO<sub>2</sub> capture refers to a physical separation process operating at sub-zero temperatures, which induces the anti-sublimation and, or liquefaction of CO<sub>2</sub> from process streams that require CO<sub>2</sub> removal, often combustion flue gases. Prior to cryogenic CO<sub>2</sub> capture, the flue gas should be completely dehumidified to prevent extensive frost formation in the pipeline and the process vessels. The advantages of this separation process include little or no usage of chemicals, a high rate of recovery, and high purity of the CO<sub>2</sub> product. In general, cryogenic CO<sub>2</sub> capture is considered economically viable when the feed stream is appropriately conditioned (Berstad *et al.*, 2013), or when sufficient cold energy is available with fairly low cost.

The phase diagram for pure CO<sub>2</sub> is shown in Figure 5.14. With a triple point at -56.6 °C and 5.1 bar, cooling the process stream at CO<sub>2</sub> partial pressures below 5.1 bar would produce dry ice, while cryogenic capture with CO<sub>2</sub> partial pressure above 5.1 bar would produce liquid CO<sub>2</sub> upon direct cooling. To decarbonise flue gases from thermal powerplants with a typical CO<sub>2</sub> concentration of ca. 3-14%, depending on fuel sources, cryogenic carbon capture can be retrofitted as a post-combustion capture technology. For instance, to achieve 90% capture rate from a coal-fired powerplant (with a typical CO<sub>2</sub> concentration of 13 vol%), a maximum operating temperature of -120 °C is required at 1 atmospheric pressure. To capture CO<sub>2</sub> from the flue gases of natural gas-fired powerplants (e.g. NGCC powerplant)

that contains ~5 vol% CO<sub>2</sub>, a maximum operation temperature of -140 °C is required to achieve 90% capture rate.

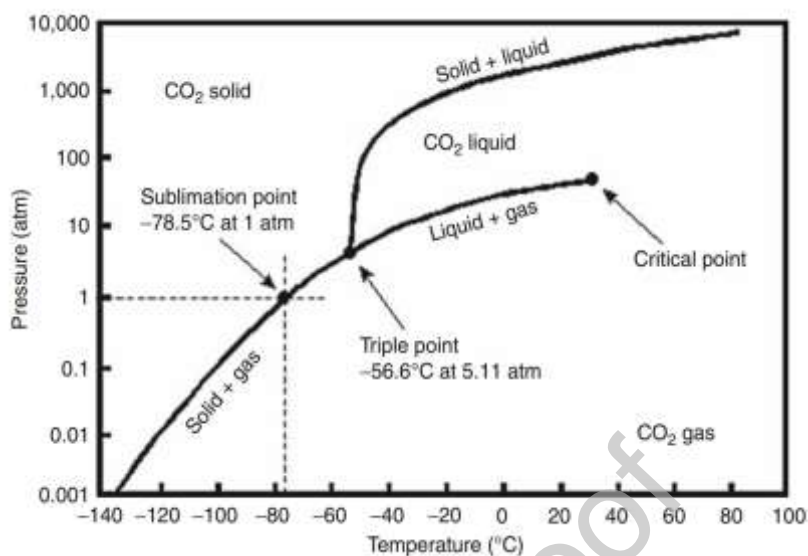


Figure 5.14. Phase diagram for pure CO<sub>2</sub>. Image reproduced from (McCullom, 2011).

### 5.3.2 Vapor-to-liquid cryogenic separation

Distillation is the most common type of separation technique. As shown in Figure 5.15, the traditional Ryan-Holmes process has been proposed for the purification of natural gas (Holmes and Ryan, 1982). Cryogenic distillation is a technique for separating biogas, natural gas and flue gas with careful consideration of CO<sub>2</sub> freezing temperature and pressure. The specific process of cryogenic distillation is as follows: The feed gas is pre-cooled and then chilled to a cryogenic temperature by a heat exchanger and enters the distillation column, which usually has a certain number of gas-liquid contact devices (e.g. trays or packing materials). After the distillation column, the raw gas is divided into two parts: the gas product at the top and the liquid product at the bottom of the column, respectively. Normally, in the biogas upgrading process, the methane after upgrading is discharged at the top of the column through a partial condenser, and the condensed CO<sub>2</sub> is passed through a reboiler at the bottom of the column to provide the heat required for evaporation. Eventually, the purified liquefied CO<sub>2</sub> is obtained through the separator.



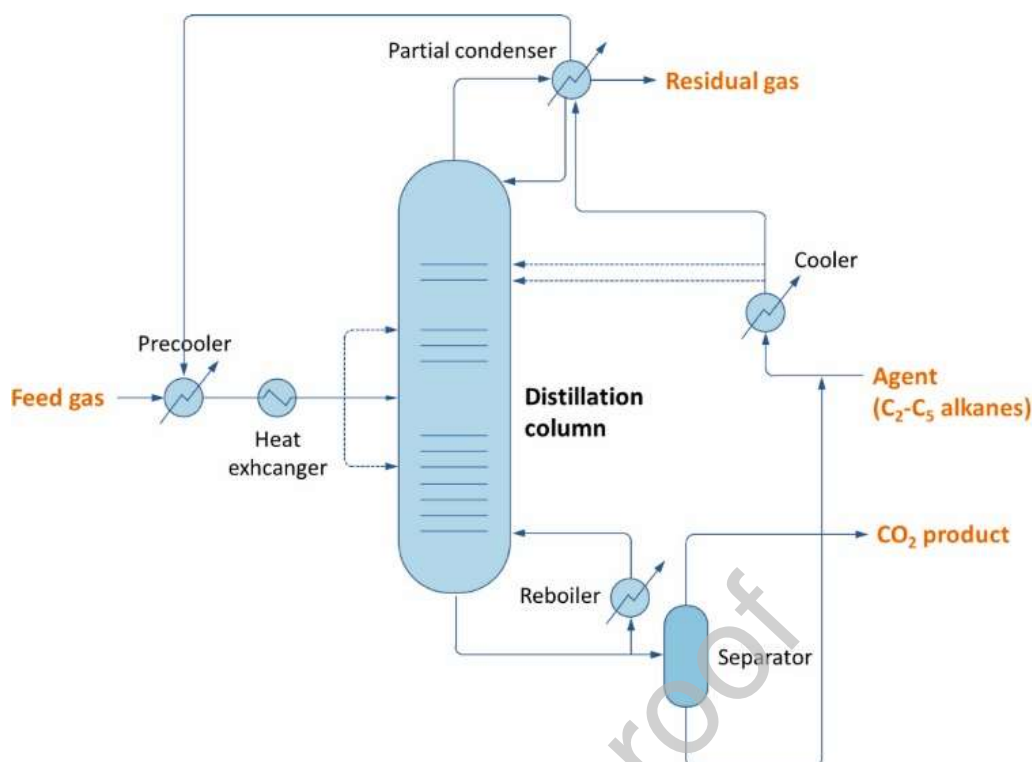


Figure. 5.15. The schematic flow diagram of Ryan Holmes process (Holmes and Ryan, 1982).

Avoiding CO<sub>2</sub> freezing out during the cryogenic distillation process is an important point worth noting. Yousef et al. investigate the effect of tray temperature on CO<sub>2</sub> freezing by pressurizing biogas to 4.9 MPa and cooling it to -61°C to obtain liquefied CO<sub>2</sub> at the bottom of the column and biomethane with 94.4% purity at the top of the column (Yousef et al., 2018a). Although widely used in industry, cryogenic distillation is still characterized by high energy consumption, often reaching more than half of the overall operating costs (Ebrahimzadeh et al., 2016; Li and Bai, 2012b). A dual column cryogenic distillation process was proposed to use the cold energy of biomethane to pre-cool the biogas, thus reducing energy consumption to 0.236 kWh/Nm<sup>3</sup> CH<sub>4</sub>, while the purity of biomethane was improved to 97.16% (Yousef et al., 2018b). Process intensification and mixed hybrid cryogenic distillation networks were explored in Maqsood's work, and the result shows a significant reduction in energy reduction and an enhancement in purification performance (Maqsood et al., 2014a; Maqsood et al., 2014b). In addition, a number of energy-efficient methods have been applied to the distillation process, such as recompression distillation (Kazemi et al., 2016), and heat integrated distillation column (Jana, 2016). In general, studies on cryogenic distillation focus on the reduction of energy consumption and the improvement of methane purity.

The controlled freeze zone (CFZ) is a solution based on single-tower cryogenic distillation for the removal of acidic impurities from natural gas because the presence of acidic gases (CO<sub>2</sub> and H<sub>2</sub>S) in natural gas has a negative impact on both its combustion and transportation (Rufford et al., 2012). In this technology, the cryogenic distillation column consists of three parts: a controlled freezing zone, an



upper distillation section and a lower distillation section. After dehydration and cooling, the feed enters the CFZ through a nozzle where the  $\text{CH}_4$  evaporates above due to the higher temperature above than below. The solidified  $\text{CO}_2$  is collected in the melt tray, and the temperature is kept moderately above the  $\text{CO}_2$  solidification temperature so that  $\text{CO}_2$  leaves at the bottom as a high concentration of liquefied  $\text{CO}_2$  (Michael E. Parker et al., 2011). The ExxonMobil Upstream Research Company developed this technology in 1983 and successfully demonstrated it in a commercial demonstration plant (Michael E. Parker et al., 2011). The project results show that the technology has a natural gas processing capacity of  $0.02 \text{ MNm}^3$  and a maximum operating capacity of  $28.3 \text{ MN}^3/\text{day}$ , and that most of the captured  $\text{CO}_2$  can be used for enhanced oil recovery (EOR). However, it should be mentioned that CFZ is not economical when there is a high content of ethane or higher hydrocarbon in the feed gas (Kelley et al., 2011).

### 5.3.3 Vapor-to-solid cryogenic separation

Antisublimation carbon capture technology is a vapor-to-solid cryogenic process in which  $\text{CO}_2$  is converted directly from the gas phase to the solid phase at atmospheric pressure (or below the three-phase point pressure). The process of antisublimation  $\text{CO}_2$  capture can be roughly divided into five steps (Pan et al., 2013): 1) chilling of flue gas to  $-40^\circ\text{C}$  and removal of moisture and other impurities, 2) heat exchange between rich and poor flue gases, 3) refrigeration integrated cascade (RIC) process, 4) freezing heat exchange of  $\text{CO}_2$ , 5) recovery of  $\text{CO}_2$ .

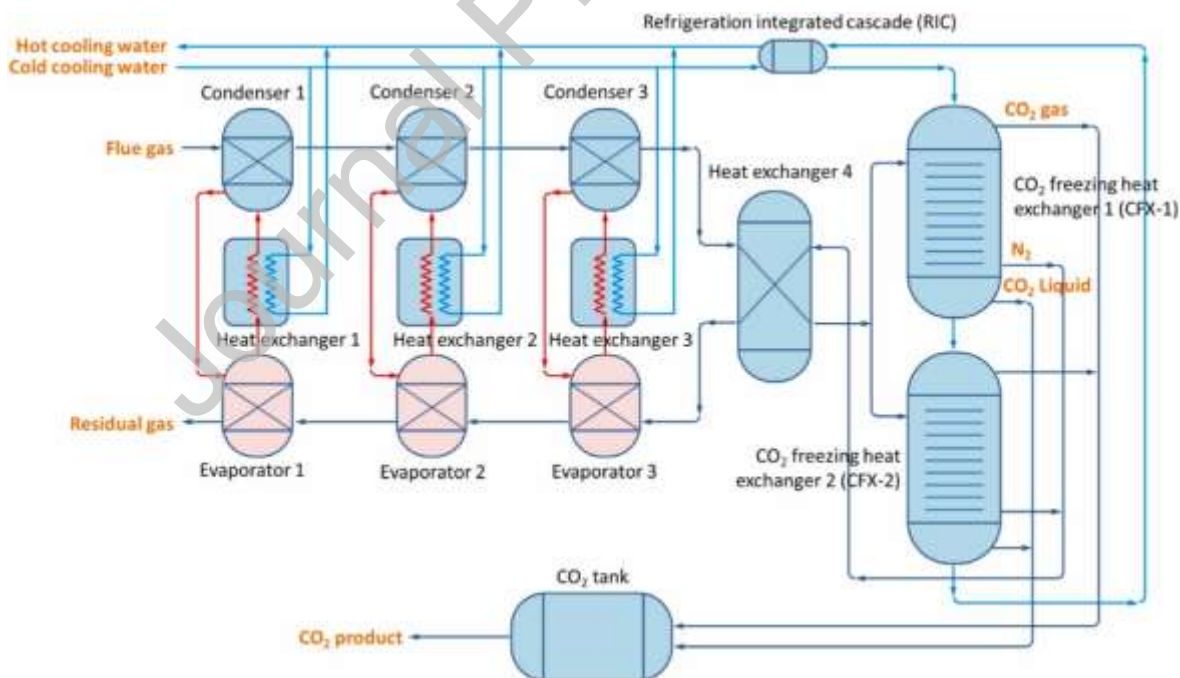


Figure. 5.16. Process flow diagram of the anti-sublimation  $\text{CO}_2$  capture process (AnSU) (Clodic et al., 2005b).

Clodic et al. used lab-scale tests for an antisublimation carbon capture process in a 660 MW boiler under flue gas conditions of 15.47% CO<sub>2</sub> concentration at 60 °C and 120 KPa, respectively (Clodic et al., 2005a; Clodic et al., 2005b). The result shows that the energy loss in total power efficiency is controlled between 3.8% and 7.2%, which is a relatively low level compared to other technologies (Clodic et al., 2005a). Schach et al. performed simulations by reproducing the gas-liquid and solid-liquid phase equilibrium models, where the flue gas was chilled to 155 K at 100 KPa, and the specific electric demand was 0.286 kWh/kgCO<sub>2</sub> (Schach et al., 2011). In this process, the carbon capture performance is further improved by improving the compression cooling cycle, and the power consumption is further reduced to 0.193 kWh/kgCO<sub>2</sub>, but the high equipment investment cost is a major bottleneck problem. A similar process mechanism was reported by Spitoni, where the optimized process was able to recover both liquid CO<sub>2</sub> and liquid biogas with an electrical power consumption of 1.093 kWh/kgCO<sub>2</sub>, which is 23% and 22% lower than the energy consumption levels of the alternative processes (Spitoni et al., 2019).

The CO<sub>2</sub> concentration in raw biogas has a significant effect on electricity consumption, which varies from 1.093 to 1.574 kWh/kgCO<sub>2</sub> when the CO<sub>2</sub> concentration is raised from 5% to 50%. CO<sub>2</sub> concentration also affects its freezing point during flue gas carbon capture. The freezing point of pure CO<sub>2</sub> gas is -78.5°C. However, it reduces to -99.3 °C when the CO<sub>2</sub> concentration is low to 15% that in the flue gas condition, undoubtedly increasing the overall energy consumption (Song et al., 2014). Therefore, low CO<sub>2</sub> concentration and high expected capture target increase the overall energy consumption of the antisublimation process in flue gas (Clodic et al., 2005a). For the carbon capture process in biogas, even though the overall energy consumption increased and the liquid biogas revenue decreased when the feed CO<sub>2</sub> concentration was in the worst condition (50% CO<sub>2</sub> content), the total energy cost increased up to 5% due to 50% increment of by-product (liquefied CO<sub>2</sub>) (Spitoni et al., 2019).

Generally speaking, the advantage of antisublimation carbon capture is that it has lower energy requirements in certain carbon capture scenarios (Clodic et al., 2005a; Spitoni et al., 2019). Another advantage of antisublimation technology is that the CO<sub>2</sub> thawed on the heat exchanger surface can be used for heat recovery, providing pre-cooling (Clodic et al., 2005b; Spitoni et al., 2019). At the same time, the latent heat during melting can be used to cool the refrigerant before evaporation (Clodic et al., 2005a). However, there are some limitations with the antisublimation process. For example, the moisture in the flue gas and raw biogas must be removed to less than 5 ppm to avoid clogging and other adverse effects. In addition, the choice of heat exchanger material is crucial to the effect of heat transfer efficiency after frosting. Finally, the concentration of CO<sub>2</sub> in the flue gas and raw biogas plays an equally important role in the evaluation of economic technology.

Stirling coolers are specific for their small size and low refrigeration temperature and can be used in the antisublimation capture process of flue gas and biogas. Song et al. designed a Stirling-based cryogenic

capture process for post-combustion flue gas (Song et al., 2012c). This carbon capture system consists of three parts. The pre-cooling tower removes the water from the flue gas to avoid blockage. The dehydrated flue gas is continuously cooled down to  $-99.3\text{ }^{\circ}\text{C}$  by cooling towers. The  $\text{CO}_2$  in the flue gas is frosted on the storage tower, the solid  $\text{CO}_2$  is collected by scrapers, and the remaining flue gas (the main component is  $\text{N}_2$ ) is discharged to the atmosphere. The parameter analysis, energy consumption, study and energy integration of the system are also reported in the relevant articles, where the energy consumption of the simulated flue gas carbon capture at the experimental scale is controlled below  $0.55\text{ MJ/kgCO}_2$  (Song et al., 2012a; Song et al., 2012b; Song, C.F. et al., 2017). However, the antisublimation carbon capture technology based on the Stirling cooler may be limited by the real flue gas conditions (impurities, high temperature, atmospheric volume, etc.), which is the focus of further research.

#### 5.3.4 Heat exchangers

Heat exchangers can be utilized to cryogenically antisublimation  $\text{CO}_2$  concentrations at atmospheric pressure for both high concentrations of  $\text{CO}_2$  found in the flue gas of post-combustion processes ( $\sim 13\text{-}15\%$ ) and for very low concentrations of  $\text{CO}_2$  found directly in the atmosphere ( $\sim 0.04\%$ ). While the idea of antisublimating  $\text{CO}_2$  directly from exhaust gas streams at atmospheric pressure using a cryogenic heat exchanger has been around for around 20 years, newer studies are beginning to explore thermally capturing  $\text{CO}_2$  directly from the atmosphere utilizing massive heat exchangers placed in arctic climates. Even though the two situations have drastically different  $\text{CO}_2$  concentrations, the technology needed to design cryogenic heat exchangers to antisublimation  $\text{CO}_2$  is analogous.

##### 5.3.4.1 Heat Exchangers: $\text{CO}_2$ Cryogenic Flue Gas Capture at Atmospheric Pressure

While considerable research to directly capture  $\text{CO}_2$  from the atmosphere via chemical- and adsorption-based methods (Deng, Y. et al., 2021; Lai et al., 2021; Sanz-Perez et al., 2016b) is ongoing, due to the immaturity of the technology, questions remain on how and at what cost these techniques will scale to the gigaton level (Baxter et al., 2009; Keith et al., 2006; Lackner et al., 2012). On the other hand, cryogenic  $\text{CO}_2$  removal is better understood, making potential faster scale-up possible. Cryogenic heat exchangers may be used for post-combustion carbon removal as well as for direct-air capture. Cryogenic  $\text{CO}_2$  removal directly from the atmosphere or from power plant effluent is based on the thermal sublimation of  $\text{CO}_2$  at very low temperatures, thus creating solid  $\text{CO}_2$  for disposal. Post-combustion carbon removal from power plant exhaust streams using cryogenic heat exchangers is a mature technology that has been utilized for some time. Recently, several researchers have been exploring potential direct air capture cryogenic  $\text{CO}_2$  heat exchanger designs for placement in Arctic and/or Antarctic climates (Boetcher, S. K. S. et al., 2020; Perskin et al., 2022; von Hippel, 2018).

Clodic and Younes (Clodic and Younes, 2003) investigated the energy consumption associated with antisublimating CO<sub>2</sub> from flue gas using cryogenic refrigeration at atmospheric pressure. Theoretically, they determined that more than 93% of a 15% flue-gas CO<sub>2</sub> concentration could be captured at plate-heat-exchanger surface temperatures between -99 and 122 °C. Since flue gases exit at high temperatures, above 85 °C, water must first be condensed out of the mixture, then, after the CO<sub>2</sub> “frosts” onto the surface, it must be removed by a “defrosting process,” so a multi-step process is needed cryogenically removing CO<sub>2</sub> from effluent at atmospheric pressure. Follow-on test-bench work by Clodic et al. (Clodic et al., 2005b) presented an experimental examination of the defrosting process. Water from flue gas, at 15% CO<sub>2</sub> concentration, is first removed to equal 0.01 g of water per kg of dry flue gas, by multi-stage condensation. The flue gas is then routed to a low-temperature evaporator, where the flue gas is cooled to -120 °C, energy recovery is utilized, and an energy cost is determined by process steps. Excluding other steps, such as pre-cooling to remove condensate, the energy cost of the cryogenic process was determined to be approximately 1.12 MJ/kg CO<sub>2</sub>, including a defrosting waste-energy recovery of around 0.26 MJ/kg CO<sub>2</sub>.

In the process proposed by Baxter et al. (Baxter et al., 2009), the flue gas is cooled, dried, and moderately compressed before it is cryogenically formed into a solid. In their process, with a concentration of CO<sub>2</sub> less than 15%, 99% of the CO<sub>2</sub> is antisublimated at -135 °C. The advantage of the system proposed by Baxter et al. (Baxter et al., 2009) is that it can be easily retrofitted to existing carbon removal systems. Energy cost per mass CO<sub>2</sub> was not reported.

Haddad et al. (Haddad et al., 2019) modelled the frost growth and formation of CO<sub>2</sub> cryogenically antisublimating on a flat plate from biogas and flue gas stream utilizing simplified heat and mass transfer equations. The heat and mass transfer equations include heat and mass transfer coefficients which are determined using existing correlations in the literature. The exact starting CO<sub>2</sub> concentrations in the biogas and flue gas streams are unclear. Utilizing parabolic trough solar collectors to power a vapor absorption refrigeration cycle, Sateesh et al. (Sateesh et al., 2021) tried to capture post-combustion CO<sub>2</sub>. The authors assumed a flue-gas composition of 15% CO<sub>2</sub>, 75% N<sub>2</sub>, and 10% H<sub>2</sub>O and claimed a 100% CO<sub>2</sub> capture rate at an energy penalty of 1.25 MJ/kg of CO<sub>2</sub>.

#### 5.3.4.2 Heat Exchangers: Cryogenic Direct Air Capture of CO<sub>2</sub>

Pure CO<sub>2</sub> at 1 atm pressure antisublimates (changes phase from vapor to solid) at -78.5 °C. However, for CO<sub>2</sub> in the atmosphere, which has partial pressures much below 1 atm, a much lower temperature is required to extract solid CO<sub>2</sub> from power plant streams or the air. Power plant exhaust CO<sub>2</sub> concentrations can reach up to 14%. Recent measurements of the concentration of CO<sub>2</sub> in the atmosphere at the Muana Loa Atmospheric Baseline Observatory have reached 419 ppm (NOAA, 2022), which equals a partial pressure of 0.000419 atm, which corresponds to an antisublimation temperature of -141.5 °C. However, it should be noted that the CO<sub>2</sub> continues to antisublimates, and the partial

pressure also decreases, which corresponds to a decrease in antisublimation temperature. Temperatures as low as  $-162\text{ }^{\circ}\text{C}$  may be required to antisublime 99% of the  $\text{CO}_2$  from the atmosphere. Air is primarily made up of  $\text{N}_2$  and  $\text{O}_2$ . At 1 atm,  $\text{O}_2$  and  $\text{N}_2$  begin to liquefy at  $-181\text{ }^{\circ}\text{C}$  and  $-195.8\text{ }^{\circ}\text{C}$ , respectively. Since the partial pressures of those components in the air are less than 1 atm, the liquefaction temperature will be even lower, allowing  $\text{CO}_2$  to be cryogenically removed before liquefying  $\text{O}_2$  or  $\text{N}_2$ .

In the last decade, due to the urgency of the global  $\text{CO}_2$  problem, research has emerged on thermally capturing  $\text{CO}_2$  directly from the environment via antisublimation using a cryogenically cooled plate heat exchanger. The heat exchanger would be a part of a  $\text{CO}_2$  deposition plant placed in Antarctica. The cold-air temperatures in Antarctica allow the inlet temperature to be as low as possible and closer to the  $\text{CO}_2$  antisublimation temperature, thus reducing the cooling the sensible load needed to reach that temperature. Another advantage of Antarctica is that at those low temperatures, the air is virtually completely dry. Agee et al. (Agee, E. et al., 2013) were one of the first to conceptually propose such a system, referring to it as a  $\text{CO}_2$  “snow” maker. An initial laboratory prototype was analyzed by Agee and Orton (Agee, E. M. and Orton, A., 2016). The prototype was a benchtop-scale sequestration chamber situated with an aluminum plate interfaced with  $\text{LN}_2$ . This experiment showed proof-of-concept, but the authors did not perform an in-depth energy analysis.

A systems-level energy analysis for a  $\text{CO}_2$  deposition plant hypothetically placed in three candidate arctic climate scenarios (Snag, Yukon, Oymyakon, Russia, and Vostok Station, Antarctica) was performed by von Hippel (von Hippel, 2018). Using a simplified energy balance, von Hippel determined that  $\text{CO}_2$  heat exchanger antisublimation in an arctic environment may be competitive with other technologies. Follow-on work, using a more sophisticated thermodynamic model and investigating more cases, including exploring pre-compression, was conducted by Boetcher et al. (Boetcher, S. K. S. et al., 2020) and Perskin et al. (Perskin et al., 2022). There, the energy performance of a waste-heat (or better, a “waste-cool”) precooler heat exchanger attached to the antisublimation heat exchanger was evaluated. It was found that this type of system could theoretically antisublime 90% of 405 ppmv concentration ( $\sim 0.04\%$ ) atmospheric  $\text{CO}_2$  for as low as 133 MJ/kg in an arctic environment.

### 5.3.5 Cryogenic liquids

In addition to heat exchangers, cryogenic liquid as a cold source can directly take away the heat of flue gas containing  $\text{CO}_2$ , resulting in the solidification of  $\text{CO}_2$ . Then, the mixture liquid slurry of  $\text{CO}_2$  and the cryogenic liquid goes through a filter to produce a  $\text{CO}_2$ -rich product (Jensen et al., 2015). Generally, the vapor pressures of cryogenic liquids should be low in order to reduce losses during evaporation. Fazlollahi et al. have chosen isopentane to prevent  $\text{CO}_2$  solidification on the surfaces, which would end the process (Fazlollahi et al., 2015). In Jensen’s work, the heat duty is provided by an internal  $\text{CF}_4$

refrigeration and an external cooling loop of CH<sub>4</sub>, and the result shows that the parasite power loading is about 15% (82.6 MW<sub>e</sub>) and the energy consumption is 0.74 MJ<sub>e</sub>/kgCO<sub>2</sub> (Jensen et al., 2015).

In most carbon capture processes, the biggest challenge is the high energy consumption. For the cryogenic carbon capture process, the waste cold energy like LNG (liquefied natural gas) is a promising approach to reduce the energy consumption by a thermal process, an inertial carbon extraction system or an external cooling loop. A hybrid cryogenic carbon capture process with an external cooling loop (CCCECL) was proposed (Baxter et al., 2009; Jensen et al., 2015). Briefly, the CCCECL system concludes: 1) dehydrated and cooled flue gas was sent from the system to the CCCECL process, 2) the flue gas was compressed and chilled to a temperature above the solidification of CO<sub>2</sub>, 3) the gas was expanded to be further chilled, 4) an amount of CO<sub>2</sub> was precipitated, 5) the CO<sub>2</sub> was pressured and reheated via the inlet gases, 6) the liquid CO<sub>2</sub> product was achieved for further utilization and the N<sub>2</sub>-rich exhausted gas was discharged. Some configurations of the CCCECL process can store energy as LNG (Jensen et al., 2015). In such system, the refrigerant was regenerated during low-demand periods, and then it was used to drive the cryogenic carbon capture process during peak demand periods. As a result, the parasitic load to the grid reduces. Besides, renewable intermittent power sources could be integrated with conventional power generation systems via CCCECL, resulting in a low energy intensive compared to the conventional capture process (0.98 MJ<sub>e</sub>/kgCO<sub>2</sub>) (Safdarnejad et al., 2015).

### 5.3.6 Packed beds

Packed beds have been worked as a heat transfer surface for the cryogenic carbon capture process that is usually filled with cold bed materials like steel monolith structure (Tuinier et al., 2011b). The capture process follows the steps: 1) chilled N<sub>2</sub> stream is sent to precool bed material, 2) the N<sub>2</sub> steam is stopped, and the flue gas is sent to cryogenic packed bed, 3) CO<sub>2</sub> frost on the surface of bed materials till saturation, 4) a CO<sub>2</sub> frost front happen through the column, 5) a regeneration step is required when the packed column is saturated. The advantages of a cryogenic packed bed are that both CO<sub>2</sub> and H<sub>2</sub>O can be separated from flue gas simultaneously via the difference of their dew and solidification points and the cold energy can be provided by LNG (Tuinier et al., 2010). Tuinier proposed a dynamically cryogenic packed bed, and the results show that the low volume fraction of frosted CO<sub>2</sub> leads to a low requirement of the elevated pressure value (Tuinier et al., 2011b). This indicated that the pressure drop and clogging phenomenon are mitigated in the cryogenic packed bed process. Apart from the carbon capture process in flue gas, cryogenic packing is also applied to the biogas upgrading process (Tuinier and van Sint Annaland, 2012). A novel cryogenic packed bed has been proposed for biogas treatment, and the result shows that the purity and recovery of biomethane products are higher. Meanwhile, the bed capacity is much higher (350.2 kg CH<sub>4</sub> h<sup>-1</sup> m<sup>-3</sup> packing), and the energy consumption is lower (2.9 MJ/kgCH<sub>4</sub>), compared to the conventional vacuum pressure swing adsorption process (Tuinier and van

Sint Annaland, 2012). Moreover, the removal of H<sub>2</sub>S content in raw biogas can be simultaneously achieved when the initial cryogenic packed bed temperature as low as -150°C (Abatzoglou and Boivin, 2009). However, this may lead to an augment in operating cost on required cold energy. Fortunately, the cold energy required in the cryogenic packed beds process may be provided by LNG, making it competitive (Abatzoglou and Boivin, 2009). Moreover, the thermal insulation of cryogenic packed bed is another challenge that should be taken into consideration to reduce latent heat loss.

### 5.3.7 Compression

Compression is an important part in the cryogenic carbon capture process. The vapor-to-liquid and vapor-to-solid routes are determined by the pressure and cryogenic temperature of the carbon capture process. In Baxter's work, flue gas was compressed to 5-7 bar before cooling and chilled and then was expanded to form CO<sub>2</sub> solidification, which was called cryogenic carbon capture with compressed flue gas (CCC-CFG) (Baxter et al., 2009). Similarly, in the cryogenic distillation process, the feed gas is compressed to 4.9 bar via four stage compressor and then cooled to 35 °C by water (Yousef et al., 2018a, b, 2019). Maqsood et al. compared the effect of pressure on liquid and solid formation during cryogenic separation. The result showed that the vapor-solid region decreased with the pressure (-60 to -98 °C for 20 bar and -62 to -75 °C for 40 bar) and the CH<sub>4</sub> purity was higher at 40 bar under the same cryogenic temperature (Maqsood et al., 2017).

The energy consumption in the cryogenic process is one of the main challenges for the scale-up application of cryogenic carbon capture processes. In the cryogenic distillation process, the power penalty for the compression process accounts for 43.1-50.9% of the total biogas upgrading energy consumption, and the energy consumption for CO<sub>2</sub> capture is 1.66-1.79 MJ/kgCO<sub>2</sub> (Yousef et al., 2018a, b). Energy saving technologies have been applied to cryogenic carbon capture processes. Compared with the conventional distillation carbon capture process, more than 34% energy reduction was observed when the multibed hybrid network was introduced into cryogenic distillation for the natural gas sweetening process (Maqsood et al., 2014c). Moreover, the energy consumption can be further reduced when the capture process is applied with intensified side mounted and integrated switch cryogenic antisublimation bed, resulting in a 69.24% profit increment (Maqsood et al., 2017). Moreover, Pellegrini et al. compared three cryogenic purification technologies for natural gas upgrading, including the dual pressure cryogenic distillation process, Ryan-Holmes and antisublimation process (Pellegrini et al., 2018). Compared with Ryan-Holmes process, the mechanical power consumption of dual pressure cryogenic distillation is higher because the raw biogas required to be compressed to 50 and 40 bar, and for antisublimation process, 99.84% of the energy requirement is the cooling duties consumption (Pellegrini et al., 2018). Up to now, the reduction of energy consumption in the cryogenic carbon capture processes requires further development and research to be applied in practical sceneries.

### 5.3.8 Life cycle assessment of cryogenic CO<sub>2</sub> capture

An overview of cryogenic-based carbon capture pathways and technology challenges, which mean the extreme utilization of cold energy and energy consumption barriers, is provided by Shen et al. (Shen, M.H. et al., 2022). A recent review paper by Song et al. (Song et al., 2019b) focused on cryogenic carbon capture technology progress, including cryogenic system structure and optimal system parameters, which revealed that cryogenic carbon capture technology provided remarkable cost and efficiency benefits. However, most of the studies involved cryogenic carbon capture considering its energy consumption (Esfilari et al., 2018), technical feasibility (Naquash et al., 2022) and economic performance, without taking its carbon abatement and other environmental impacts into consideration (Markewitz et al., 2013). Only a few studies provided a far-reaching insight into the life-cycle environmental impacts or life-cycle cost analysis of systems combined with cryogenic technologies and other carbon capture pathways, which shows a possibility to be deployed in biogas upgrading (Hiloidhari and Kumari, 2021), air separation unit (Schreiber et al., 2013; Troy et al., 2016; Zhang, X.P. et al., 2014), natural gas purification (Rocco et al., 2019) and biomass-coal co-gasification (Esfilari et al., 2018). Herein, all selected LCAs report significant carbon capture processes with regard to cryogenic technologies. However, global warming potential (GWP) can hardly be compared, since each cryogenic LCA exhibits specific system boundary and functional unit, use different life cycle inventory source and database, such as Ecoinvent, Simapro and Gabi. The uniform and comprehensive framework principles should be further investigated and paid more attention to, including system boundaries, functional units and inventory analysis.

**System boundaries:** System boundaries vary to different extents for all kinds of cryogenic capture systems, but it is necessary to take some vital processes into consideration, such as raw material production and transportation, energy conversion, carbon capture and storage. Biogas-related cryogenic systems usually contain the whole supply chain of biogas from cradle to gate, which includes biomass feedstocks cultivation, harvesting and transportation processes, and bioenergy conversion processes (Florio et al., 2019). However, there are still few studies that considered the product end-use process (Adelt et al., 2011). Cryogenic air separation units are the most common forms while talking about cryogenic carbon capture, which can be deployed in steel production, liquefied natural gas (LNG) production and combined with membrane capture. Some studies have taken the whole life cycle of air separation and carbon capture processes into consideration, which included up-stream processes (O<sub>2</sub> production process, MDEA and membrane production), main processes (steel production and CO<sub>2</sub> capture), and down-stream processes (CO<sub>2</sub> transport and storage), but not considering the end-of-life processes of different equipment (Luca and Petrescu, 2021). More comprehensive frameworks have considered waste treatment processes in the life cycle of IGCC and oxy-fuel plants (Schreiber et al., 2013; Zhang, X.P. et al., 2014).



**Functional unit:** Per unit of product (biogas, biomethane, electricity, heat etc.) produced (Adelt et al., 2011; Florio et al., 2019) or per unit CO<sub>2</sub> removal from biogas (Starr et al., 2012) are usually selected as functional units of biogas upgrading systems. Electricity or heat supply is selected to be functional units since air separation is usually connected with generation processes.

**Environmental categories:** Most of the LCAs of cryogenic-related systems considered ReCiPe 2016 midpoint (H), CML 2001 and Eco-indicator 99 Hierarchist as the impact assessment methods with various impact categories, among which GWP is the most cared one. Hence, it seems that there is an agreement to consider multiple environmental impact categories for the assessment of cryogenic systems.

Cryogenic carbon capture technologies have been studied for thermodynamic performance and technical feasibility with a limited understanding of overall environmental implications. Because of the lack of large-scale deployment or pilot demonstration, there is a huge knowledge gap in the availability of operation parameters and related energy/resource consumption data on cryogenic carbon capture, which is the direct reason for the shortage of LCAs about cryogenic carbon capture. This part aims to conclude the LCA of the cryogenic carbon capture situation to fully understand the environmental benefits and potential trade-offs associated with cryogenic carbon capture technologies. Based on the available body of cryogenic carbon capture LCA literature, we conclude that existing LCA results for most cryogenic technologies are not representative of cryogenic carbon capture schemes since these studies are all related to cryogenic air separation or biogas upgrading processes. However, a high-purity CO<sub>2</sub> product in either a compressed liquid or solid phase and utilization of organic solvents and sorbents is the main advantage of cryogenic carbon capture technologies, indicating the environmental benefit potential for ecosystems. Furthermore, due to dramatic temperature variations and high-pressure conditions, large exergy losses exist during the whole capture process. Therefore, more efficient cryogenic carbon capture option designing will be an inevitable challenge for commercial applications. In order to explore more possibilities for the application of cryogenic carbon capture technologies, life-cycle environmental or cost assessments should be deployed under comprehensive and suitable evaluation frameworks. Moreover, life cycle environmental assessment should also quantify the environmental burden shift to reveal more realistic environmental benefits connecting with various ecologic co-benefits and compare with different conventional CCS options.

#### 5.4 Process Intensification

Currently, the improvement of carbon capture efficiency generally needs high investment, including more expensive materials and increasing operating cost. This scenario has sent researchers fleeing to the application of process intensification (PI) techniques in the field of carbon capture for saving energy

and decreasing consumption. For example, in the commonly alkanolamine method, the chemical reaction is fast while the efficiency of carbon capture is limited by the gas-liquid/gas-solid mass transfer in most cases. Therefore, it is promising to break through the limitation of low-speed heat and mass transfer via drastic improvement of equipment and process efficiency. According to the principle of PI (Van Gerven and Stankiewicz, 2009), the intensified strategies for carbon capture can be classified into four domains: spatial, functional, energy, and temporal. Specifically, the PI of carbon capture can be achieved by (1) developing novel structures to enhance mass transfer; (2) combining a variety of technologies to maximize the synergistic effect; (3) designing rational process to minimize the energy cost; and (4) shortening the process time to improve the whole efficiency.

#### 5.4.1 Spatial domain: Novel structure for ample transfer

With the aim to enhance mass transfer, many researchers tried to optimize the internal structure of the absorption columns, such as the geometry of aperture and baffles (Garcia-Abuin et al., 2010), the structure of packing (Smith et al., 2015), etc. and adjust the operating conditions, including gas velocity, gas-liquid ratio, and liquid height in the column (Yan et al., 2019). The experimental results of these studies showed that installing baffles and using smaller apertures, lower sorption temperature, higher regeneration temperature, and lower regeneration pressure exerted positive effects on CO<sub>2</sub> capture. The principle of above studies is to increase gas-liquid mass transfer coefficient by enhancing fluid turbulence or enlarge the gas-liquid contact area by changing the fluid flow patterns, including the deformation, splitting, stretching and breakup of bubbles (Yin et al., 2022).

With the idea of intensifying gas-liquid mass transfer, microchemical technology has recently attracted great attention in the field of CO<sub>2</sub> capture due to the various advantages including efficient mass and heat transfer, safer operation, higher integration and superior controllability. By performing the processes in the scale of sub-millimeter, micro-reactors can dramatically intensify the gas-liquid mass transfer. As reported, the volumetric mass transfer coefficient in the micro-reactor can be several orders of magnitude higher than that in traditional gas-liquid vessels, such as plate column, packed column and stirred tank (Ganapathy et al., 2016). For example, Yue et al. (Yue et al., 2007) investigated the absorption of pure CO<sub>2</sub> in a 667  $\mu\text{m}$  channel. The experimental demonstrated an enhancement in mass transfer characteristics, as compared to conventional absorption systems. A comparison of mass transfer performance among different gas-liquid contactors reveals that the gas-liquid microchannel contactor of this study can provide at least one or two orders of magnitude higher liquid side volumetric mass transfer coefficients and interfacial areas than the others. Besides, Ganapathy et al. (Ganapathy et al., 2015) compared a microreactor to most conventional absorption systems including packed columns, plate columns, bubble columns, tube reactors, bubble reactors and venturi reactors. The experimental results showed that the interfacial areas and liquid-side volumetric mass transfer coefficients achieved

using the present reactors are between 1 and 4 orders of magnitude higher than the mentioned conventional macroscale gas–liquid absorption systems, which is considered an indication of the high level of process intensification and enhancement that can be achieved by using microreactors. The high mass transfer efficiency of micro-reactors is bound to reduce the operating consumption of carbon capture. Shao et al. (Shao et al., 2010) investigated the influence of channel length of micro-reactors on their absorption efficiencies of CO<sub>2</sub> and found that when the channel length increased by 100%, the mass transfer coefficient was higher by 290%, improving utilization of the absorption capacity of the amine solution for a given reactor volume.

Although microchemical technology has exhibited promising performance in carbon capture, the industrial application of this method still faces many obstacles. First, smaller diameters yield substantial enhancement in mass transfer characteristics, while the pressure drop is also considerably higher (Niu et al., 2009). For the various microchannel contactors tested, an enhanced mass transfer rate was observed for smaller microchannel contactors. The shortening of the diffusion length from channel size reduction is beneficial to achieve fast mass transfer rates, and this is the size effect of mass transfer (Ganapathy et al., 2014). However, the rapidly increasing pressure drop limits the application of micro-reactors for large handling capacity. Besides, the strong interfacial force makes it very difficult to operate counter-current at microscale, not only for absorption but also for stripping, distillation and extraction (Wang, Jiashuo et al., 2021), which limits the design of more rational structures. Therefore, in order to better utilize the advantages of microscale to carbon capture, the micro-channel should be optimally designed to ensure the inherently higher surface area to volume ratio of these systems substantially while keeping the pressure drop at moderate levels.

#### **5.4.2 Functional domain: Hybrid techniques for maximal synergism**

Apart from the optimization of reactor structures, the combination of two or more standalone CO<sub>2</sub> capture technologies, named as hybrid processes, has also provided novel ideas to overcome the challenges of standalone CO<sub>2</sub> capture technologies due to the potentially high capture efficiency and low energy requirement. The hybrid processes usually consist of two or more conventional technologies (*i.e.* absorption, adsorption, membrane, cryogenic and hydrate, *etc.*). The integration of different technologies may be superior to the standalone process and avoid their disadvantages. Currently, there are four types of hybrid carbon capture technologies, including (1) absorption-based processes, including membrane contactor (Zhao, S. et al., 2016) and absorption-adsorption (Breault et al., 2016); (2) adsorption-based processes, including adsorption-catalysis (Marono et al., 2015) and adsorption-hydrate (Yang, M. et al., 2014); (3) membrane-based processes, including membrane-cryogenic (Burdyny and Struchtrup, 2010), and membrane-absorption (Kundu et al., 2014); (4) low-

temperature-based processes, including cryogenic-hydrate(Suroutseua et al., 2011) and low temperature-absorption(Hanak et al., 2015b).

Appropriate hybrid CO<sub>2</sub> capture strategy can be a potential alternative of exiting standalone processes in terms of efficiency, as screening of suitable hybrid carbon capture processes highly depends on the properties of feed gas (e.g. CO<sub>2</sub> concentration, gas temperature and pressure, *etc.*), the requirement of product (e.g. purity, *etc.*) and the availability of the capture equipment. In addition, CO<sub>2</sub> recovery and energy consumption are also significantly affected by the source of CO<sub>2</sub> emission when using different capture technologies(Song et al., 2018b). For example, Song et al.(Song et al., 2018a; Song, C. et al., 2017) employed a membrane-cryogenic hybrid system to CO<sub>2</sub> capture and exhibited that compared to the standalone methods, hybrid processes showed the superiority not only in CO<sub>2</sub> recovery and energy penalty, but also in the installation investment.

The synergistic effect existed in the hybrid processes can no doubt lead to energy saving and consumption reduction. Liao et al.(Liao et al., 2019) designed and optimized a hybrid membrane-cryogenic system for both pre-combustion and post-combustion carbon capture, which reduced 33% of operating cost and 28% of total annualized cost. Besides, Scholes et al. (Scholes et al., 2013) postulated a post combustion capture process equipped with three membrane stages and a cryogenic separation to ensure the feed burner air supply is not oxygen-deficient. By employing this strategy, \$43/ton CO<sub>2</sub> can be avoided, and the carbon capture cost of membrane contactor technology can be decreased to \$48/ton CO<sub>2</sub> with over 90% CO<sub>2</sub> recovery and 97% CO<sub>2</sub> purity.

Although increasing interest in the CO<sub>2</sub> capture by hybrid processes has been attracted in recent years and exciting results have been reported, amount of existing research is undertaken by simulation or lab-scale, because the overall cost of the hybrid process has to be taken into consideration in terms of capital costs, operating costs and maintenance costs. Most costs are very site-specific, and for a full-scale system these costs strongly depend on properties (e.g. CO<sub>2</sub> concentration, flow rate, temperature and pressure) of feed gas, the configuration of separation units, as well. Meanwhile, the concentration of CO<sub>2</sub> is limited to higher than 15%, and the capture condition is also moderate than that in industrial emissions. In addition, the hybrid processes may result in the more stringent requirements on materials and equipment, such as cold resistance of membrane in the membrane-cryogenic system, and poison resistance of membrane in the adsorption-catalysis-membrane hybrid system etc. To overcome these problems, it is essential to understand the interactions between membranes and absorbents/solvents and develop novel membranes and green solvents for hybrid processes, which requires further investigation.

### 5.4.3 Energy domain: Process optimization for low cost

From the perspective of energy domain, it is necessary for industrializing carbon capture technologies to design rational processes via the combination of flowsheet design and rigorous optimization, with the aim to lower the energy cost and higher the environmental performance. In order to deliver better performance in recovery rates, energy consumption and solvent slip, the design and improvement of a stand-alone CO<sub>2</sub> capture flowsheet generally follows these steps: (1) Design equilibrium-based process flowsheet to obtain process specifications; (2) Conduct sensitivity analysis on the process variables to obtain process model and variables; (3) Perform multi-objective optimization to obtain the results of energy and mass balances; (4) Calculate equipment dimension and process productivity(Sharma et al., 2016). These processes are always achieved by using commercial software packages, including Aspen Plus, HYSIS, or gPROMS, because these tools contain the required physicochemical models and can provide property databanks for numerical calculation.

Different with traditional flowsheets design, the decision makers in the current society focus more on emission reduction efficiency, energy penalty, and carbon cyclic capacity among different solvents, rather than just energy consumption (Ji et al., 2021). However, the multi-objective problem leads to a time-consuming design process because of the highly non-linear nature of the model equations and the high complexity of the processes. In this case, many researches abstracted this problem as a Mixed Integer Non-Linear Problem (MINLP) to assist them in the selection of optimal retrofitting options of CO<sub>2</sub> capture technologies. Take a design process for a coal-fired plant as example, post-combustion capture by monoethanolamide (MEA) scrubbing is currently the commercial technology used worldwide, while oxy-fuel combustion is still on an earlier stage of development(Zhu and Fan, 2011). Many preliminary studies have shown that the latter technology is technically and economically feasible for retrofitting existing coal-fired power plants(Hu and Yan, 2012). In order to evaluate these two techniques, Bravo et al.(Bravo et al., 2021) considered economic and environmental criteria at the early stages of the process development and conducted multi-objective optimization to address the trade-off problems between different economic and environmental indicators. The numerical results indicated that carbon capture with MEA scrubbing performs better for soft environmental limits while oxy-fuel combustion is the preferred choice when more stringent environmental limitations are considered.

However, the optimal design of carbon capture processes is always time-consuming due to the highly non-linear nature of the model equations and the high complexity of the processes. Besides, the convergence management of the process simulations limits the combined flowsheet design. Hence, novel computing methods should be further developed for economy-environment multi-objective problems.

#### 5.4.4 Temporal domain: External-field intensification for high efficiency

The traditional method of carbon capture suffers from severe corrosion problems, considerable energy loss, high sorbent cost, lower gas–liquid interfacial surface area, and ineffective regeneration (Bhown and Freeman, 2011). In the temporal domain, the principles of PI indicate that manipulation of the time scales may mean for instance bringing molecules under extreme temperature conditions for a very short time, which can shift the process beyond the equilibrium limitation, or it can improve heat management in multifunctional systems. For example, the regeneration of absorbents used for capture CO<sub>2</sub> usually employs temperature-swing adsorption (TSA) but the regeneration time usually is more prolonged due to slow heating and cooling of the adsorbent during TSA, thereby increasing the adsorbent inventory and investment costs (Leung et al., 2014). Thus, alternative (e.g., electrical) heating methods are being explored to develop an energy-efficient and rapid TSA cycle process for carbon capture. Alternative electrical heating methods for TSA include Electric Swing Adsorption (ESA), which uses the Joule Effect (Zhao, Q. et al., 2017), induction heating (Sadiq et al., 2016), and microwave heating (Li, Hong et al., 2019). These techniques could offer distinct advantages over the more traditional adsorbent regeneration techniques in terms of energy efficiency, faster heating rate, and simple and compact equipment designs.

Among the above novel heating methods, microwave heating can directly deliver energy to the targeted composition; this selective heating characteristic leads to the formation of local overheating domains in microscopic scale (called “hot spots”), which has been directly observed in the previous study (Zhao et al., 2022b). This phenomenon can be used to accelerate desorption of CO<sub>2</sub> absorbent. For instance, regeneration of a zeolite 13X under microwave irradiation for acetone and toluene capture resulted in higher desorption rates when compared to conductive heating regeneration (Cherbanski and Molga, 2009). Besides, Yassin et al. (Yassin et al., 2021) reported a similar result in CO<sub>2</sub> capture from flue gases using pelletized activated carbons. The acceleration of absorbent regeneration in the above studies can be ascribed to the formation of hot spots, inducing a much locally higher temperature over the surface of absorbents than the overall temperature in the equipment (Yang, Z. et al., 2017). Apart from the selective heating characteristic, the rapid heating rate of microwave irradiation can also lead to the atomization of liquid droplets and bubble-enhanced flow, enhancing the gas-liquid mass transfer during desorption (Liu, K. et al., 2021; Zhao et al., 2021).

Although microwave irradiation has shown great potential to accelerate the desorption process and therefore decrease the solvents amount, the further applications of microwave irradiation to absorbent regeneration processes in industrial scale should consider the uneven heating problems caused by the inhomogeneous electromagnetic field distribution (Shen, X. et al., 2022; Zhao et al., 2022a). Therefore, the interaction between microwaves and absorbents/solvents should be further investigated before developing microwave-assisted desorption techniques.

### 5.5 Bio-Energy with Carbon Capture and Storage (BECCS)

Bio-Energy with Carbon Capture and Storage (BECCS) is a special technology in CCS, which can capture and store CO<sub>2</sub> generated in the process of biomass combustion or conversion (Figure 5.16)(Almena et al., 2022). The difference with traditional CCUS technology is that it can achieve negative emissions. The idea is to use plant photosynthesis to convert atmospheric CO<sub>2</sub> into organic matter and store it as biomass, which can be burned directly to generate heat or chemically synthesized into other high-value clean energy sources. Most climate change mitigation pathways which limit global warming to 1.5 °C or 2 °C rely on negative emission technologies, in particularly BECCS(Fajardy et al., 2021).

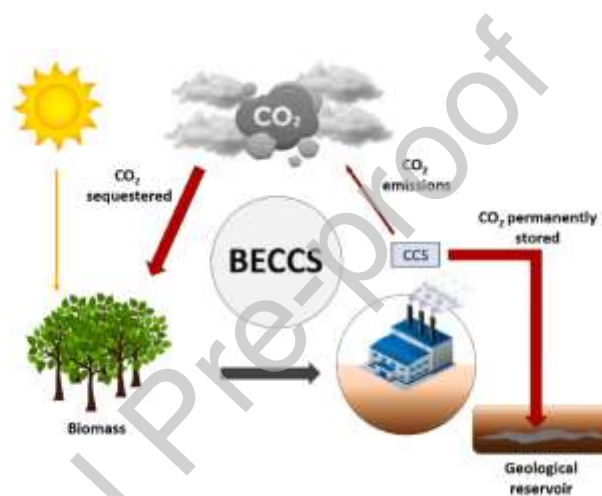


Figure 5.16 The carbon flow of BECCS. When BECCS systems are employed, a negative carbon flow from the atmosphere into storage is created.(Almena et al., 2022)

The development of BECCS technology can solve the problem of harmless and reduced treatment of all kinds of organic waste in urban and rural areas. If biomass waste is not effectively used, under the condition of natural decomposition, methane and other gases with stronger greenhouse effect will be released. Under the general background of comprehensively promoting the rural revitalization strategy, the future development of biomass energy will need to take a road of "agriculture-environment-energy-agriculture" green and low-carbon closed cycle development. BECCS plays an important role in both power generation and non-electricity utilization, and promotes the overall improvement of the energy structure of villages and towns.

### 5.5.1 Biomass power generation

Biomass power generation is the largest and most mature modern biomass energy utilization technology. The number of biomass power generation projects that have been put into operation from 2016 to 2020 are shown in Figure 5.17. China is rich in biomass resources, mainly including agricultural waste, forestry waste, livestock and poultry waste, municipal solid waste, organic wastewater and waste, etc. The total amount of biomass resources for energy is equivalent to about 460 million standard coal. Biomass power generation technology can be divided into three categories according to the working principle: direct combustion power generation technology, gasification power generation technology and coupled combustion power generation technology.

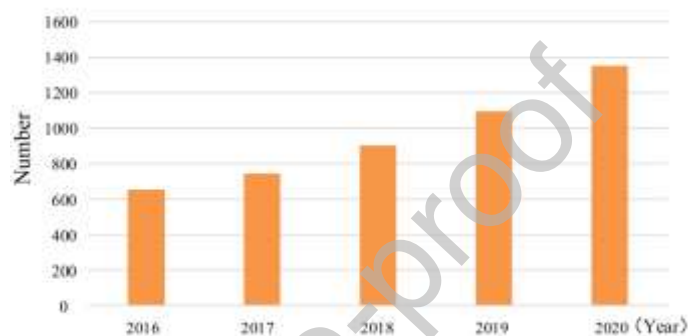


Figure 5.17 Number of biomass power generation projects in operation (Guo, H. et al., 2022).

Direct combustion of biomass for power generation is very similar to coal-fired boilers in principle. It is to add biomass fuel into appropriate steam boilers for biomass combustion, convert chemical energy in biomass fuel into internal energy of high temperature and pressure steam through high temperature combustion process, convert into mechanical energy through steam power cycle. Finally, the mechanical energy is eventually converted into electricity by a generator.

Biomass gasification power generation should go through the following steps: (1) biomass gasification, after crushing and drying and other pretreated biomass pyrolysis gasification under high temperature environment, to produce gas containing combustible components such as CO, CH<sub>4</sub> and H<sub>2</sub>; (2) Gas purification, the combustible gas generated in the gasification process is passed into the purification system to remove impurities such as ash, coke and tar, so as to meet the inlet requirements of downstream power generation equipment; (3) Gas combustion power generation, purified gas into the gas turbine or internal combustion engine combustion power generation, can also be passed into the boiler combustion, the use of high temperature and high pressure steam to drive steam turbine power generation.

Due to the dispersion of biomass resources, low energy density, and difficulty in collection and transportation, direct combustion of biomass for power generation is highly dependent on the sustainability and economy of fuel supply, resulting in high cost of biomass power generation. Biomass



coupled power generation is a power generation method that uses biomass fuel to replace some other fuels (usually coal) for mixed firing. It can improve the flexibility of biomass fuel and reduce the consumption of coal at the same time, so as to achieve CO<sub>2</sub> emission reduction of coal-fired thermal power units. At present, biomass coupled power generation technology mainly includes: direct mixed combustion coupled power generation technology, indirect combustion coupled power generation technology and steam coupled power generation technology.

As we all know, biomass itself is generally considered to have zero carbon emissions. In other words, the CO<sub>2</sub> produced by biomass combustion or conversion is equal to the CO<sub>2</sub> absorbed during the growth process, so the CO<sub>2</sub> stored by biomass becomes negative carbon emissions after deducting the additional emissions in related processes. The life cycle assessment (LCA) method was used to evaluate CO<sub>2</sub> emissions from different power generation technologies. The system boundary consists of three parts: forest management (FM), collection, processing and transportation (CPT), and electricity generation with Carbon Capture and Storage (EG-CCS) through a Biomass Heat & Power Plant (BHP-CCS) (Figure 5.18) (Briones-Hidrovo et al., 2022). The life analysis of the entire system is 25 years. As opposed to integrated coal gasification combined cycle (IGCC), biomass integrated combined cycle (BIGCC) combined with CO<sub>2</sub> capture can greatly reduce CO<sub>2</sub> emissions.

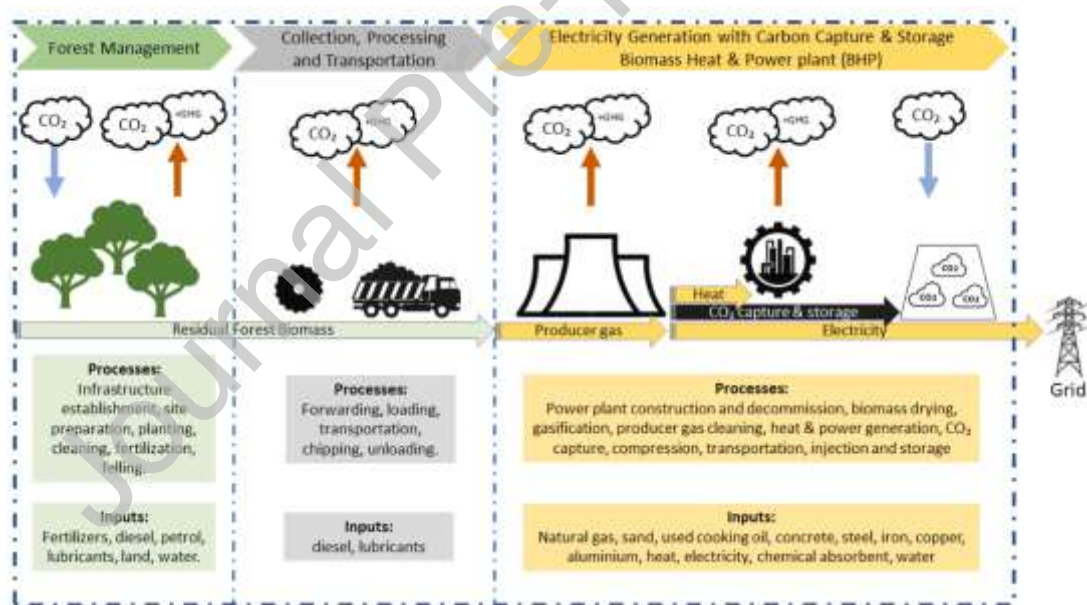


Figure 5.18 System boundaries of the Biomass Heat and Power Plant with Carbon Capture and Storage.(Briones-Hidrovo et al., 2022)

### 5.5.2 Biomass liquid fuel

Biomass is the only renewable carbon resource that can be converted into liquid fuel. It has the potential to replace petroleum, provide diversified clean energy supply for transportation, and greatly reduce

carbon emissions. At present, the raw materials of aviation biofuel mainly include animal and vegetable oil, lignocellulose, sugar and starch, etc. Animal and vegetable oil based jet fuel has great development potential, with its high energy density, molecular structure close to aviation biofuel, and high blending degree with fossil jet fuel (up to 50%). It is an important source of sustainable jet fuel at present (Gnanasekaran et al., 2022).

Microalgae biosequestration technology is a process that uses microorganisms to convert a large amount of carbon dioxide into biomass. Algae cells synthesize organic matter through photosynthesis using CO<sub>2</sub> and light energy and release oxygen to realize photosynthetic carbon sequestration. Micrococcoid genetically engineered using tools including CRISPR-Cas9 can produce twice as much oil as its wild parent and grow at a similar rate (Ajjawi, 2017). Zhang et al. found a novel "blue light" enhancement pathway and established an induction pathway for related oil synthesis, achieving a peak productivity of triacylglycerol twice that of unmodified microalgae (Zhang, 2022). The advantages of microalgae carbon sequestration technology are high carbon sequestration efficiency, strong environmental adaptability, reduction of industrial carbon emissions, production of high value-added products, and creation of economic value.

### 5.5.3 Biomass based materials and chemical

At present, there are also many studies that use waste biomass as raw materials to generate zero-carbon plastics. By providing long-chain bio-based epoxides and innovating and efficient synthesis of CO<sub>2</sub> to produce polymers such as biomass polycarbonate materials, the secondary utilization of waste biomass and CO<sub>2</sub> brings greater emission reduction potential. Sichuan University has made a breakthrough in the efficient depolymerization of biodegradable cyclic ester copolymer to obtain its copolymerized cyclic ester monomer under mild conditions (no catalyst, no solvent, 120°C). Through the repolymerization of recovered monomer, a regenerated copolymer with the same structure and properties as the original depolymerization copolymer was synthesized under controlled control (Figure 5.19). The closed-loop chemical cycle of the polymer was realized for the first time (Yan et al., 2022). Based on the characteristics of biomass unit structure, it is advisable to vigorously develop bioenergy, biochemical and biological materials, and cultivate and strengthen the biomass industry.

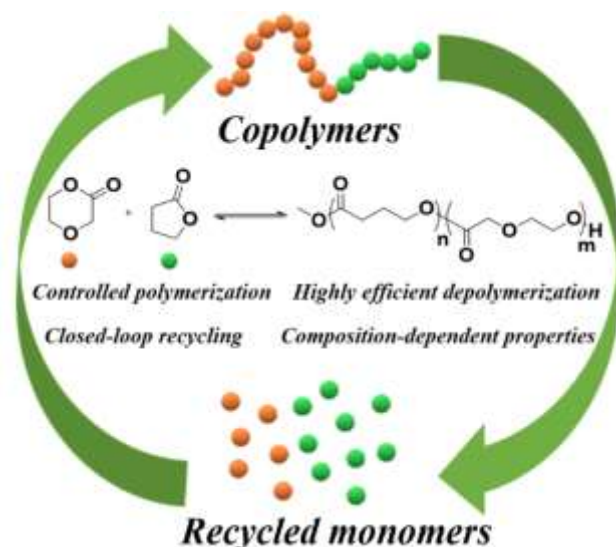


Figure 5.19 Schematic diagram of controlled synthesis and closed loop chemical cycle of biodegradable copolymers(Yan et al., 2022).

#### 5.5.4 BECCS project distribution

The application of BECCS technology in the power industry is still in a stage of rapid development. In 2019, the UK Drax 6\*660MW biomass fuel power plant started to capture CO<sub>2</sub>, capturing 1000 kg of carbon from flue gas emissions every day. This is the first time in the world that CO<sub>2</sub> is captured from 100% biomass combustion.

As of 2019, the distribution of 8 BECCS projects in the global geological sequestration is shown in Table 5.6. Five of these are already in operation, including one large-scale demonstration project and four demonstration and pilot-scale projects, with an annual CO<sub>2</sub> capture of about 1.5 Mt. Among them, the Illinois Industrial Carbon Capture Project in the United States is currently the largest BECCS project and the only BECCS project in operation in the world. The project captures high-purity CO<sub>2</sub> from maize ethanol production for geological storage in the saline aquifer on a capture scale of 1 Mt/a. The capture sources for the remaining four operating BECCS projects are small-scale ethanol production plants, all of which capture enhanced oil recovery (EOR). In addition, three BECCS geological storage projects are still being planned, with CO<sub>2</sub> capture sources from power plants and cement plants.

Table 5.6 Global BECCS project distribution

Project title	Capture source	Capture scale /(Mt a <sup>-1</sup> )	CO <sub>2</sub> storage method
Illinois Industrial Carbon Capture	Bioethanol plant	1.0000	Saline sequestration
Arkalon CO <sub>2</sub> Compression Facilities	Bioethanol bioplant	0.2900	EOR
Bonanza Carbon Capture	Bioethanol plant	0.1000	EOR
Husky CO <sub>2</sub> Inject	Bioethanol plant	0.0900	EOR

Farnsworth Inject	Bioethanol/fertilizer plants	0.0070	EOR
Mikaua Power plant capture after combustion	Biomass power plants	0.1800	Offshore storage
Drax Power CCS	Biomass power plants	0.0003	Geological storage
Norwegian Full Process CCS	Waste-to-energy/cement	0.8000	Geological storage

Note: EOR (Enhanced Oil Recovery) refers to enhanced oil recovery or enhanced extraction.

### 5.5.5 BECCS development trend and potential

Biomass energy is highly integrated with fossil energy to provide electricity, gas, heat and oil in a stable and secure manner without changing the existing energy infrastructure and architecture to achieve seamless energy replacement. Moreover, in the period of adjusting the energy structure in our country, only biomass energy can cover all the energy goods of industrial civilization and assume the task of new energy transformation, which is not possessed by other renewable energy.

The influence factors of BECCS technology application potential include biomass resource quantity and biomass utilization technology maturity. Biomass resources are mainly divided into agricultural and forestry residues, solid wastes and energy crops, and the availability of resources is uncertain. It is predicted that the total biomass resources will be 17.24 EJ/a in 2050. In terms of biomass utilization technology, biomass processing, combustion, anaerobic digestion, densification technology and final products have reached the commercial level. Some advanced biomass energy utilization technologies, for example, cellulosic ethanol, F-T synthetic biofuel and biomass integrated gasification combined cycle (BIGCC) are still in the demonstration stage of development, and the future development is more uncertain.

BECCS is likely to play an important role in climate change mitigation and energy transition along with renewables, other negative emission technologies, and deep emission reduction technologies. The efficient conversion of biomass into energy, chemicals and materials to replace petrochemical based products is an important zero-carbon/negative-carbon technology to achieve the dual carbon target. Earlier deployment of BECCS greatly increases its climate change mitigation potential, suggesting that policymakers should use BECCS alongside measures for GHG abatement and carbon removal.

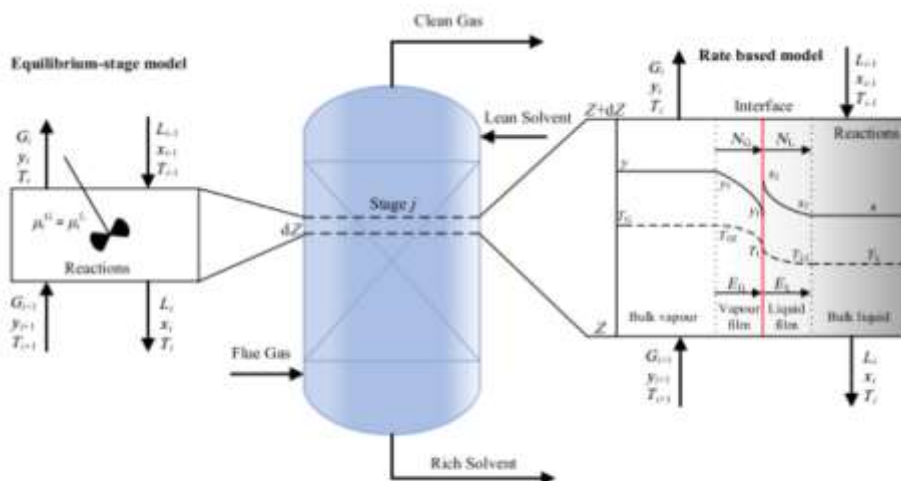
## 6. Process modelling and techno-economic analysis

### 6.1 Modelling, simulation and TEA for PCC based on chemical absorption using packed bed

Different mathematical models have been developed and reported in literature to describe the operation of the PCC process based on chemical absorption using packed bed (PB) column. Most of these studies have focused on steady state operation. It is imperative that the models are realistic and accurate to perform model-based application such as process design, operation and control. Investigations on the PCC process using dynamic models are required to investigate the dynamic operations such as start-up, shutdown and load following, capturing the interactions within the PCC process and the influence of the disturbances on the PCC process. Commonly used commercially available software to carry out modelling and simulation studies of the PCC-chemical absorption process using PB include Aspen Plus<sup>®</sup>, Aspen HYSYS<sup>®</sup>, gPROMS<sup>®</sup>, Aspen Custom Modeller<sup>®</sup>, Aspen Dynamics<sup>®</sup>. Amongst these software, Aspen Dynamics<sup>®</sup>, Aspen Custom Modeller<sup>®</sup>, gPROMS<sup>®</sup> are tools capable of developing efficient dynamic models that could adequately explain the process (Bui et al., 2014).

#### 6.1.1 Modelling Principles

Modelling and simulating the solvent-based PCC process is vital for the quick prediction of CO<sub>2</sub> capture efficiency by avoiding many expensive experimental tests (Chatziasteriou et al., 2022). PCC based on chemical absorption using a PB column involving simultaneous gas-liquid mass transfer and chemical reactions, is best described using either the equilibrium-stage or the rate-based model approach. The equilibrium-based approach assumes theoretical stages, where liquid and vapour attain equilibrium. This assumption is unrealistic and does not reflect the real stage performance of the column (Bui et al., 2014; Chatziasteriou et al., 2022). The rate-based approach, however, accounts for multicomponent mass transfer, heat transfer and chemical reactions within the column, making it more appropriate for describing the PCC process based on chemical absorption as it gives an accurate representation of the process (Lawal et al., 2009; Otitoju, 2022). In the rate-based modelling approach, the gas-liquid mass transfer can be described using different established theories such as the penetration theory (Rahimpour and Kashkooli, 2004), the surface renewal theory (Danckwerts, 1970), and the two-film theory (Biliyok et al., 2012; Lawal et al., 2009; Nittaya et al., 2014; Otitoju, 2022). The two-film theory whereby the mass transfer within the film arises from steady-state molecular diffusion, mass transfer resistance is assumed only in the vapour film and liquid film is the most widely used (Kenig et al., 2001). The Maxwell-Stefans equations are used to describe the diffusion in the film, the compositions for both bulk liquid and gas phases are assumed to be uniform.



**Figure 6.1 the equilibrium-stage model and rate-based model approaches for the PCC based on chemical absorption using PB.** Adapted from (Otitoju, 2022)

The reaction of  $\text{CO}_2$  with an amine in PCC based on chemical absorption using PB column is described using three reaction mechanisms: the Zwitterion mechanism, the termolecular mechanism and the base-catalysed hydration mechanism. The details of these reaction mechanisms have been extensively discussed in literature (Aboudheir et al., 2003; Littel et al., 1992). The reaction kinetics of fast-reacting solvents such as MEA and PZ can be approximated, assuming these reactions reach equilibrium. For slow-reacting solvents such as DEA and MDEA, accurate reaction kinetics is therefore needed to describe the reactions (Zhang et al., 2009). In first-principle modelling, the reaction kinetics is accounted for using the enhancement factor based on pseudo-first-order reaction kinetics. Thus, based on the level of detail required in the mass transfer and reaction kinetics, the model of the PCC process based on chemical absorption can be developed according to the level of complexities shown in Figure 6.2. The level of accuracy increases with complexity thus, Model 5 is the most accurate as it accounts for mass transfer and reaction kinetics via the rate-based approach. Model 1 is regarded as the least accurate of all. The main assumptions in most of the models for chemical absorption process using PB column include (Koronaki et al., 2015):

- Adiabatic absorber is considered with constant pressure inside it.
- All reactions take place in the liquid film, while the liquid bulk is at chemical equilibrium.
- A plug flow model describes the movement of both gas and liquid streams into the column.
- The flowrates of gas and liquid phases are constant in the absorber.
- Axial diffusion and solvent evaporation may be ignored.
- The interface and bulk phase temperatures are equal.
- The two phases are considered as ideal.

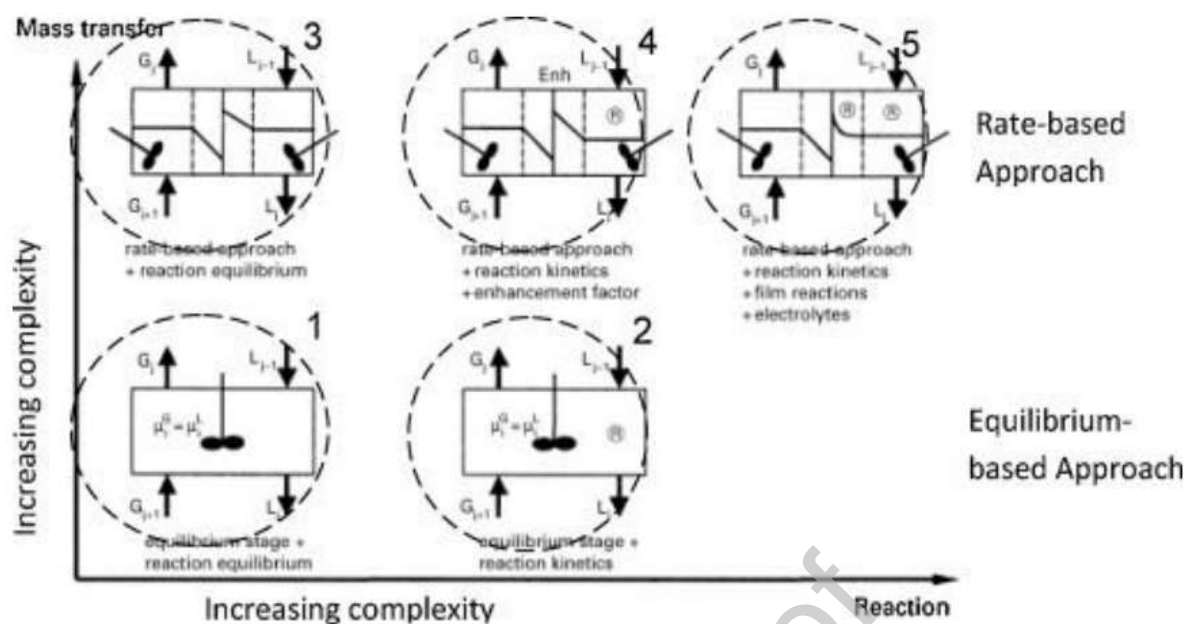


Figure 6.2 Complexity in models for PCC based on chemical absorption using PB column.

Adapted from (Kenig et al. 2001; Wang et al. 2011)

### 6.1.2 Modelling, simulation and process analysis of PCC based on chemical absorption using RPB

Some studies on the modelling and simulation of the PCC process using MEA in PB have focused on the development of single components such as absorber and stripper (Kvamsdal et al., 2009; Lawal et al., 2009; Zhang et al., 2009; Ziari et al., 2009), the whole solvent-based PCC plant (Gaspar and Cormos, 2012; Harun et al., 2011; Lawal et al., 2010), and integration of the PCC plant to CO<sub>2</sub> emitters such as power plants (Biliyok et al., 2012; Lawal et al., 2012). These studies have been analyzed and summarized in various review papers (Bui et al., 2014; Oko et al., 2017; Wang, M. et al., 2011). Zhang et al. (Zhang et al., 2009) presented a rate-based model for PCC using MEA solvent in Aspen Plus<sup>®</sup>. The developed model was validated against pilot plant experimental data and accurately predicted using the measurements for lean and rich CO<sub>2</sub> loadings, capture level and temperature profile. Khan et al. (Khan et al., 2011) investigated the impact of various mass transfer correlations on the predictability of the rate-based model. The selection/suitability of mass transfer and hydraulic correlations depends on the type of alkanolamines, packing and flow conditions. Thus, it is important to benchmark the correlations against experiments based on various operating conditions and packing types (Gaspar and Cormos, 2012). Razi et al. (Razi et al., 2013) investigated the impact of mass transfer coefficient correlation, kinetic models and effective interfacial area correlation on the model prediction of the pressure drop, CO<sub>2</sub> capture level and temperature profile in the column. The study revealed that the model prediction accuracy is dependent on the kinetic model and mass transfer correlations. As established in literature, the MEA solvent is volatile, corrosive and requires high regeneration energy

(Yoro and Daramola, 2020; Yoro et al., 2019). Thus, it is imperative to focus on PCC process using alternative solvents with lower regeneration energy, high reactivity with CO<sub>2</sub>, high resistance to degradation and environmentally friendly (Zhou et al., 2010). Modelling and simulation studies of PCC process using alternative solvent such as PZ (Otitoju et al., 2021) and AMP and PZ blend (Zhang, W. et al., 2017) solvent. For example, Otitoju et al. (Otitoju et al., 2021) developed a rate-based model for the PCC process using PZ. The model was validated at pilot scale and scaled-up to treat flue gas from a 250 MWe NGCC power plant. Therefore, further modelling and simulation studies of PCC process using suitable novel solvents should be explored.

The model development of the solvent-based PCC process with process configuration modifications has received much attention because the modified process has shown better economic performance and flexibility in operation (Wu, X. et al., 2020). Mostafavi et al. (Mostafavi et al., 2021) proposed combinations of process modifications such as absorber intercooling, lean vapour recompression and parallel exchanger arrangement to reduce the reboiler duty and cost of the PCC process. They found that the combination of the absorber intercooling and the lean vapour recompression resulted in an 8% reduction in steam consumption for regeneration and consequently a significant reduction in the total costs (i.e. fixed and variable costs).

Karimi et al. (Karimi et al., 2011; Karimi et al., 2012) developed rate-based models for five different stripper configurations of the PCC process including: standard configuration, split-stream, multi-pressure stripper, vapor recompression and compressor integration. The capital cost and CO<sub>2</sub> avoidance cost are calculated to evaluate the steady-state performance of different processes (Karimi et al. 2011). The dynamic performance of PCC processes with standard configuration, split-stream and vapor recompression configurations were then investigated. The simulation results showed that the standard configuration has the best dynamic behavior and is the most stable one. For the other two configurations, the vapor recompression configuration can handle disturbances better than the split-stream configuration (Karimi et al., 2012).

In the same vein, Biliyok et al. (Biliyok et al., 2012) developed a dynamic model for the PCC process with inter-cooled absorber in gPROMS<sup>®</sup>. The model was validated with dynamic experimental data and accurately predicted the behavior of the plant, especially for the trend of dynamic change. Analysis of the impact of inter-cooled solvent and flue gas moisture content on the CO<sub>2</sub> capture process performance was investigated using the validated model. Results revealed that the inter-cooling can slightly enhance the absorber performance when the temperature bulge is located around it. However, the moisture content in flue gas could strongly influence the temperature profile of the absorber but only had a trivial influence on the capture level. Similar study by Walters et al. (Walters et al., 2016) using PZ solvent revealed that PZ solvent capacity could be improved by absorber intercooling.



Investigating the PCC process integrated with either a power plant or industrial process is critical to improving its operation performance. Lawal et al. (Lawal et al., 2012) integrated dynamic models for a 500MWe sub-critical coal-fired power plant with PCC in gPROMS. The simulation results illustrated that the PCC process response was much slower than the coal-fired power plant. Olaleye et al. (Olaleye et al., 2016) investigated the dynamic behaviour of a large-scale PCC model integrated with a 600 MWe super-critical coal-fired power plant on load following mode of operation of the coal-fired power plant. The simulation results showed that about 4.67% of the maximum power of the coal-fired power plant could be quickly produced by the stripper stop mechanism, which has potential benefit for the wide-range load-varying operation of the power plant.

### 6.1.3 Techno-economic analysis (TEA) of PCC based on Chemical absorption using PB

Several studies have focused on the model-based optimization of PCC process based on chemical absorption to establish the operating conditions that achieve the CO<sub>2</sub> capture targets at minimum cost. Abu-Zahra et al. (Abu-Zahra et al., 2007) investigated the minimal thermal energy duty required for MEA solvent regeneration. Studies revealed significant energy savings could be achieved by optimizing lean solvent loading, amine solvent concentration, and stripper operating pressure. A minimum thermal energy requirement of 3.0GJ/ton CO<sub>2</sub> was attained at a lean MEA loading of 0.3, using 40wt% MEA and stripper operating pressure of 210 kPa compared with the base case of 3.9 GJ/ton CO<sub>2</sub>. Comprehensive sensitivity analysis and optimization of solvent-based PCC process using MEA based on total annual cost was carried out by Arias et al. (Arias et al., 2016). The study revealed that rich solvent, lean solvent, and flue gas temperatures are very sensitive to the total annual cost.

Further studies on TEA of the chemical absorption process focused on the process configuration modification. Dubois and Thomas (Dubois and Thomas, 2018) presented a technical analysis of different CO<sub>2</sub> capture process configurations (rich solvent recycle (RSR), solvent split flow (SSF), lean/rich vapour compression (L/RVC)) using different solvents (MEA, PZ, PZ-MDEA blend). The study revealed that the configurations studied attained regeneration energy savings within 4-18% range. The minimal regeneration energy of 2.38 GJ/ton CO<sub>2</sub> was obtained with PZ-MDEA blend (30wt% PZ and 10wt% MDEA) solvent and RVC process configuration.

Oh et al. (Oh et al., 2020) conducted a TEA on various modified PCC processes using 30wt% MEA. Five stripper configurations modified with two or more components of lean vapour compression (LVC), cold solvent split (CSS), and stripper overhead compression (SOC) were investigated to reduce the total equivalent work. The study revealed that the thermal energy required from the reboiler could be reduced by 8.1- 32.8% through the modified configurations. The study suggested that for a combined configuration implementation, the total equivalent work could be up to 9.0%, and the operating cost

could be saved by up to 10.2%. However, an increase in capital cost is attained due to the process modifications.

An investigation by Zhang et al. (Zhang, W. et al., 2017) on the energy performance of CO<sub>2</sub> capture process with AMP and PZ aqueous solvent with process modifications, including intercooled absorber (ICA), lean vapour compressor (LVC) and rich solvent split (RSS) revealed that the energy demand were reduced by 6.7%, 2.7%, and 8.5%, respectively. The combination of LVC +RSS, ICA +LVC and ICA+ RSS modifications obtained energy savings of 9.3%, 8.5% and 14% respectively. The energy demand for the combination of ICA+RSS+LVC was reduced by 15.2%.

Otitoju et al. (Otitoju et al., 2021) investigated the technical and economic performance of three different PCC process configurations using PZ solvent for 250 MWe NGCC compared with the standard process using 30wt% MEA solvent. Results revealed that the total energy demand of the standard CO<sub>2</sub> capture process using 30wt% PZ is 3.56 GJ/ton CO<sub>2</sub>, which is 33% less than the energy demand of the standard PCC process using 30 wt% MEA. Amongst the configurations considered, the lowest energy demand of 2.76 GJ/ton CO<sub>2</sub> was attained using an advanced flash stripper (AFS) using 40 wt% PZ. Results also showed that the lowest CO<sub>2</sub> capture cost of \$34.65 per ton CO<sub>2</sub> was achieved using the AFS process configuration with 40wt% PZ.

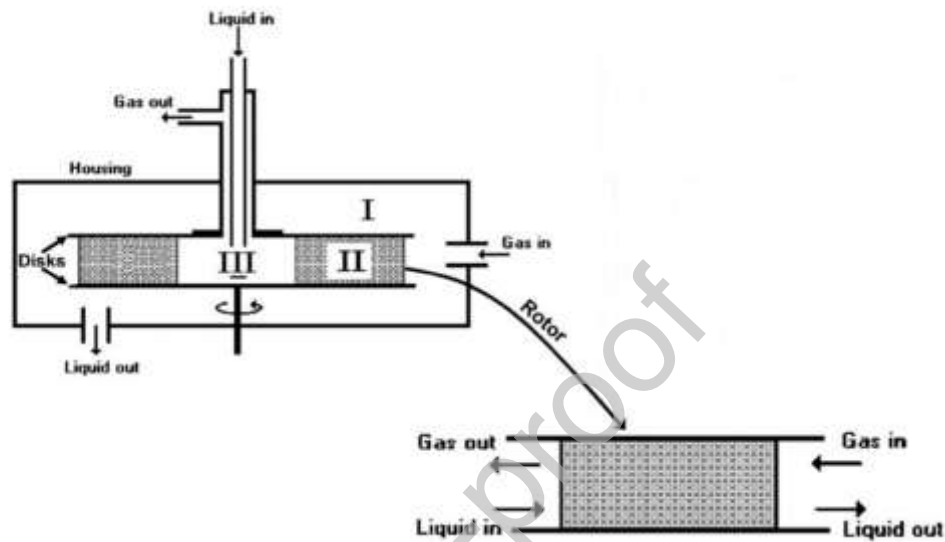
#### **6.1.4 Summary: advantages, limitations and future prospect**

Modelling and simulation of the PCC process based on chemical absorption using PB column has matured through many years of development and improvement. Many models have been developed to gain in-depth knowledge or insights into the PCC process using different solvents and configurations under steady-state and dynamic conditions. However, dynamic operating/experimental data is still insufficient to verify PCC dynamic models at different process configurations. From the validation point of view, more experimental tests should be carried out on the PCC process with different process configurations at pilot scale.

## **6.2 Modeling, simulation and techno-economic assessment of intensified PCC based on chemical absorption using RPB**

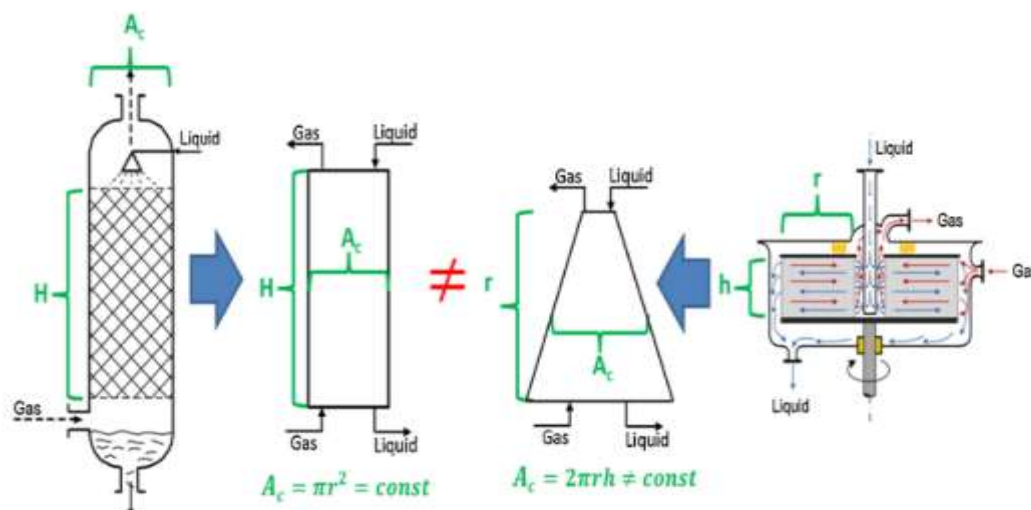
The rotating packed bed (RPB) is the most commonly used Higee (high gravity) technology for the solvent-based PCC process. It comprises an annular packed bed connected to two disks erected on a rotating shaft. A cross-sectional view of the RPB is shown in Figure 6.3. The RPB assembly is housed in a casing and operates in a high centrifugal field attained by rotating a cylindrical rigid bed (Cortes Garcia et al., 2017). The liquid and the vapour flow either co-currently or counter-currently in the horizontal direction. This is in opposition to the packed bed (PB) where liquid and vapour flow is

vertical. Thus in RPB, the separation efficiency and capacity are determined by the rotor diameter and the axial height respectively. This is in contrast with PB where capacity is determined by the column diameter and the separation efficiency is determined by column height (see Figure 6.4) (Cortes Garcia et al., 2017; Kiss, 2014).



**Figure 6.3** The cross-sectional view of the RPB (Chavez and Larachi, 2009)

Because of these fundamental structural differences, the modelling and simulation of the PB are significantly different from that of the RPB. For instance, mass transfer is considered to occur only along the packing in PB modelling whereas, mass transfer is considered to occur both along the packing and in the space between the rotor and the casing in modelling of RPB. Additionally, unlike the PB which is modelled as a straight bed with a constant cross-sectional area and constant gas and liquid velocities, the RPB is modelled as a tapered bed with a varied cross-sectional area and varied gas and liquid velocities (Cortes Garcia et al., 2017). This leads to varying gas and liquid mass transfer coefficients along the radius in RPB. The schematic of the PB and RPB, which highlights their structural and modelling differences, is shown in Figure 6.4.



**Figure 6.4 Schematic of the PB modelling (left) vs RPB modelling (right) (Neumann et al., 2018)**

There are many research activities on the modelling and simulation of the PCC process using the RPB technology (Joel et al., 2014,2017; Borhani et al., 2018, 2019; Oko et al., 2018; Im et al., 2020; Luo et al., 2021). The majority of these studies have focused on the modelling and simulation of CO<sub>2</sub> capture either in the RPB absorber (Joel et al., 2014; Borhani et al., 2018; Oko et al., 2018; Luo et al., 2021) or in the RPB stripper (Joel et al., 2017; Borhani et al., 2019). The modelling and simulation of the whole intensified carbon capture process consisting of the RPB absorber, RPB stripper, heat exchanger, pumps etc. have also been reported (Im et al., 2020). Discussions on these are provided in the following subsections.

### 6.2.1 Modelling and simulation of CO<sub>2</sub> absorption in RPB absorber

Modelling and simulation of CO<sub>2</sub> absorption with different solvents in RPB absorbers have been reported. The absorption of CO<sub>2</sub> using Benfield solution (amine-promoted hot potassium carbonate) was investigated in an experimental and modelling study conducted by Yi et al.,(2009). The steady-state model was developed in Matlab<sup>®</sup> based on the two-film theory and accounted for kinetics and CO<sub>2</sub> balance in the liquid droplets. The model was validated with experimental data collected in RPB with an inner radius of 0.040 m, outer radius of 0.10 m and axial height of 0.031 m. The model generally predicted the CO<sub>2</sub> mole fraction in the outlet gas and revealed the presence of an end effect zone at the inlet region of the packing where mass transfer efficiency in the RPB was the highest(Yi et al., 2009). Zhang et al.,(2014) developed a steady-state model of CO<sub>2</sub> absorption with an MDEA concentration of 10-30 wt% in a pilot-scale RPB absorber packed with multi-layer stainless steel. The model was implemented in Fortran<sup>®</sup> and uses Higbie's penetration theory. The model was validated and accurately predicted the CO<sub>2</sub> capture level at rotating speeds less than 1100 rpm. Beyond this rotating speed, there

were sharp deviations between the experimental values and model predictions. The CO<sub>2</sub> capture levels were generally lower than 50% due to slow reaction and low concentration of MDEA.

More studies have focused on the modelling and simulation of CO<sub>2</sub> absorption with MEA in RPB absorbers. Joel et al.,(2014) modified the rate-based model in Aspen Plus® to simulate a steady-state process of CO<sub>2</sub> absorption with MEA in an RPB absorber. The default mass transfer and hydrodynamic correlations in the rate-based model were modified by replacing the gravitational acceleration term ( $g$ ) in the correlations with centrifugal acceleration ( $r\omega$ ). The modified correlations were written in visual Fortran® and linked dynamically with the rate-based model in Aspen Plus®. The model was validated at the pilot scale and was used to investigate the effects of various operating variables on the CO<sub>2</sub> capture level. Process analysis showed that no temperature bulge was observed in the temperature profile of the pilot-scale RPB absorber because of the high liquid-to-gas (L/G) ratio (30 kg/kg). Furthermore, It was reported that the RPB absorber achieved a 12 times volume reduction factor compared to a PB absorber when 30 wt% MEA was used. A steady-state rate-based model of an MEA-based RPB absorber was developed by Kang et al., (2014). The model equations and the different correlations were implemented and solved in gPROMS ModelBuilder®. Their model used a modified enhancement factor which is based on the apparent reaction rate constant of Aboudheir et al., (2003) to improve the agreements between the model predictions and experimental data. Additionally, they investigated the effects of various mass transfer and liquid holdups correlations on model predictions of CO<sub>2</sub> mole fraction,  $K_{Ga}$  and CO<sub>2</sub> capture level. It was concluded that a combination of Onda et al.,(1968) for liquid phase mass transfer coefficient and interfacial area, Burns et al.(Burns et al., 2000) for liquid holdup and Tung and Mah, (1985) for gas phase mass transfer coefficient improved model predictions and were adequate to predict the effect of changes in liquid and gas flow rates in the RPB absorber.

Thiels et al., (2016) examined the process design for the RPB absorber to achieve varying CO<sub>2</sub> capture levels in Aspen Custom Modeler. They proposed a series arrangement of the RPB and PB absorbers to minimize the absorber packing volume. Borhani et al.,(2018) studied the effect of different reaction models and enhancement factors on CO<sub>2</sub> absorption in a pilot-scale RPB absorber operated with MEA concentrations of 55 wt% to 75 wt%. In addition to this, the influence of rotor speed, lean MEA concentrations, flow rates and temperatures on CO<sub>2</sub> capture level was also evaluated. Oko et al., (2018) used their steady-state RPB absorber model developed in gPROMS ModelBuilder® to show that the liquid phase temperature in RPB could rise significantly and hence demonstrated the need for intercoolers in RPB absorbers. Following this, the authors proposed and investigated various intercooler design options suitable for application in RPB absorbers. In a recent study, Otitoju et al., (2023) developed, validated and scaled up a steady-state rate-based model of an RPB absorber in Aspen Custom Modeller®. The authors reported that the large-scale RPB absorber achieved a 4–13 times reduction in volume and a 3-35% reduction in capital expenditures compared to a PB absorber. Recently Luo et al.,(2021) reported the dynamic modelling and simulation of CO<sub>2</sub> absorption in a pilot-scale RPB

absorber based on the surface renewal mass transfer theory. The RPB absorber model was developed in gPROMS ModelBuilder® and the embedded SAFT-VR EOS was used for the modelling of the thermodynamic properties. They performed steady-state process analysis to investigate the effects of key process variables such as rotating speed (300 rpm -1450 rpm), L/G ratio (2-6 kg/kg) and MEA concentrations (30 wt% - 80 wt%) on the absorption performance. They also carried out dynamic simulations of the RPB absorber to study its response to changes in the flow rates of both the flue gas and the solvent. It was concluded that the RPB absorber responds quickly to process changes (Luo, X. et al., 2021).

### 6.2.2 Modelling and simulation of CO<sub>2</sub> desorption in RPB stripper

Although there are many experimental studies of CO<sub>2</sub> desorption in RPB strippers, experimental data collected from two of those studies are commonly used to validate the model of the RPB stripper. Table 6.1 shows the specifications of the RPB used in those studies (Jassim et al., 2007; Cheng et al., 2013). There are fewer model-based studies on CO<sub>2</sub> desorption using an RPB stripper compared to their RPB absorber counterpart. There are only two studies in the open literature on the modelling and simulation of CO<sub>2</sub> desorption in RPB stripper (Joel et al., 2017; Borhani et al., 2019). This may be due to the complexity and difficulty involved in modelling the RPB Stripper compared to the RPB absorber. The first modelling and simulation study for CO<sub>2</sub> desorption in a RPB stripper was reported by Joel et al.,(2017). The rate-based RPB stripper model was developed using Aspen Plus® and Fortran®. Their model was validated with experimental data from Jassim et al., (2007) and Cheng et al., (2013). Model validation results were in agreement with experimental data for specific reboiler duty and lean CO<sub>2</sub> loading. Process analysis indicated that the regeneration efficiency increases with rotor speed, but with an increase in heat and mass transfers that subsequently resulted in a decrease in regeneration energy. The authors also reported that the RPB stripper volume was reduced by 9.692 times compared to that of a PB stripper. Borhani et al., (2019) used an equation-oriented approach to develop the model of the RPB stripper. The partial pressure, the heat of desorption and K-values were calculated from correlation developed by regression of experimental data collected for different concentrations of MEA. The model was implemented in gPROMS ModelBuilder® and was used to analyse the effect of changes in liquid flow rate, pressure, rotor speed and reboiler temperature on the regeneration energy of the RPB stripper. They concluded that the desorption energy reduces with an increase in reboiler temperature until 120 °C. Beyond this temperature, desorption energy increases.

**Table 6.1 Specifications of RPB stripper**

Institutions	Dimensions $r_i, r_o, h$ (m)	Packing type	$a_t$ ( $m^2/m^3$ )	$\epsilon$	References
Newcastle University	0.078, 0.199, 0.02	Expamet	2132	0.76	(Jassim et al., 2007)
National Tsing Hua University, Taiwan	0.038, 0.08, 0.02	Wire mesh	803	0.96	(Cheng et al., 2013)

### 6.2.3 Modelling, simulation and optimization of the whole solvent-based intensified PCC process

Modelling and simulation of the CO<sub>2</sub> absorption/desorption using RPB have been carried out mostly for individual RPB absorbers and RPB strippers. Only one study reported the modelling and simulation of the RPB absorber and RPB stripper as a connected system for the solvent-based PCC process at the lab scale (Im et al., 2020). In that study, the authors first developed and validated the model of the MEA-based RPB absorber and RPB stripper separately and then they developed the whole intensified PCC system by integrating the RPB absorber and RPB stripper with other process units in gPROMS ModelBuilder®. The integrated process was operated with varied MEA concentrations (30 wt% - 80 wt%). Optimal design and workable operating conditions for the integrated intensified PCC process were investigated using a flue gas flow rate of 71 kg/h and design specifications including 90% CO<sub>2</sub> capture level, lean solvent temperature of 40 °C, absorber and stripper pressures of 1 atm and 1.6 atm, CO<sub>2</sub> lean loading of 0.364 molCO<sub>2</sub>/molMEA, flash drum temperature of 40 °C, temperature approach of 10 °C, condenser temperature of 40 °C and rotor speeds of 800 and 600 rpm for the RPB absorber and RPB stripper respectively. Steady-state optimization of the whole intensified process was performed by setting the minimization of the total energy consumption (reboiler, rotation and pumps) as the optimisation objective and parameters such as rotor speed, MEA concentration, reboiler temperature, lean solvent flow rate, condenser temperature and stripper pressure as decision variables. In addition to this, the CO<sub>2</sub> capture level, CO<sub>2</sub> purity and percentage flooding in the absorber and the stripper were chosen as constraints. The optimization results showed that the lowest total energy consumption of 4.62 GJ/ton CO<sub>2</sub> (3.04 GJ/ton CO<sub>2</sub> for reboiler duty and 1.57 GJ/ton CO<sub>2</sub> for rotational energy) was achieved at 90% CO<sub>2</sub> capture level and 73 wt% MEA concentration. The authors concluded that although the specific reboiler duty was lower for the MEA-based PCC process using RPB its overall energy consumption could be higher than that of the MEA-based PCC process using PB due to the additional energy consumed for rotating the RPB.

#### 6.2.4 Scale-up of RPB for solvent-based PCC

Unlike the solvent-based PCC process using PB as absorbers and strippers, there are not many scale-up studies on solvent-based PCC with RPB as absorbers and strippers. Hence existing studies on CO<sub>2</sub> capture in RPB are based on small RPB rigs with a maximum outer diameter of 0.396 m and flue gas capacity of 0.66 kg/s or less (Jassim et al., 2007). Otitoju et al., (2023) performed the first scale-up study by scaling up a validated pilot-scale model of an MEA-based RPB absorber to a large-scale MEA-based RPB absorber with capacity for flue gas flow rate (356 kg/s) from a 250 MW<sub>e</sub> CCGT power plant. The large-scale RPB absorber was designed by estimating its basic dimensions (i.e. inner radius, outer radius, axial height and casing) using a rigorous iterative scale-up procedure developed by the authors based on the design approach of Agarwal et al., (2010). The scale-up uses the area of a transfer unit (ATU) to address the polar coordinate issue in RPBs. The results of the scale-up studies showed that a large-scale RPB absorber operated with 55 wt% would require an inner radius of 1.48 m while the one with a 75 wt% MEA would require an inner radius of 1.47 m. According to the authors, this inner radius would be sufficient to house the liquid distributor, not lead to excessive gas velocity and allow for gas withdrawal from the RPB without causing a very high pressure drop. Furthermore, the outer radius of the large-scale RPB absorber with 55 wt% MEA and 75 wt% MEA were estimated to be 4.86 m and 4.61 m, respectively, while their axial heights were estimated to be 1.26 and 1.19 respectively. The author used the scale-up results to carry out a techno-economic assessment and quantified the size and cost of a large-scale RPB absorber operated with MEA concentration of (55 wt% - 75 wt%).

#### 6.2.5 Techno-economic assessment of the solvent-based intensified PCC process

Although there are existing techno-economic studies for systems where RPBs are used for distillation (Sudhoff et al., 2015), recovery and purification of bioethanol (Gudena et al., 2013) and absorption of aroma from a bioreactor off-gas (Lukin et al., 2020). So far only Otitoju et al., (2023) has reported on the techno-economic assessment of the solvent-based PCC process using RPB, though the study was limited to the RPB absorber only. Technical assessments of the MEA-based RPB absorber performed by Otitoju et al., (2023) included the effects of certain process variables (i.e. lean solvent CO<sub>2</sub> loading, lean MEA flow rate and rotor speed) on the CO<sub>2</sub> absorption performance. The authors reported that the RPB absorber operated with 55 wt% MEA has a 4–11 times volume reduction factor while that operated with 75 wt% MEA has a 5–13 times volume reduction factor when compared to those of the PB absorbers. Furthermore, economic assessments showed that the capital expenditure (CAPEX), operating expenditure (OPEX) and CO<sub>2</sub> capture cost of the RPB absorber were lower compared to that of the PB absorbers. For instance, the CAPEX was lowered by 3–53% with the RPB absorber while the CO<sub>2</sub> capture cost was lowered by \$8.5/tCO<sub>2</sub> – \$15/tCO<sub>2</sub> with the RPB absorber compared to that of the PB absorbers.



### 6.2.6 Summary: advantages, limitations and future prospect

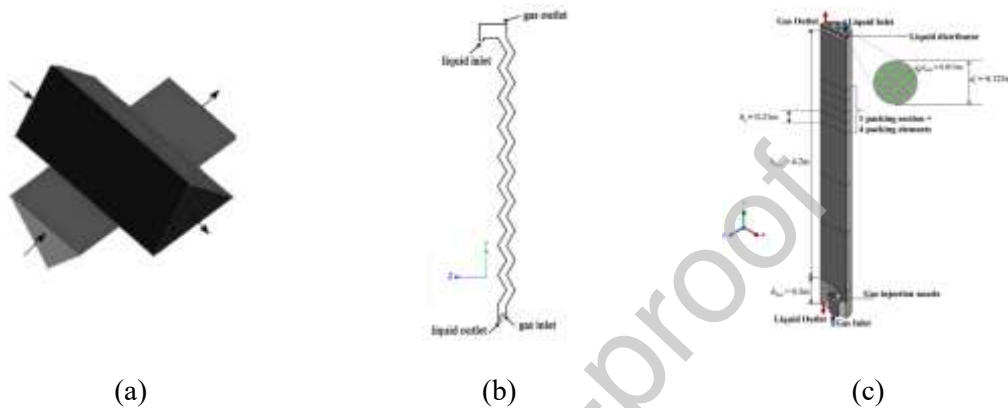
The RPB is the most commonly used technology in the intensified solvent-based PCC process because of its lower flooding tendency and ability to operate at higher gas and/or liquid flow rates compared to PBs. RPB is self-cleaning and can intensify the mass transfer process in the CO<sub>2</sub> capture process. It can reduce the process equipment footprint by reducing the size of the absorber by 5-13 times (Joel et al., 2014) and that of the stripper by 9.69 times compared to PB (Joel et al., 2017). Hence, RPB could be used in space-limited applications like ships and mobile skid plants. Furthermore, it can fulfil larger flue gas treatment than PB because mass transfer intensification in RPB could lead to a gas retention time below 1.5 s. This is significantly lower than a gas retention time of 20.4 s obtained in PBs. RPB can deal with viscous solvents and has been mostly operated with higher solvent concentrations (eg. 55 wt% or 80 wt% MEA). The cost of the solvent-based PCC process could also be reduced by RPB technology.

Despite the many advantages of RPB, its modelling and application in the solvent-based PCC process are limited to being used separately as an absorber or as a stripper. This is due majorly to the lack of experimental data to validate the model of the whole solvent-based PCC process using RPB. Additionally, existing studies on solvent-based PCC using RPB are conducted at lab and pilot scales. Only the study of Otitoju et al., (2023) was conducted for a large-scale RPB absorber. To accelerate the commercial deployment of the process, there is a need for more studies involving the detailed and accurate modelling and scale-up of the whole intensified PCC process using RPB. Such studies are critical to gaining insights into the design and operation of the whole intensified process. Additionally, a detailed economic assessment of the whole process is necessary to quantify the CO<sub>2</sub> capture cost for the entire process. Detailed optimization studies incorporating environmental and life cycle analysis (LCA) of the intensified PCC process should be carried out and the results thereof compared with the that of solvent-based PCC process using PB.

### 6.3 CFD Study of Post-Combustion Carbon Capture Based on Chemical Absorption Using Packed Bed

Packed bed (PB) has been used as multiphase contactors and reactors for post-combustion carbon capture (PCC). Like many other industry sectors, computational fluid dynamics (CFD) has been employed to design and optimize the packed bed technology for PCC. By solving a series of governing equations for fluid flows, chemical reactions, and heat and mass transfers, CFD simulation can reveal details of hydrodynamics, heat and mass transfer performance inside the packed beds.

Due to the packed bed's multi-scale nature, CFD simulation of the CO<sub>2</sub> capture processes in large scale PBs is still prohibitively computational expensive when the processes at the pore scale are to be resolved. In order to reduce the computational costs, two general approaches to the CFD PB simulations are employed, i.e. the micro- and macro-scale approaches. For example, the details of the flow behaviour in the PB can be investigated using the micro-scale modelling approach, whereas the overall column performance, such as the CO<sub>2</sub> capture rate and pressure drop, can be analyzed using the macro-scale approach (Li, Q. et al., 2016). Different models, such as the element scale, corrugation scale, and column scale models, have been proposed, as illustrated in Figure 6.5.



**Figure 6.5 Typical computational models employed. (a) element scale model (Chen et al., 2009); (b) corrugation scale model (Hosseini et al., 2012); (c) column scale model (Kim, Jeongeun et al., 2016).**

### 6.3.1 Element scale model

For mesoscale simulations, 3D representative element units (REUs) can be employed (Petre et al., 2003). The REU can be viewed as the smallest element in the PB, representing the bed dissipation mechanisms. Petre et al., (2003) and Larachi et al., (2003) utilized numerous REUs to resemble the flow at different positions in the column and they were used to simulate the gas flows over a wide range of Reynolds numbers: from pure creeping flows to fully developed turbulent flows. The overall pressure drop across the column was reconstructed based on each REU's obtained pressure loss. Furthermore, Said et al., (2011) investigated the dry pressure drop for the fully developed turbulent gas flow using two periodic REUs with different slice directions. In addition, the counter-current gas-liquid flow in the PB was studied using the VOF method based on a 3D REU, and the total liquid holdup and wetted area were estimated by Chen et al., (2009). It should be noted that although the use of the REUs can save the computing resources and time, the accuracy of the simulation results is directly related to the setting of the boundary conditions for the REUs, especially the wall effects, which may lead to an inaccurate result. It has been reported that the predicted pressure drop using REUs is usually more significant than

the pressure drop measured from the experiment due to the intersection of the two adjacent flow channels (Raynal et al., 2004).

### 6.3.2 Corrugation scale model

The 2D corrugation scale model is usually employed to study the two-phase flow behaviours in the PB, such as the dry pressure drop, liquid holdup, and liquid film thickness using the VOF method. For example Szulczewska et al., (2003), Gu et al., (2004), and Valluri et al., (2005) studied the counter-current gas-liquid flows on inclined plates using the VOF method for various packing surface microstructures, fluid properties and gas flow rates. It was concluded that the gas flow rate noticeably influenced the liquid flow pattern and film thickness. Further, the complex geometry of the structured packing in the PB was simplified as a 2D vertical cross-section channel between two neighbouring packing sheets (Raynal et al., 2004; Hosseini et al., 2012). The process of the liquid film formation on the packing surface was simulated, and the liquid film thickness and pressure drop were compared with the experimental data. In addition, Haroun et al., (2012) investigated the liquid holdup and the non-reacting mass transfer rate based on co-current gas-liquid flows in a 2D corrugation scale model. The results showed that the liquid flow rate and packing geometry mainly affected the mass transfer. Nevertheless, the use of the 2D geometry for the simulation of two-phase flow in the PB, although generally successful, has limitations due to the presence of highly anisotropic structured packings.

### 6.3.3 Column scale model

In general, the hydrodynamics and mass transfer processes have been explored in a packing column considering gas flow only or gas-liquid flows using the VOF and Eulerian methods. For the simulations of the gas flow, Wen et al., (2007) investigated the single-component (air) and two-component (air and CO<sub>2</sub>) gas flows in a column with complex packing geometries. Then, the influence of the geometry features of the packing on the dry pressure drop was explored (Sun, B. et al., 2021). Haghshenas Fard et al., (2007) modelled the dry and wet pressure drops in a packing column model similar to the actual geometry of the structured ceramic packing. The simulation showed that the wet pressure drop was larger than the dry pressure drop under the same gas load. This indicates that the modelling of the dry pressure drop cannot accurately describe the actual pressure drop in the packing column, where both the upward gas and downward liquid stream flows exist. Therefore, the simulations of both gas and liquid flows are essential for better understanding the flow dynamics in the packed bed.

It should be noted that the size of the column models employed in most studies such as those in the above-mentioned works, are relatively small but the required numbers of the computational mesh are still quite large. A promising approach for modeling a large-scale or industrial column is to take the

packing as a porous medium without resolving the details of the packing geometry, i.e. using the Eulerian porous medium model. To utilize this approach, it is very important to accurately determine a proper resistance force model to describe the gas-liquid interfacial force and drag force from the packing (Kołodziej and Łojewska, 2009). Mirzaie et al., (2020) estimated the porous resistance using the general Ergun's equation. However, the force models employed did not consider the effect of the various geometry of the packing, which may cause an inaccurate flow behaviour prediction. As a result, various porous medium resistance force models, such as those for spherical packing (Ergun, 1952; Attou et al., 1999; Lappalainen et al., 2008), structured slit packing (Iliuta et al., 2004), wire gauze packing (Kołodziej and Łojewska, 2009), and tube bundle packing (Zhang and Bokil, 1997) have been proposed. These models are developed based on the packings of different types and they consider the influence of the packing geometry on the fluids across the packing region. It has been shown that the flow characteristics could be accurately predicted in the packed beds by employing these models (Fourati et al., 2013; Iliuta, I. et al., 2014; Pham, Dung Anh et al., 2015; Pham, Dung A. et al., 2015; Uwitonze et al., 2021; Zhang, M. et al., 2017).

In addition, liquid dispersion occurs in the packed bed. Figure 6.6(a) shows the experimentally observed spreading of the liquid in a 3D column model with a point liquid jet source located at the top of the packing. Without considering the dispersion forces in the CFD model, the predicted liquid maldistribution can be quite different (Tan et al., 2021).

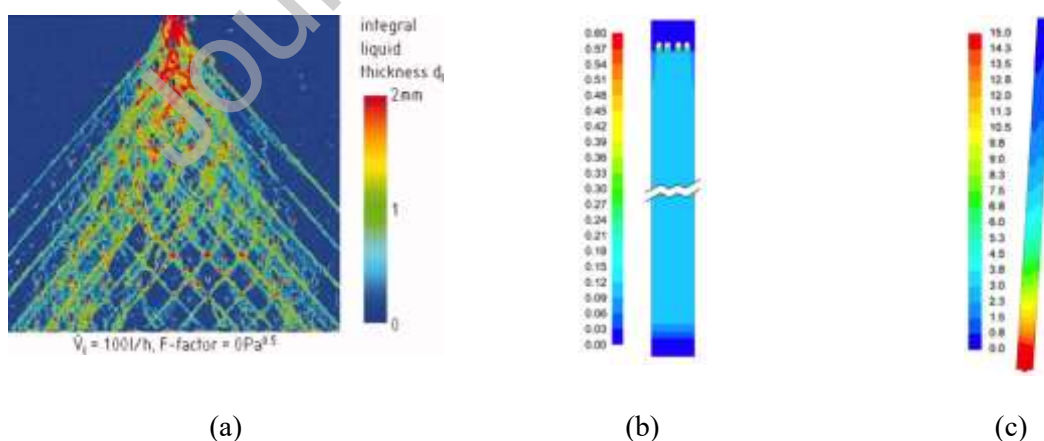
Liquid dispersion in the packed bed may be divided into the capillary pressure induced dispersion and mechanical dispersion (Wang, Y. et al., 2013). The capillary pressure force is produced by the difference in the pressures across the fluid interface. Two main models, i.e. the Grosser model (Grosser et al., 1988) and the Attou and Ferschneider model (Attou and Ferschneider, 1999), have been widely used to model the liquid dispersion resulting from the capillary dispersion (Boyer et al., 2005; Gunjal et al., 2005; Iliuta, I. et al., 2014; Jiang et al., 2002; Wang, Y. et al., 2013). In Grosser's models, it was assumed that the capillary pressure force was inversely proportional only to the packing's porosity and particle diameter. It is reported that the Grosser model may fail to reproduce the steep rise in the capillary pressure as the liquid saturation approaches zero, and thus fail to catch the effect of the capillary pressure force in some packed bed models (Zhang, Guojun et al., 2022).

The mechanical dispersion is caused by the complex advection of the momentum by the fluid at the pore scale (Fourati et al., 2013) or, in other words, the variation in the velocity with respect to the main flow at the macroscopic scale (Carney and Finn, 2016). The gas dispersion force is relatively small compared with the liquid dispersion force because the momentum exchange between the gas and liquid is usually small. As a result, the gas dispersion force is usually ignored (Fourati et al., 2013) in the CFD simulations. The drift velocity, which is a function of the gradient of the phase volume fraction, will lead to a driving force to cause the liquid to flow from the high liquid concentration region to the low liquid concentration region and subsequently increase the liquid holdup. Although many mechanical

dispersion force models have been developed, the model proposed by (Lappalainen et al., 2009) based on spherical particle packings is the most popular, and it has been employed in many works for the PB simulations (Kim, Jeongeun et al., 2016; Kim et al., 2017; Lappalainen et al., 2011; Lappalainen et al., 2009; Solomenko et al., 2015).

Lappalainen et al. (Lappalainen et al., 2009) employed their porous resistance model and dispersion force models to investigate the liquid dispersion phenomenon in a trickle bed. The results showed that the mechanical dispersion force was always larger than the capillary dispersion force under different particle sizes. Also, it was reported that the capillary dispersion force could be ignored for large particles and high packing porosity (Fourati et al., 2013). Thus, the mechanical dispersion force is the only force employed in most simulation works (Pham, Dung Anh et al., 2015; Pham, Dung A. et al., 2015). Furthermore, Hossain et al. (Hossain et al., 2020) used the mechanical dispersion model to simulate the liquid dispersion in a structured packed bed, and the simulation results agreed with the experimental data. It was proven that the mechanical dispersion model that initially derived from the random packing was also suitable for structured packings (Fourati et al., 2013), thus indicating that this model had a wide range of adaptability to model the flow in different types of packings.

Based on the column scale models combining the porous resistance and dispersion forces, the fluid flows were investigated in randomly and structured packed beds (Dung Anh Pham et al., 2015a; Kim et al., 2016; Uwitonze et al., 2021). An example of the simulated liquid holdup contour is shown in Figure 6.6(b). By further coupling with the mass transfer model and some empirical correlations of the effective interfacial area and mass transfer coefficient, the CO<sub>2</sub> capture process could be successfully analysed (Gbadago et al., 2020; Pan et al., 2018). Then, the effect of the sloshing on the liquid flow mal-distribution and CO<sub>2</sub> capture performance (see Figure 6.6(c)) may be investigated by using the sliding mesh method (Kim et al., 2017; Zhang et al., 2017; Dashliborun et al., 2019).



**Figure 6.6** Contours of (a) the spreading of the liquid fed from a point source (Mahr and Mewes, 2008); (b) the liquid holdup (Kim, Jeongeun et al., 2016); and (c) CO<sub>2</sub> concentration (Pham, Dung Anh et al., 2015).

### 6.3.4 Summary on CFD simulations of the PB

The PB's flow characteristics and mass transfer have been studied using the CFD method, mostly for small lab and pilot scale models. It has been demonstrated that employing the CFD is an efficient and effective way to simulate the carbon capture processes inside the PB, either for simulating the single or multiphase flows and for evaluating the hydrodynamics and/or mass transfer performances. Also, it can achieve much more detailed information about the processes occurring in the bed, which may not be obtained from the experimental measurements.

In order to model the gas-liquid flow and mass transfer in the PBs, different approaches have been employed. The details of the flow behaviour in the PB are usually investigated in the micro-scale model. When using this model, small and complex packing geometry can be considered and it requires a large mesh number. Some methods, such as using the REUs could be used to save computing resources and time. However, the accuracy of the simulation results is directly related to the setting of the boundary conditions and the established packing geometry. Some overall column performance parameters can be obtained using the macro scale model, such as the CO<sub>2</sub> capture rate and pressure drop. To make the simulation of large scale PB feasible and accurate, the Eulerian porous medium model can be used without resolving the complex geometry of the packing structure, but the sub-models for expressing the forces, including the porous resistance and dispersion forces, should be carefully considered.

## 6.4 CFD Study of Post-Combustion Carbon Capture based on Chemical Absorption using Rotating Packed Bed

The rotating packed bed (RPB) has shown great potential to capture CO<sub>2</sub> due to its increased effective interfacial area between the gas and liquid phases under the centrifugal force and excellent mass transfer performance. Among the studies on the RPB, CFD has been widely used to investigate the gas and liquid flows inside the 2D and 3D RPB models. For the single-phase, the gas flow behaviours, including the pressure drop and its distribution, have been studied in various RPB models. While for the gas-liquid flows, two methods, i.e. the VOF and Eulerian methods, have been employed to investigate the wet pressure drop, liquid holdup, liquid dispersion, etc., within the RPB. In addition, the mass transfer performance has been explored by using the CFD method coupled with user-defined functions (UDF).

### 6.4.1 Fluid flow study in the RPB

The flow characteristics, such as the gas pressure drop and liquid holdup, affect the CO<sub>2</sub> capture performance within the RPB and these have been investigated by using the CFD.

#### 6.4.1.1 Single phase gas flow and pressure drop

The distribution of the dry gas pressure and pressure drop were simulated for the gas flow passing through a 3D packing region with a complex wire mesh matrix by Liu et al., (2017); Wojtasik-Malinowska et al., (2022) and Yang et al., (2010). The influence of the liquid flow was not considered in these simulations. Liu et al., (2017) concluded that a considerable part of the gas pressure drop usually occurred from the gas pressure drop in the inner cavity zone of the rotating bed. Also, strong turbulence and mixing, named as the gas-side end effect, were observed in the outer packing zone of the RPB. In this study, a grid of over 90 million computational cells was used to accurately describe the gas flow by resolving at the pore scale in the wire mesh packing of a volume of just 0.009 m<sup>3</sup>.

In addition, the packing region may be regarded as a porous medium without computationally resolving the geometry of the packing in order to reduce the required computing resources. In this way, Llerena-Chavez and Larachi, (2009), Yang et al., (2015) and Wu et al., (2018) investigated the mal-distribution of the gas pressure in the 3D RPB models. Then the optimum design of the RPB was obtained by modifying the gas feed configurations and inserting internals or baffles in the packing region to reduce the mal-distribution and increase the gas-side mass transfer. Again, the simulations did not consider the influence of the liquid phase on the gas flow. The difference between the dry and wet pressure drops in the RPB can be pretty significant (Liu et al., 1996; Lin and Chen, 2008; Zheng et al., 2000; Sandilya et al., 2001).

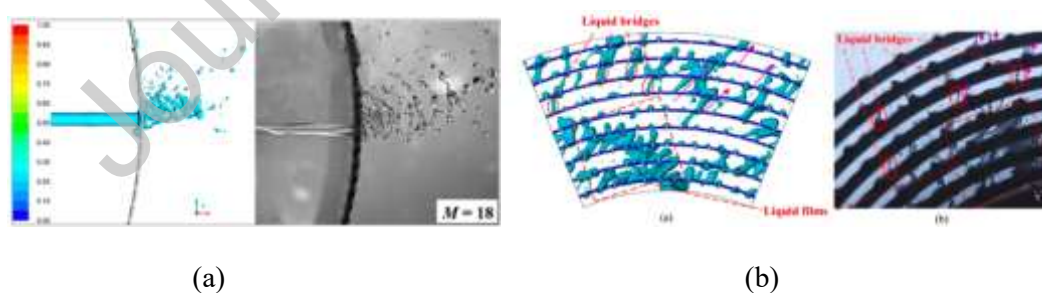
#### 6.4.1.2 Characteristics of the liquid flow

The characteristics of the liquid flow, such as the liquid holdup, liquid velocity, and liquid residence time, significantly influence the CO<sub>2</sub> capture in the RPB and therefore attract more attention than the gas flow. A two-phase flow model, either the VOF or the Eulerian model, must be adopted to investigate the liquid flow behaviors accurately. In particular, the VOF method has been widely used since it is well-suited for capturing the gas-liquid interface and the evolution of droplets when impacting on the packing surface, if sufficiently fine computational meshes are employed.

Using 2D VOF method, the liquid flow patterns in wire mesh and foam packings have been obtained under various operating conditions. The flow patterns can be primarily divided into three types: pore flow, droplet flow and film flow (Shi et al., 2013; Xie et al., 2017; Ouyang et al., 2018a,2018b,2019; Liu et al., 2019, 2020). In addition, the simulation investigations showed that the flow patterns varied mainly depending on the rotational speed of the RPB. The liquid distribution in the packing region became more uniform with the increased rotational speed, thus producing improved micro-mixing. Furthermore, Yang et al., (2016) and Liu et al., (2020) visually explored the liquid holdup and the liquid distribution within the packing under different operating conditions using the VOF method. The predicted liquid holdup agreed well with the correlations of Burns et al., (2000) and Yang et al., (2016). However, the actual liquid flow in the RPB is 3D. The flow characteristics obtained under the 2D

assumption are limited (Shi et al., 2013). Xie et al., (2019) analysed the gas-liquid flow by using 3D REUs of the RPB where different gravitational forces were employed in the REU to model the flow at different locations across a typical RPB, so that the overall characteristics of the liquid flow in the RPB was successfully assembled. In addition, the correlation of the effective interfacial area was proposed which has been further utilized in the work of Lu et al., (2019) and Zhang et al., (2022a, 2022b). In addition, using the VOF method, Guo et al., (2017) and Zhang et al., (2020) investigated the liquid holdup, liquid droplet size and residence time in a complete RPB model in 3D. However, the multilayer wire mesh packing was simplified as straight wires parallel to the rotor axis without considering the effect of the horizontal wire meshes. Thus, the difference of the liquid holdup obtained from the experiment, simulation and Bruns correlation was large. Therefore, it is important to model the packing geometry exactly in 3D when using VOF method. However, this would lead to a huge computational mesh.

Recently, (Zhang, W. et al., 2021) and (Li, Y.B. et al., 2022) modeled a sector of the 3D RPB model using the VOF model incorporating a periodic boundary condition. The model considered both the latitude and longitude structured wires to predict the liquid flow behaviours in the packing region accurately. Using this model, the formations of the liquid droplets when impacting on the single-layer or multi-layer wire meshes were simulated (Guo et al., 2017; Xu, Y.C. et al., 2019; Zhang, Wei et al., 2020; Zhang, W. et al., 2021). The results obtained were compared with the photographs recorded using high-speed cameras, as shown in Figure 6.7. The observed liquid dispersion indicated that the gas-liquid contact area and the mixing were enhanced at the inner edge of the packing (Zhang, J.P. et al., 2017). Although various liquid flow characteristics could be clearly captured by employing the VOF method in this study, it will become computationally prohibitively expensive to be used for the simulations of large/full scale RPBs (Li, Y.B. et al., 2022; Liu, Y. et al., 2017).

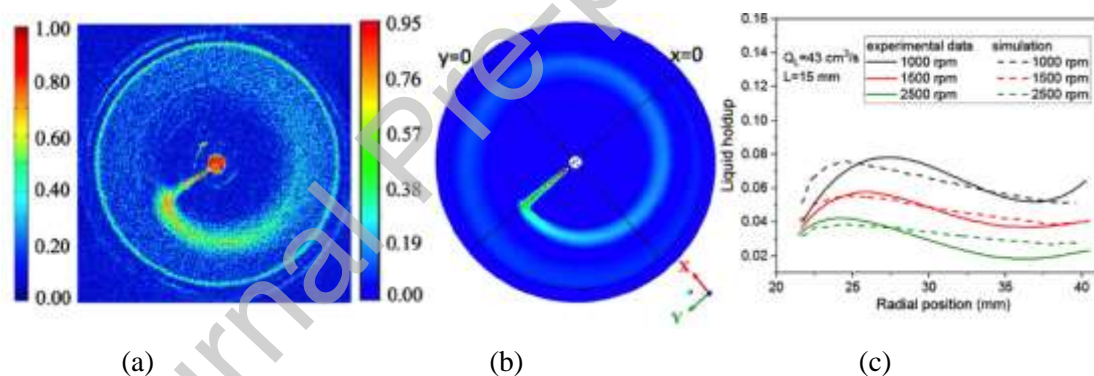


**Figure 6.7 Comparison of the simulated and visualized liquid flow across the rotating (a) single-layer wire mesh packing (Xu, Y.C. et al., 2019); and (b) multi-layer wire mesh packing (Zhang, W. et al., 2021).**

The Eulerian approach has shown great potential for reducing the computational cost in modelling the RPBs (Vlahostergios et al., 2020). Eulerian porous medium method has been utilized in the single-phase model to investigate the dry gas pressure drop in RPBs. When it is employed to study the liquid flow,



the appropriate mathematical models need to be added to the governing momentum equations, such as the porous resistance and liquid dispersion forces. (Lu et al., 2018,2019) proposed some beneficial mathematical models for estimating the gas-liquid interfacial force and the drag forces from the packing to be used with the two-phase Eulerian porous media model for simulating liquid flow in the RPB. These equations were derived based on the correlations originally proposed by Kołodziej and Łojewska, (2009) for single-phase flow through a wire mesh. The equations have been successfully employed to investigate the gas-liquid flows in the RPBs to predict the liquid holdup and gas pressure drop. Recently, G. Zhang et al., (2022) further developed this model by considering the dispersion forces mentioned in Section 6.3.3, including the capillary and mechanical dispersion forces. The results showed that the predicted liquid holdup matched the experimental data after considering the liquid dispersion force, as shown in Figure 6.8. Employing the Eulerian porous medium models and the proposed models by Lu et al., (2018, 2019) and G. Zhang et al., (2022; 2023), the simulation time for a full pilot scale RPB in 3D was significantly reduced. Although the trade-off of the Eulerian porous medium model is that it does not allow a clear capture of the gas-liquid interface, it does provide a feasible and effective way to simulate the CO<sub>2</sub> capture process in a full-scale RPB in 3D.



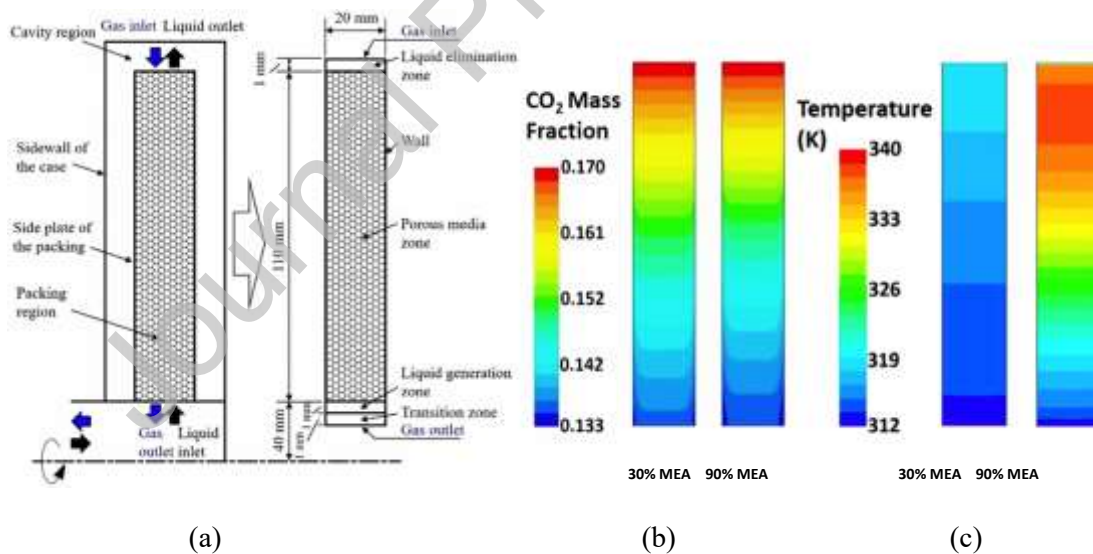
**Figure 6.8 (a) Map of the liquid holdup from the experiment(Yang, Y. et al., 2015); (b) contour of the liquid holdup from the simulation; (c) comparison of the liquid holdup along the radial position(Zhang, Guojun et al., 2022).**

#### 6.4.2 Predicting the mass transfer performance in the RPB

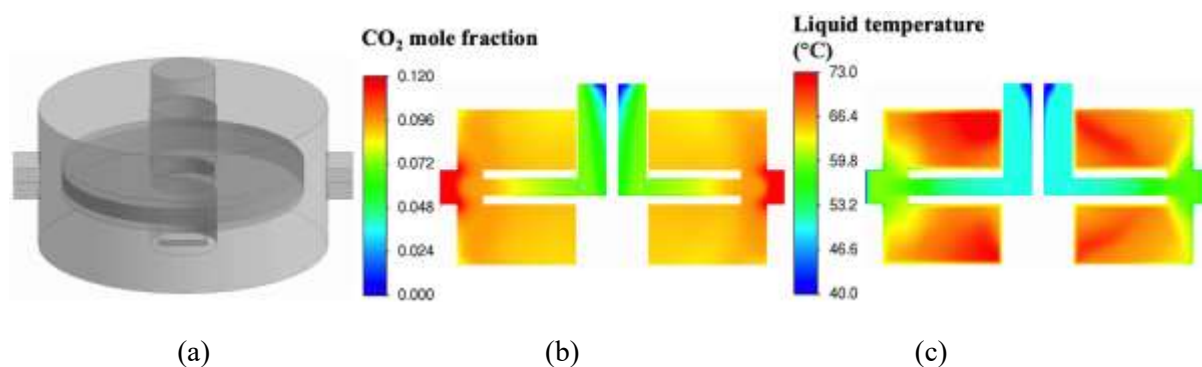
As is well known, the mass transfer can be greatly enhanced in the RPB due to the centrifugal force resulting from the rotation of the packed bed. Both the VOF and the porous medium approaches have been employed in studying the mass transfer process within the RPB, especially for CO<sub>2</sub> capture. Guo et al.,(2016) employed the VOF, together with Yang et al., (2016) investigated the oxygen absorption in the water in the packing region by employing the VOF model and Chen's liquid side mass transfer coefficient correlation via a UDF. They found that the micro-mixing behaviour was extreme in the 'end effect' zone due to the liquid dispersion produced by the collision between the liquid and the packing.

Since the semi-empirical mass transfer correlation was used, it may not be able to accurately predict the mass transfer process in a practical RPB as the correlation was too general. As mentioned before, using VOF method requires a prohibitively large number of computational cells to model a full-scale RPB where multiple-length scales which exist in the RPB have to be resolved in order to obtain an acceptable accuracy of the CFD simulation. Therefore, the Eulerian porous medium approach is preferred.

Lu et al., (2019) developed a 2D axisymmetric Eulerian porous medium model incorporating the two-film chemical-enhanced mass transfer model to investigate the CO<sub>2</sub> capture in an RPB, as is illustrated in Figure 6.9(a). The model uses a much coarser computer mesh than that typically employed in a VOF model without resulting in significant errors in the model results. The two-film reaction-enhanced mass transfer model has shown sufficient accuracy for expressing the CO<sub>2</sub> mass transfer among the phases in many PB investigations (Kim, Jeongeun et al., 2016; Kim et al., 2017; Pham, Dung A. et al., 2015). Figures 6.9(b) and 6.9(c) show the predicted CO<sub>2</sub> capture and temperature distributions in the RPB. The results are in good agreement with the experimental observations. Using a similar approach, a complete 3D RPB model, including the packing, inner and outer cavity zones, has been simulated (Zhang et al., 2023). Figure 6.10 shows the CO<sub>2</sub> and liquid temperature distributions in the RPB with a 50% MEA concentration solvent. The simulation results showed that the CO<sub>2</sub> capture performance agreed well with the experimental data, indicating that the porous medium approach can accurately predict the carbon capture process within the entire RPB.



**Figure 6.9 (a) Schematic diagram of the physical 2D RPB model; contours of the (b) CO<sub>2</sub> mass fraction in the gas phase and (c) liquid temperature for 30% MEA and 90% MEA (Lu et al., 2019).**



**Figure 6.10 (a) Schematic diagram of the physical 3D RPB model; contours of the (b) CO<sub>2</sub> mole fraction in the gas phase and (c) liquid temperature for 50% MEA(Zhang et al., 2023).**

### 6.4.3 Summary on CFD for the RPB

The flow characteristics and mass transfer in the RPB have been successfully investigated using CFD. Unlike modelling the static packing in the PB, the RPB models usually employ multiple reference frames or a dynamic mesh to simulate the rotation of the packed bed. To model the gas-liquid flow and CO<sub>2</sub> capture in the RPBs, both the VOF and Eulerian methods have been employed. The VOF can clearly capture the gas-liquid interface and the process of droplet formation when a sufficiently fine computational mesh is employed. However, it is computationally time-consuming and can become prohibitively expensive to simulate large-scale RPBs using the VOF method. Using the Eulerian method coupled with the porous medium sub-models could save computational resources and simulation time significantly. Therefore, it has shown an excellent potential to be used to simulate large-scale RPBs for process design optimization and scaling up. Nevertheless, the model's accuracy depends on the sub-models employed, such as the porous resistance force model, effective interfacial area model, etc. Finally, as for any CFD model development, including those for both PB and RPB simulations, model validation needs to be performed before it is employed for the modeling of a specific type of packing for CO<sub>2</sub> capture.

## 6.5 Modelling, Simulation and Techno-Economic Analysis of Solid adsorbent-based Post combustion Carbon Capture (PCC)

### 6.5.1 Introduction for Modelling, Simulation and Techno-Economic Analysis of Solid adsorbent-based Post combustion Carbon Capture (PCC)

Post combustion CO<sub>2</sub> adsorption is usually done in fixed bed columns(Siahpoosh et al., 2009), but it is also done in fluidized beds (Akinola et al., 2022). The design of an adsorption column based on empirical data can be expensive and time-consuming, due to the extensive experimentation required. However, predictive models that consider all important transport phenomena can be used to understand

the behavior of adsorption column systems and to screen adsorbents without the need for experimentation (Maring and Webley, 2013a).

Pai et al. (Pai et al., 2021) described three main concepts involved in modelling adsorption columns, i.e., mass transfer, heat transfer and fluid dynamics. Mathematical models that include solving coupled partial differential equations with appropriate boundary conditions are used to describe the mass and energy balance and fluid flow, to predict the behavior of the adsorption process. The models are then validated with experimental data before they are used for design, optimization, and economic analysis (Yan et al., 2016). Solving partial differential equations simultaneously can be tedious and time-consuming. Therefore, simplified models can usually be used satisfactorily by developing assumptions that simplify the representation of mainly the mass transfer phenomena within the adsorbent particles, to decrease the complexity of the model and the computational time (Shafeeyan et al., 2014). In general, mathematical models of fixed bed adsorption reflect a dynamic state, since a steady-state condition is never attained during adsorption (Valenciano et al., 2015).

## 6.5.2 Current Status on Model Development of Solid Adsorption-based Carbon Capture

### 6.5.2.1 Fixed bed adsorption column modelling

A set of partial differential and algebraic equations derived from the conservation of mass, energy, and momentum balance are typically used in the modelling of bed columns described in the literature. These equations are used to predict the transient concentration and temperature profile in a fixed bed column. For the equations to be solved, initial conditions for a few key factors, such as concentration, temperature, and flow rate, are necessary. By using the appropriate transport rate equations and equilibrium isotherms, these conservation equations consider the restrictions imposed by the mass transfer rate and the equilibrium between the gas phase and the solid particles. Fixed-bed adsorption models differ in terms of mass transfer rate, equilibrium isotherms, thermal effect and the pressure drop equations used.

### 6.5.2.2 Mass balance model

Eq.(6.1) is the mathematical equation used to determine the concentration distribution of components in the gas phase along the bed. It includes the terms for: axial dispersion, convection flow, accumulation of the components in the gas phase and the mass transfer term that accounts for the adsorption process on the adsorbent particles.

$$-D_{zi} \frac{\partial^2 c_i}{\partial z^2} + \frac{\partial}{\partial z} (uc_i) + \frac{\partial c_i}{\partial t} + \left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) \rho_p \frac{\partial \bar{q}_i}{\partial t} = 0 \quad (\text{eq.6.1})$$

- $D_{zi}$  is the axial dispersion coefficient, which lumps together the effects that contribute to axial mixing. It can be estimated using the following correlation:

$$\frac{\varepsilon_b D_{zi}}{D_{mi}} = 20 + 0.5 Sc Re \quad (\text{eq.6.2})$$

Where  $D_{mi}$ ,  $Sc$  and  $Re$  are the molecular diffusivity of component  $i$ , the Schmidt number and the Reynolds number respectively.

- $c_i$  is the adsorbate concentration in the gas phase;  $z$  is the distance along the bed length;  $u$  is the fluid velocity;  $t$  is the time;  $\varepsilon_b$  is the bed voidage;  $\rho_p$  is the particle density.
- $\bar{q}_i$  represents the average concentration of component  $i$  in the adsorbent particle. It is the link between the gas and solid phase mass balance equations.
- It is often assumed that there is no radial variation in concentration in both the gas and the solid phase, therefore  $c_i$  and  $\bar{q}_i$  represent radial average concentrations.
- The axial mixing term,  $-D_{zi}(\partial^2 c_i / \partial z^2)$  is often assumed to be insignificant and therefore excluded from eq.(6.1). This assumption is reasonable for large industrial adsorption units (Simo et al.; Zhao, R. et al.).

In eq.(6.1),  $\frac{\partial \bar{q}_i}{\partial t}$  is the rate of mass transfer to the solid adsorbent. It can be expressed as function of the concentration in the gas and solid phase as shown in eq.(6.3). It is a kinetic model that describes the mass transfer mechanism within an adsorbent. There are different models for different adsorbents, which provide an accurate representation of the mass transfer mechanism (Zhao, R. et al., 2019a).

$$\frac{\partial \bar{q}_i}{\partial t} = f(q_i, c_i) \quad (\text{eq.6.3})$$

The main types of mass transfer kinetic models include the local equilibrium model and the mass transfer resistance model.

The local equilibrium model assumes a fast mass transfer rate between the gas and solid phase and local equilibrium is reached at every point and time in the column. The equilibrium relationship between the gas and the solid phase can be represented using equilibrium isotherms. The most common isotherms used by researchers include the Langmuir, Freundlich and Toth isotherms (Zhao, R. et al., 2019a). An example of these models can be found in Zhao et al. (Zhao, R. et al., 2019a), who have used various equilibrium isotherms to evaluate the performance of a PCC adsorption system when using different adsorbents. The local equilibrium models exclude the effect of mass transfer resistance in the particle and thus do not accurately represent what is observed in adsorption columns. However, due to their simplicity, they can be used to provide an approximate representation of column behavior and they can

provide valuable information about the process dynamics and the behavior of the system during the preliminary design stage of the process. Equilibrium models are also useful for designing systems in which the adsorptive selectivity depends on the difference in the equilibrium of the species in the gas mixture, but they will not be useful when the selectivity is based on kinetics when separation is achieved by the difference in the gas-adsorbent mass transfer rates between the components (Hassan et al., 1986). Therefore, a non-equilibrium model will be required to describe the behavior of such processes.

Mass transfer resistance models are based on the three potential types of resistance to diffusion into the adsorbent particles, namely: external fluid resistance and intraparticle diffusion resistance, macropore diffusion resistance, and micropore diffusion resistance. These models have been shown to predict the behavior of adsorbents in a column adequately (Mulgundmath et al., 2012). A detailed description of these models can be found in Shafeeyan et al., (2014). Although these models provide a close approximation of reality in adsorption columns, their main drawback is the complex mathematical formulation, which is difficult and time-consuming to solve, which makes them impractical for column design and optimization. In general, simplified models are adopted by applying assumptions that increase the practicability of the model without reducing its accuracy. The most used of such models is the Linear Driving Force (LDF) approximation, which suggests that the mass transfer rate of a component into the adsorbent is proportional to the linear difference between the concentration on the outer surface of the adsorbent particle and the average concentration inside the particle. The outer surface concentration is assumed to be at equilibrium with the bulk gas phase concentration. The mass transfer is therefore expressed as follows (Shafeeyan et al., 2014):

$$\frac{\partial \bar{q}_i}{\partial t} = k_i (q_i^* - \bar{q}_i) \quad (\text{eq.6.4})$$

Where  $q_i^*$  is the adsorbed-phase concentration in equilibrium with the gas phase concentration of component  $i$ , which can be obtained from various equilibrium isotherms models (Zhao, R. et al., 2019a), an example of which is the Langmuir isotherm. This can be expressed as shown in eq.(6.5), where:  $q_i^s$  is the saturation loading of the adsorbent;  $K$  is the Langmuir isothermal equilibrium constant.

$$q_i^* = q_i^s \frac{K(T)P_i}{1 + K(T)P_i} \quad (\text{eq.6.5})$$

In eq.(6.4),  $k_i$  is the effective linear driving force rate coefficient that lumps together all the resistance to mass transfer. To predict  $k_i$  accurately, many forms that have been developed can be found in the literature, with these depending on what type of mass transfer resistance is dominant. For instance,

Farooq and Ruthven (1990) suggested the following model for  $k_i$ , if both macropore and micropore diffusion resistance are dominant:

$$\frac{1}{k_i} = \frac{R_p q_0}{3k_{fi} c_0} + \frac{R_p^2 q_0}{15\epsilon_p D_{pi} c_0} + \frac{R_c^2}{15D_{\mu i}} \quad (\text{eq.6.6})$$

Where:

- $q_0$  is the value of  $q$  (concentration in the solid state) at equilibrium, while  $c_0$  is the concentration in the gas phase at feed temperature.
- $D_{pi}$  and  $D_{\mu i}$  are the effective macropore diffusivity and the micropore diffusivity respectively.
- $R_p$  and  $R_c$  are the macropore and micropore radius.
- $k_{fi}$  is the external film mass transfer coefficient.

### 6.5.2.3 Energy balance

Although there are several isothermal adsorption models that do not take the energy balance into account (Moreira et al., 2006; Shen et al., 2010), temperature variations in the adsorption column can affect adsorption equilibrium and the adsorption rate. Therefore, in order to accurately predict packed bed adsorption, the effect of heat generation due to the adsorption process must be considered. Three control volumes are usually considered - the gas, the solid and the wall of the column - and the heat transfer rate in these volumes can be modeled as follows (Shafeeyan et al., 2014):

The gas phase energy balance that is used to determine the gas temperature profile in the bed:

$$-\lambda_L \frac{\partial^2 T_g}{\partial Z^2} + \rho_g C_g \frac{\partial(uT_g)}{\partial Z} + \rho_g C_g \frac{\partial T_g}{\partial t} + \left(\frac{1-\epsilon_b}{\epsilon_b}\right) h_f a_s (T_g - T_s) + \frac{4h_w}{\epsilon_b d_{int}} (T_g - T_w) = 0 \quad (\text{eq.6.7})$$

Where:

- $T_g$ ,  $T_s$  and  $T_w$  are the gas, solid particles, and wall temperature, respectively.
- $C_g$  and  $\rho_g$  are the bulk heat capacity and density of the gas.
- $h_f$  is the coefficient of the film heat transfer between the gas and the solid particles;  $h_w$  is the coefficient of the internal convective heat transfer between the gas and column wall;  $a_s$  is the ratio of the particle's external surface area to its volume;  $d_{int}$  is the internal diameter of the column;  $\lambda_L$  is the effective axial heat dispersion given by Grande and Rodrigues, (2005).

The solid phase energy balance:

$$\rho_p C_s \frac{\partial T_s}{\partial t} = h_f a_s (T_g - T_s) + \sum_{i=1}^n (-\Delta H_i) \frac{\partial \bar{q}_i}{\partial t} \quad (\text{eq.6.8})$$

Where:  $\rho_p$  and  $C_s$  are the particle density and heat capacity, respectively;  $\Delta H_i$  is the isosteric enthalpy of adsorption for component, which can be calculated as given in Yang et al., (1997).

The column wall energy balance:

$$\rho_w C_w \frac{\partial T_w}{\partial t} = h_w a_w (T_g - T_w) + U a_a (T_\infty - T_w) \quad (\text{eq.6.9})$$

Where:  $\rho_w$  and  $C_w$  are the density and the heat capacity of the wall, respectively;  $a_w$  is the ratio of the internal surface area to the volume of the column wall;  $a_a$  is the ratio of the external surface area to the volume of the wall;  $U$  is the external overall heat transfer coefficient between the wall and the air outside the wall;  $T_\infty$  is the temperature of the outside air.

#### 6.5.2.4 Momentum balance

The moment balance accounts for the pressure drop and the change in gas velocity in the column. Any model that estimates the pressure drop across a fixed bed can be used. The most common in the Ergun equation:

$$\frac{\partial P}{\partial Z} = - \frac{150 \mu (1 - \epsilon_b)^2}{\epsilon_b^3 d_p^2} + \frac{1.75 (1 - \epsilon_b) \rho_g}{\epsilon_b^3 d_p} u^2 \quad (\text{eq.6.10})$$

Where:  $P$  is the total pressure;  $\mu$  is the gas viscosity;  $d_p$  is the particle diameter.

#### 6.5.2.5 Fluidized bed adsorption modelling

When compared to fixed-bed systems, where hotspot generation is frequently unavoidable due to insufficient heat and mass transfer across the bed, fluidized-bed adsorption has the main advantage of improved adsorption due to enhanced heat and mass transfer caused by uniformity of temperature in the bed. However, modelling the behaviour of a fluidized bed is more difficult and requires the use of a complex computational method to describe the different fluidization regimes (Lee and Miller, 2013).



In addition to the gas-solid interactions phenomena that we have addressed for fixed bed column modelling, fluidized bed adsorption modelling also requires characterization of the hydrodynamics (Jung and Lee, 2022b; Li, W.L. et al., 2022). Simple models that consider the important hydrodynamic characteristics of a fluidized bed and require less computational power have been used (Akinola et al., 2022). In recent years, the use of computation fluid dynamic (CFD) has become more prevalent among researchers due to the advances in computational power (Balice et al., 2022; Cai, W. et al., 2022; Lian and Zhong, 2022; Luo et al., 2022). According to Nikam et al., (2022) and Ren et al., (2022), two approaches are used in these models: the Eulerian-Eulerian approach, which considers two fluid phases, i.e., the gas phase and the fluidized solid phase; the Eulerian-Lagrangian approach, which treats the solid fluidized phase as a discrete phase and keeps track of the position of individual particles in the bed. The latter approach provides a more precise description of the fluidized phase, although it requires more processing power.

### 6.5.3 Study of the Adsorption-based Carbon Capture Process Based on Process Simulation

The simulation and modelling of PCC processes are usually done to screen and evaluate the performance of different adsorbent materials, and to evaluate different process configurations. According to Nikolaidis et al., (2018), the relationship between ideal process performance, operating conditions, and adsorbent properties is complicated and cannot be quantified by only considering isotherms, selectivity and data of equilibrium working capacity: detailed simulation and optimization are required. The common performance indicators used in most PCC simulations and modelling include CO<sub>2</sub> purity and recovery, energy efficiency, productivity, and economics (Akinola et al., 2022). Simulation and modelling packages such as gPROMS, Matlab and Aspen Adsorption are often used when evaluating these processes (Hasan et al., 2013; Leperi et al., 2019; Subraveti et al., 2019a). Several authors, including (Farmahini et al., 2018), Hasan et al., (2013), Leperi et al., (2019) and Subramanian Balashankar and Rajendran, (2019) have used simulation and modelling to screen adsorbent materials. Recently, Burns et al. (2020) screened 1632 metal-organic framework (MOF) materials for PCC by integrating molecular simulation with a macroscopic process simulation of vacuum swing adsorption (VSA). They concluded that: 482 materials met the regulatory target of 95% purity and 90% recovery of CO<sub>2</sub> (95/90 CO<sub>2</sub> PRT); 365 of these materials had a parasitic energy requirement below that of solvent-based capture of 290 kWh per metric ton of CO<sub>2</sub>. They also used a machine learning model to predict a given material's ability to achieve the required 95/90 CO<sub>2</sub> PRT.

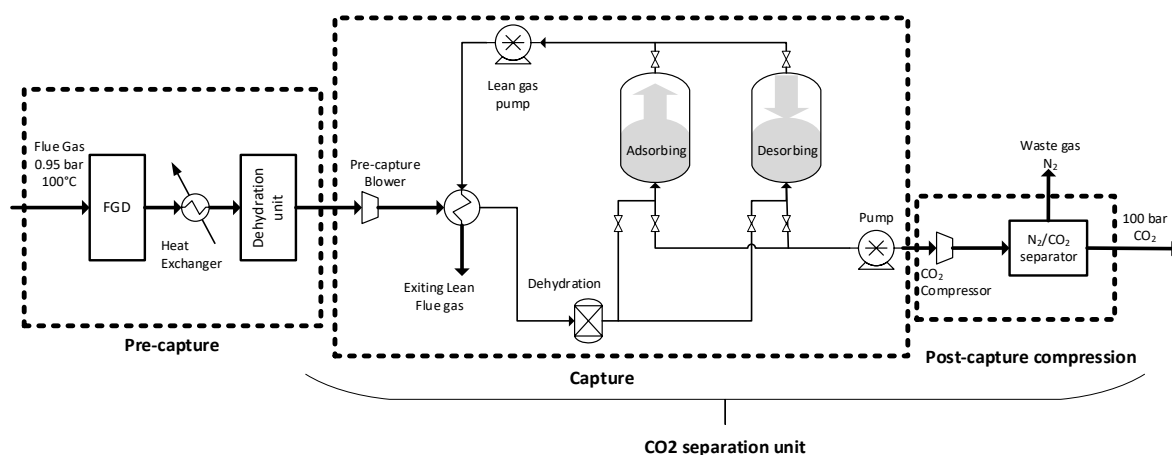
Energy consumption is one of the important parameters, which has been extensively investigated using modelling and simulation in adsorption-based PCC and which ties up closely with process operating conditions such as feed pressurisation and blowdown pressure, plant productivity and capital cost. For instance, Haghpanah et al., (2013) did a simulation exercise in which they optimized pressure-vacuum swing adsorption (PVSA) using Zeochem zeolite 13X. They concluded that a minimum energy requirement of 149 kWh/ton of CO<sub>2</sub> is achievable when the process operates at low pressure, with an

inlet pressure of 1 bar and a vacuum blowdown pressure of 0.02 bar to achieve a productivity of 0.49 mol of CO<sub>2</sub>/m<sup>3</sup> of adsorbent corresponding to an 11% energy penalty. They also noted that energy consumption increases with higher productivity and that a combination of feed pressurization and low blowdown pressure can reduce the plant size and the capital cost significantly. Similar results were obtained by Krishnamurthy et al., (2014). Nikolaidis et al., (2018) corroborated that energy consumption increases with increased productivity when they compared the optimized performance of zeolite 13X and modified zeolite 13X in a simulation of a single stage PVSA. In a simulation run by Subramanian Balashankar and Rajendran, (2019), more than 120 000 zeolite materials were compared, including hypothetical and existing zeolite materials. It was shown that low N<sub>2</sub> affinity, not high CO<sub>2</sub> affinity, is characteristic of a low energy consuming adsorbent. It was also shown that the best performing adsorbent materials consumed 16% less energy than Zeolite 13X, which is considered the current benchmark for adsorbent materials.

#### 6.5.4 Techno-economic Analysis

In industrial settings, solid adsorbents have been used to remove CO<sub>2</sub> from hydrogen and natural gas. Unlike the flue gas from power plants, these gases are typically present at high pressure and low temperature. When the International Energy Agency (IEA) conducted a study on applying PSA to adsorption-based PCC in the early 1990s (IEA, 1992); thus, the authors concluded that this technology was not suitable for the bulk capture of CO<sub>2</sub> from fossil fuel power plants.

Interest in using adsorbents for CO<sub>2</sub> PCC only surfaced in late 2000s. Ho et al., (2008) reported the first Techno-Economic Analysis (TEA) study after the publication of the IEA 1992 report. In this study, the VSA process was compared to the PSA process, as shown in Figure 6.11. Zeolite 13 X was selected as the adsorbent, with a capacity of 2.2 mol/kg of adsorbent, and CO<sub>2</sub>/N<sub>2</sub> selectivity of 54. When the four-step Skarstrom cycle was used, the VSA showed promising results compared to PSA, with a capture cost of \$51/ton of CO<sub>2</sub> avoided (2006 USD), close to MEA adsorption process, which is \$49/ton CO<sub>2</sub>. The CO<sub>2</sub> capture rate was set at 85% in the study, but the purity of the CO<sub>2</sub> in the recovery stream was less than 50%. Most of the cost comes from compression (both unit cost and energy cost), seconded by the adsorbent unit and adsorbent replacement. When a seven-step PSA cycle was applied, the capture cost was lowered to \$41/ton with an improved purity of 70%. The drawback of using the seven-setup PSA cycle is that more adsorbent is needed to compensate for the reduced CO<sub>2</sub> recovery rate. The authors proposed that the most cost can be reduced further if a better adsorbent is used (Ho et al., 2008). This result was very promising, as the estimated capture cost was close to that of the MEA adsorption processes.



**Figure 6.11: Simplified process flow diagram for the PSA/VSA CO<sub>2</sub> capture process applied by Ho et al., (2008)**

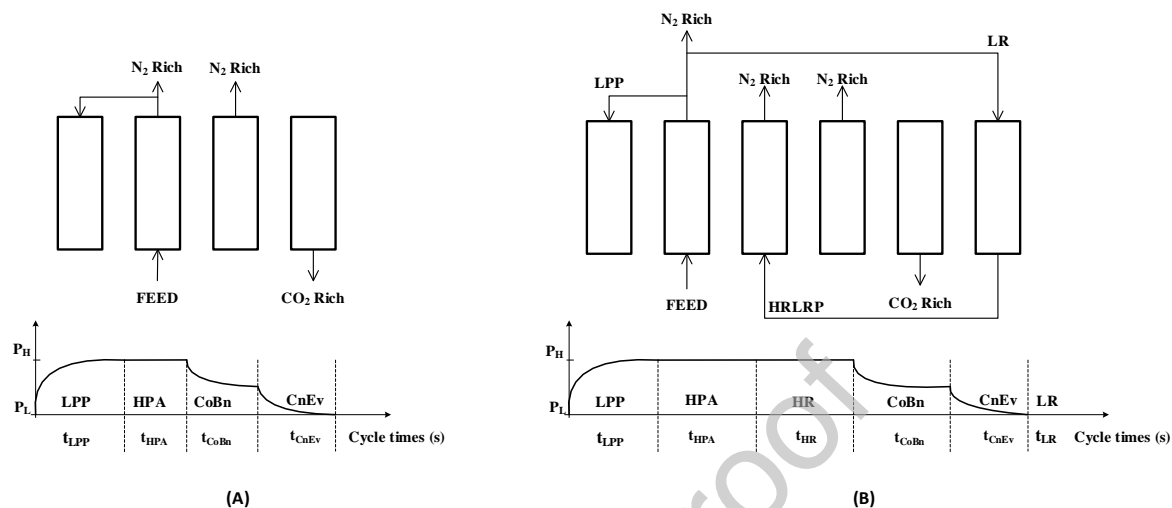
The impact of process factors on the VSA for PCC was investigated by Zhang et al., (2008). The cost results were not comparable to those reported in previous studies since a straightforward economic assessment method was used to compare the merits of various VSA situations. However, the study did show that input CO<sub>2</sub> with a high concentration increases the recovery rate and purity of CO<sub>2</sub>, which can significantly reduce the capture cost. Using a six-step VSA cycle, the study found that ordinary flue gas with a CO<sub>2</sub> concentration of about 12% by volume is good for VSA, with good recovery (>70%) and purity (>90%). Increased purity can be attained using a nine-step VSA cycle, but the cost penalty is higher.

In their review paper, Samanta et al., (2012) evaluated the studies on PCC and noted that relatively few economic analyses were done because there was insufficient data on the performance of solid sorbents in various contactor configurations. The assessment also made it clear that the reactor and process design are crucial for the development of the PCC technology and that the sorbent is not the only important factor in the process. This assessment still holds true.

The impact of water on adsorption-based PCC was taken into consideration by Leperi et al., (2016). The study found that removing water before the PSA cycle is crucial. When moisture was eliminated during the pre-treatment phase, with zeolite 13X being used as the adsorbent, it resulted in a 90% recovery rate with 90% purity at a cost of \$32.1/ton CO<sub>2</sub>. Pre-treatment can cut the overall cost of capture by about 6%.

More and more parameters can be added into the TEA as computer power and simulation models improve. Khurana and Farooq, (2019) reported on an integrated optimization platform that can use a simulator based on a non-isothermal and non-isobaric linear driving force model. This platform was demonstrated using two VSA cycles: a four-step VSA cycle with light pressurization and a six-step cycle with dual reflux Figure 6.12. The method was optimized in relation to the levelized cost of electricity (LCOE). MOF UTSA-16 was used to obtain a minimum LCOE of \$114/MWh for the four-

step cycle, which is less expensive than NETL's Shell Cansolv-based PCC solution. The cost of CO<sub>2</sub> capture is claimed to be \$21.1/ton CO<sub>2</sub> captured and \$26.3/ton CO<sub>2</sub> avoided, with CO<sub>2</sub> purity exceeding 90% (Khurana and Farooq, 2019). This is much lower than that reported in prior research, and it meets the \$40/ton CO<sub>2</sub> objective for second-generation PCC technologies.



**Figure 6.12: (A) The four-step VSA cycle with LPP and (B) the six-step dual-reflux VSA cycle studied by Khurana and Farooq, (2019)**

Danaci et al., (2020) created another screening tool. Twenty-two MOFs, two zeolites and activated carbon were tested against CO<sub>2</sub> purity, recovery rate and cost. CO<sub>2</sub> emissions from four sources were considered: natural gas power plants, coal-fired power plants, cement manufacture and the steel industry. UTSA-16, which is similar to zeolite 13X, was found to be the best MOF among the adsorbents examined; however, the cost of the adsorbent was higher than that of an amine-based adsorption technique. The study found that the most relevant qualities of the adsorbent are its low N<sub>2</sub> adsorption and moderate enthalpies of adsorption, rather than its CO<sub>2</sub> capacity or surface area. This work showed a new direction for adsorbent design, as well as the complexity of the PSA system.

Subraveti et al., (2021) confirmed that the cost of the VSA process when using the new proposed adsorbents Zeolite 13X and two MOFs, is still higher than that of the MEA process. The study reported that IISERP MOF 2 outperformed Zeolite 13X, which is the benchmark material for the four-step cycle process. When the CO<sub>2</sub> concentration in the flue gas was 20%, the capture cost was €33.6/ton of CO<sub>2</sub>, with a corresponding CO<sub>2</sub> averted cost of €73/ton, which is more than that of MEA. The study reported that optimizing the VSA process for proxy objectives, such as reducing energy used and maximizing productivity, does not automatically translate into the lowest cost. The adsorbents identified as being superior due to their high energy/productivity performance did not always result in reduced cost. The rationale offered was that the minimum cost configuration does not lay in the minimal energy vs maximum productivity Pareto curves, due to the complexity of the VSA process scaling up. This explanation adds to the already-complex VSA process and poses a new hurdle in adsorbent screening.

The study also indicated that: due to the constraint of a single VSA unit, it is difficult to profit from economies of scale; the VSA process is probably better suited to small and medium-sized operations rather than large-scale operations (Subraveti et al., 2021). It was also stated that a different strategy is required to further reduce capture costs, and the proposed solutions were to use monoliths, contact passes paired with quick cycling and using other cycles.

Jung and Lee, (2022b) claimed that the solid sorbent process outperforms the MEA process. Four processes were evaluated in their study: fluidized bed, fixed bed, moving bed and rapid thermal swing. The amine functionalized  $\text{SiO}_2/0.37\text{EB-PEI}$  powder, pellet and hollow fibre were employed as the solid sorbent. The study revealed that, except for the fluidized bed process, the proposed processes had a lower capture cost than the 30% MEA process. The best performing process had a capture cost of \$48 per ton of  $\text{CO}_2$ , which was 24% less expensive than the 30% MEA process and only 3% more expensive than the Water Lean Solvents method.

Subraveti et al., (2022) investigated the cost limits of the PVSA process. In this investigation, the cost of the adsorbent was adjusted to zero to determine the effect of sorbent characteristics. It was determined that the optimal adsorbent should have close to 0%  $\text{N}_2$  adsorption, which agrees with Danaci et al., (2020)'s conclusions, as well as linear isotherms. Based on the four-step cycle, morphological change can result in a 9 - 22% lower  $\text{CO}_2$  avoidance cost. The optimal pellet porosity and diameter was 0.42 - 0.76% and 3-5 mm, respectively. When compared to the four-step cycle, the six-step DR cycle cost 15 - 42% less. As shown in Figure 6.13, compared to the MEA process, the four stage PVSA cycle is at least 8% less expensive, and the six-step DR PVSA is at least 35% less expensive for input gasses with more than 7.5%  $\text{CO}_2$  concentration.  $\text{CO}_2$  averted costs ranged from €10.4 to 87.1/ton for feed gas with  $\text{CO}_2$  concentrations ranging from 3.50% to 30%, while MEA costs ranged from €54.8 to €76.8, which indicates that PSA is well suited to high  $\text{CO}_2$  concentration gas treatment.

The two most recent studies (Jung and Lee, 2022a; Subraveti et al., 2022) indicated that under certain conditions, the solid adsorbent could deliver a reduced  $\text{CO}_2$  capture cost. It is worth noting that in the study by Subraveti et al., (2022), the optimal  $\text{CO}_2$  adsorption isotherm varied according to the different process options and different  $\text{CO}_2$  compositions. Examples of the  $\text{CO}_2$  isotherms are shown in Figure 6.14.

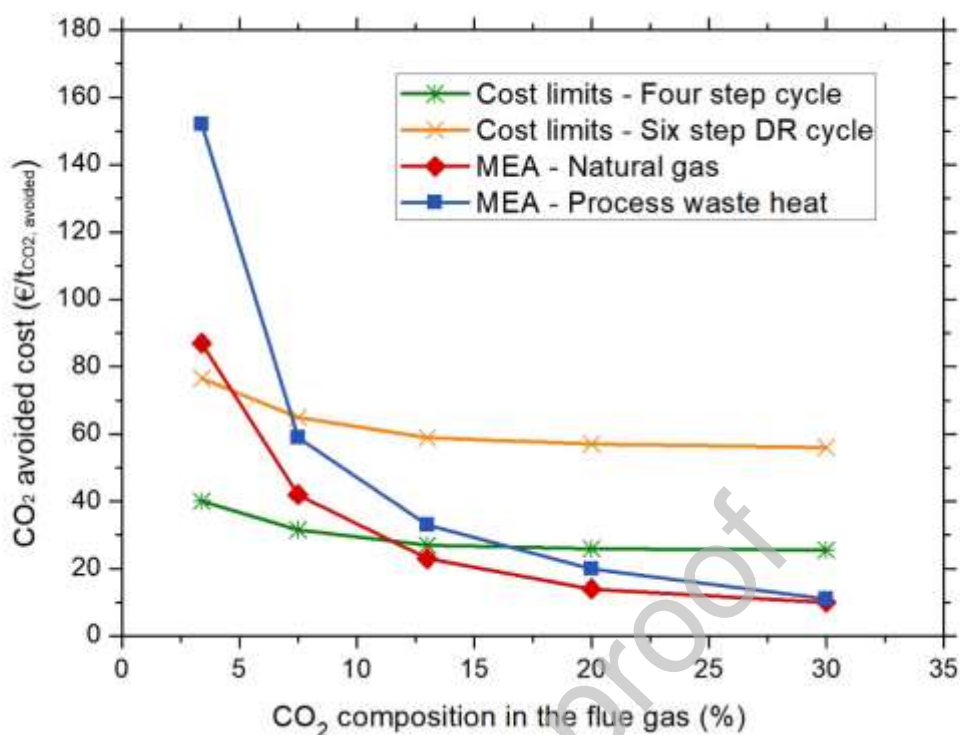


Figure 6.13: Comparison of the cost limit of the four-step and six-step DR PVSA cycles with CO<sub>2</sub> avoided cost obtained using the MEA-based CO<sub>2</sub> capture with two streams supply scenario (Subraveti et al., 2022).

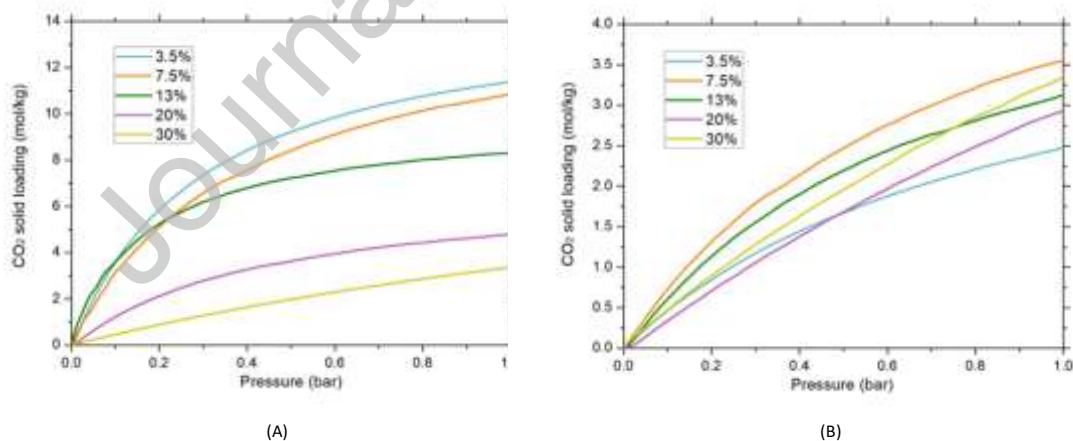


Figure 6.14: Optimal adsorbent properties that correspond to the cost limit of (A) four-step PVSA process, and (B) six-step DR cycle with different CO<sub>2</sub> feed concentrations (Subraveti et al., 2022).

According to Akinola et al., (2022), although TEA research on the solid adsorbent system for PCC is still limited, the trend over the last two decades has shown that advancements in the computational

capacity of available modelling and simulation tools has enabled detailed model development and simulation studies, particularly in the case of a fixed bed, which has thus far been seen as the most promising option. The detailed simulation demonstrated the difficulty of adsorbent and process screening, particularly when the best performing adsorbent does not always result in the lowest cost, and the best performing process for single unit operation does not always result in a superior large-scale setup. More creative cycle and column configurations are required to enable cost-effective PCC adsorption.

### 6.5.5 Summary: advantages, limitations, and prospects

Table 6.2 summarizes some of the important developments in PCC modelling, simulation, and economic analysis. Even though there are still few process simulations and economic evaluations, it is evident that more information on identifying the lowest-cost option has been reported thanks to increased computing capacity and model development. It is promising to see that the cost of solid-based PCC processes has decreased over the years, according to the simulation results. The second-generation PCC technologies' target cost of \$40/ ton of CO<sub>2</sub> has been met, and additional cost reductions are possible.

Furthermore, the work done so far has indicated that the traditional way of doing materials screening, with only the CO<sub>2</sub> capacity and surface area being considered, was not sufficient to determine the best adsorbent. Adsorption enthalpies and N<sub>2</sub> adsorption both contribute significantly to reducing capture costs. The “best adsorbent” also depends on the process configuration. Various processes have different needs in terms of the optimal adsorbent. This makes material screening more changing because the best adsorbent selected for a single unit might not be the best candidate for a large-scale operation. To reduce capture cost, it would therefore be more crucial to consider different process configuration options. As recommended by Akinola et al., (2022), the key to develop more cost-effective PCC processes would lie on the development of more creative cycle and column configurations. Setting the process performance target first, understanding the process requirements for the adsorbent to reach the target, and using this as a criterion for material screening should be the philosophy for more cost-effective PCC.

**Table 6.2 Summary of some of the work done on modelling, simulation, and techno-economic analysis of PCC processes and their results on capture cost and energy consumption.**

Application	Authors	Method	Adsorption Type	Operation mode	Cost/ Energy consumption	Software used
Adsorbent material screening	(Farmahini et al., 2018)	Molecular simulation, Equilibrium adsorption,	Fixed bed	VSA, PSA		CySim, Platypus, Python

Application	Authors	Method	Adsorption Type	Operation mode	Cost/ Energy consumption	Software used
		Process simulation				
<b>Adsorbent material screening</b>	(Hasan et al., 2013)	ZEOMICS, Isotherms, Process simulation, NAPDE, NLP	Fixed bed	VSA, PSA	\$23.63-\$41.45 per ton CO <sub>2</sub>	ZEOMICS
<b>Adsorbent material screening</b>	(Leperi et al., 2019)	Molecular Simulation, Equilibrium Isotherms, Process simulation	Fixed bed	PSA	\$30-\$40 per ton CO <sub>2</sub>	Matlab-S-ODE
<b>Adsorbent material screening</b>	(Subramanian Balashankar and Rajendran, 2019)	BAAM, Process simulation, Equilibrium Isotherms	Fixed bed	VSA	123.21 kWh/ton CO <sub>2</sub>	Matlab-S-PDE
<b>Adsorbent material screening</b>	(Burns et al., 2020)	Molecular Simulation (GCMC), Process Simulation, Machine Learning	Fixed bed	VSA	< 290kWh/ton CO <sub>2</sub>	
<b>Adsorbent material screening</b>	(Jung and Lee, 2022a)	Process simulation	Fixed bed, Fluidized bed, Moving bed	TSA	\$48.1-\$75.2/ton CO <sub>2</sub>	
<b>Energy evaluation</b>	(Haghpanah et al., 2013)	Process simulation - Finite Volume Method	Fixed bed	PSA, VSA, PVSA	148.96-499.65 kWh/ton CO <sub>2</sub>	Matlab-ode23s
<b>Energy evaluation wet flue gas</b>	(Krishnamurthy et al., 2014a)	Process Simulation, Equilibrium model	Fixed bed	VSA	177 kWh/ton CO <sub>2</sub>	Matlab-ODE
<b>Energy Evaluation</b>	(Nikolaidis et al., 2018)	Equilibrium Isotherms, LDF	Fixed bed	P/VSA	0.89-1.08 MJ/kg CO <sub>2</sub>	gPROMS/gOPT
<b>Energy Evaluation</b>	(Jung and Lee, 2022b)	Process simulation	Fluidized bed	TSA	258.6 kWh/ton CO <sub>2</sub>	

## 6.6 Machine learning application for modelling, simulation, optimization and control of carbon capture systems.

Carbon capture systems involve a highly nonlinear and complicated interplay of heat and mass transfer, thermodynamics and chemical reactions (Lawal et al., 2009). Accurately modeling their behaviour from the first principle is time-consuming, computationally difficult and requires advanced capabilities in process systems engineering. Data-based modelling using machine learning, which is simpler and easier to implement, has been proven to accurately model and predict the highly complex underlying



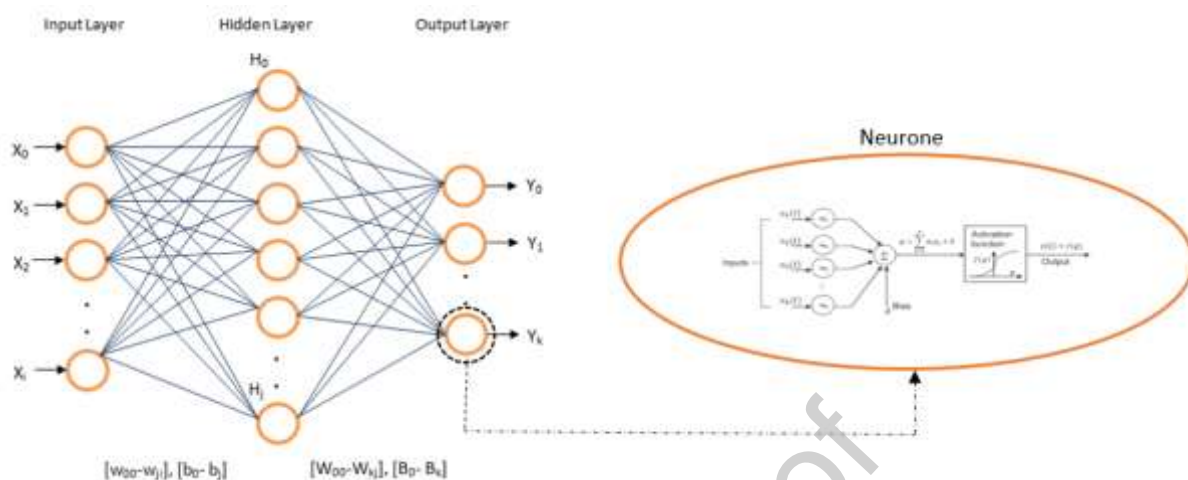
relationships in carbon capture systems with reduced computational load (Li et al., 2018). Machine learning, a branch of artificial intelligence, uses empirical data to obtain models that can predict relationships and patterns. Machine learning models use algorithms, common among which are decision trees, naïve Bayes, support vector machines, random forest, AdaBoost, k-means clustering, particle swarm, genetic algorithm and artificial neural networks (Yan et al., 2021), to achieve specific tasks such as regression, classification, clustering, outlier detection and dimension reduction. The tasks are achieved by ‘training’ the algorithms using the selected data to ‘learn’ the relationships and patterns in a dataset. The methods for machine learning model training includes supervised, unsupervised and reinforcement learning (Bonetto and Latzko, 2020). Unsupervised learning algorithms use only input datasets to ‘train’ machine learning models to ‘learn’ the commonalities within a dataset, enabling clustering or association of unlabelled datasets. On the other hand, supervised and reinforcement learning uses an input-output dataset and ‘trains’ the machine learning model to ‘learn’ the input-output relationship (Bonetto and Latzko, 2020).

Supervised machine learning has been widely used in carbon capture modelling, simulation, control and optimisation due to its relative simplicity and suitability for a wide range of machine learning algorithms. Machine learning-based modelling application in carbon capture has become expedient with the growing availability of experimental and/or operating datasets of carbon capture systems as the number of test and demonstration plants commissioned worldwide continues to increase (Okon et al., 2017). State-of-the-art machine learning applications in the wider area of carbon capture storage and utilisation (CCUS) have been reported (Gupta and Li, 2022; Rahimi et al., 2021; Yan et al., 2021). Given the wide-ranging nature of the existing reviews, their discussions on machine learning applications in carbon capture are limited with no critical analysis of existing models. Therefore, this section of this review provides an in-depth critical analysis, identifies the grey areas and limitations in existing machine learning applications in carbon capture and gives recommendations to guide future research and development.

### **6.6.1 Machine learning algorithm: Artificial neural network**

Although a handful of machine learning algorithms have been developed for handling different tasks (Yan et al., 2021), artificial neural network (ANN) is the most widely used algorithm due to their versatility and accuracy for all task categories (Shalaby et al., 2021). ANN mimics the structure of biological neural networks and their way of encoding and decoding problems and is therefore able to identify complex underlying relationships based on input-output datasets. They include the interconnection of neurones and the basic building blocks, organised in input, hidden and output layers (Figure 6.16). Feedforward ANN with signals flowing from the input to the output through a single hidden layer is very commonly used, although they are very likely to overfit the data and therefore have

poor generalisation capability (Caruana et al., 2000). To address this limitation, NN algorithms with multiple hidden layers and recurrent networks with feedback loops are emerging. The following sections describe machine learning application in different areas of carbon capture.



**Figure 6.16** Neural network showing the structure of the neurone (Shalaby et al., 2021)

### 6.6.2 Machine learning for thermodynamic and physical property prediction

The CO<sub>2</sub> solubility and other thermodynamic and physical property data, used for representing the vapour-liquid equilibria (VLE) in solutions of chemical solvent-CO<sub>2</sub>, are essential for the design and modelling of the absorber and stripper in carbon capture systems. The VLE in these systems is commonly predicted using the electrolyte Non-Random Two-Liquid (NRTL) or models such as the extended UNIQUAC, SAFT-VR and SAFT- $\gamma$  (Aronu et al., 2011; Mac Dowell et al., 2010). The electrolyte NRTL, an activity coefficient model, is the most accurate thermodynamic equilibrium model (Austgen et al., 1989). The model predictions are based on the excess Gibbs free energy model with the Pitzer-Debye-Huckel equation used to describe the long-range interaction effects. The electrolyte NRTL model has been widely used to correlate CO<sub>2</sub> solubility data in 30 wt% MEA solution. Unless where these thermodynamic models are available such as in commercial simulators, developing them is non-trivial making a strong case for machine learning-based models.

ANN has proven to successfully accurately model the VLE and physical properties of solutions of the different solvents-CO<sub>2</sub> systems as obtained in carbon capture systems (Chen et al., 2015; Norouzbahari et al., 2015; Zhang et al., 2018). Single hidden layer back-propagation neural networks (BPNN), radial basis function neural networks (RBFNN) and general regression neural networks among others have all been shown to accurately predict the CO<sub>2</sub> solubility and other properties of different amine solutions (Chen et al., 2015; Zhang et al., 2018). Although BPNN show slightly better performance, these models have limited generalisation due to the one hidden-layer structure. A more robust structure, namely multiple hidden layer BPNN, showed improved accuracy (Norouzbahari et al., 2015) although this

model appeared to have overfitted the data. Extreme machine learning algorithms where the input-hidden layer and hidden layer-output neurone weightings of the ANN are assigned random and via one-step regression respectively have also been shown to improve the predictive performance for CO<sub>2</sub> solubility and other properties (Nabipour et al., 2020). Other machine learning algorithms, namely Least Square Support Vector Machine, have comparable performance for CO<sub>2</sub> solubility predictions as an ANN-based model (Baghban et al., 2017; Nabipour et al., 2020). On the other hand, ANN has also been used to predict isotherms for CO<sub>2</sub> capture by adsorption (Khurana and Farooq, 2019). The isotherms relate the adsorbates in the surrounding phase to the adsorbates on the adsorbent at equilibrium and constant temperature conditions and is a critical thermodynamic requirement for modelling the process. The ANN-based isotherm model can be effectively and rapidly used to screen and select adsorbents.

### 6.6.3 Machine learning for modelling and simulation of the CO<sub>2</sub> capture system

ANN model with a single hidden layer has been developed and used to evaluate carbon capture performance through chemical absorption (Wu et al., 2010; Sipöcz et al., 2011). As this type of ANN model generally has poor generalisation capability beyond the training data, new solutions involving bootstrapping multiple single-layered neural networks into one network have been developed for CO<sub>2</sub> capture application (Li et al., 2015). Bootstrapped ANN models have a slow training process due to the increased number of calculations. The extreme learning machine algorithm, where the input-hidden layer and hidden layer-output neurone weightings are assigned randomly and via one-step regression respectively, can be employed to greatly enhanced the training speed of the bootstrapped ANN models (Li et al., 2017). Notwithstanding, the hidden single-layer nature of the bootstrapped primary networks, makes them vulnerable to accurately capturing the complicated phenomena in carbon capture systems as they may become trapped in the local optima (Dong and Li, 2012). More sophisticated deep belief networks (DBN) has been proposed to address this problem in carbon capture application (Li et al., 2018). DBN comprises multiple hidden layers of restricted Boltzmann machines that learn the input dataset's probability distribution, rather than the deterministic values. DBN is trained in batches including the unsupervised training phase to obtain initial weights of the neurones and a subsequent supervised phase via back-propagation. The DBN model of carbon capture systems has been shown to have better prediction accuracy than others (Li et al., 2018). Other machine learning algorithms, namely tree regression and Gaussian process regression, have also been used for modelling and simulating solvent-based carbon capture systems, but ANN generally performs better (Shalaby et al., 2021). ANN and other machine algorithms namely support vector machine, gradient boosting and tree regression have also been applied to estimate the CO<sub>2</sub> adsorption capacity for different adsorbents (Yuan et al. 2021; Fathalian et al. 2022; Irfan et al. 2022) with ANN similarly showing superior predictive capability compared to other algorithms (Fathalian et al. 2022). Many existing machine learning models for CO<sub>2</sub>

capture by adsorption are mainly for predicting the CO<sub>2</sub> adsorption capacities for different adsorbents. These models are therefore not suitable for process optimisation and control.

#### **6.6.4 Machine learning for control of the CO<sub>2</sub> capture process**

CO<sub>2</sub> capture via chemical absorption exhibits large time inertia due to the high solvent circulation rate and huge volume of the absorber and stripper(Liao et al., 2020). This impacts the capability of the plant to be operated flexibly to follow the rapid dynamics of their host power plant as required, making the process control very challenging and conventional PID controllers insufficient for achieving desired control(Liao et al., 2020). Machine learning-based predictive controllers effectively reach setpoints with zero bias at all conditions (Li et al., 2018; Akinola et al., 2020; Liao et al., 2020). Conventional model predictive controllers (MPC) are based on first principle models often linearised around the operating point to reduce the associated complexity and computational loads. Although these MPCs show better performance than PID-based controllers, their performance deteriorates quickly due to the linear models. In contrast, the machine learning-based MPC is non-linear; in some cases, the parameters can be conveniently tuned online (Li et al., 2018). The machine learning-based MPC for CO<sub>2</sub> capture has also been assessed for large-scale applications involving a carbon capture plant integrated into a 500 MW coal-fired power plant modelled via the first principle(Liao et al., 2020).

#### **6.6.5 Machine learning for optimisation of the carbon capture process**

Process optimisation, which involves an iterative solution of nonlinear equations, can be computationally challenging when based on mechanistic models of the process. As a result, reduced-order models are widely used for optimisation(Eason and Biegler, 2020). However, reduced order models sacrifice accuracy and in dynamic scenarios may not capture some critical dynamics of a process, making a case for more accurate machine learning models. Machine learning models of carbon capture systems by chemical absorption using the ANN algorithm have been used for optimising the operating condition of the process using a genetic algorithm and sequential quadratic programming algorithm(Shalaby et al., 2021). More sophisticated systems, involving reinforcement learning using actor-critic neural networks that address the limitation of standard single hidden layer ANN, have also been used to optimize carbon capture systems (Chen and Wang, 2014).

#### **6.6.6 Summary: advantages, limitations and future prospects**

Although machine learning has been largely proven for obtaining models of carbon capture and other process systems the models are rarely used. Sipöcz et al. (2011) recommended incorporating machine learning models in component libraries of commercial simulators. This will greatly promote their use and enable hybrid models to leverage the strengths of machine learning and first principle modelling,

diminishing their limitations. Machine learning models of carbon capture systems are also mostly obtained from first principle models. While this is sufficient for demonstrating the efficacy of the methodology, the models must be developed using actual operating plant data in practice as assumptions in modelling may oversimplify the practical realities. In addition, overfitting appears to go unnoticed in many reported models showing near-perfect predictions. These studies do not show any rigorous attempt to check for overfitting and the generalisation capability of the models cannot, therefore, be trusted. Finally, machine learning application in CO<sub>2</sub> capture adsorption is limited with many reported models focusing mainly on predicting the capture capacity of different adsorbents without consideration for other operating conditions.

Journal Pre-proof

## **7. Large scale applications of carbon capture technologies**

### **7.1 SaskPower Boundary Dam CCS Facility**

#### **7.1.1 Introduction for large scale carbon capture technologies**

Given the dominant role that fossil fuels continue to play in primary energy consumption for a prolonged future to come, carbon capture, use and storage (CCUS) will remain a critical greenhouse gas reduction solution. The enormous challenge for implementing CCUS lies in the integration of component technologies through large-scale commercial demonstration projects. CCS is applicable beyond the energy sectors and can be applied to industrial sources of emissions from sectors such as iron, steel, and concrete, which are hard to decarbonize. In recent years, it has been widely recognized by governments and experts that some of the world's most carbon-intensive industries may have no alternatives to CCS for deep emissions reduction.

On 2 October 2014, the first-ever, commercial-scale, coal-fired power plant incorporating amine solvent absorption carbon capture began operation near Estevan, Saskatchewan, Canada. This was a global landmark event, demonstrating a number of high-risk technology and business issues have been overcome. The project has proven to the world that commercial scale carbon dioxide capture at a coal-fired power generating station is possible rather than an elusive future option (Preston, 2015). SaskPower's Boundary Dam 3 Carbon Capture & Storage Facility (BD3 CCS Facility) is fully integrated with a coal-fired power plant. Renowned for being a key part of a full chain operation, the facility includes a power plant burning coal, a CO<sub>2</sub> capture facility, transportation infrastructure (pipelines), use and storage in enhanced oil recovery (EOR), and deep underground storage. The Province of Saskatchewan, Canada, becomes the hub for full-cycle CCUS knowledge, with the large-scale full chain of CCUS operations and demonstration, which is an ideal model for carbon capture, use and storage (CCUS) because the EOR creates revenue from the sale of carbon dioxide (CO<sub>2</sub>). Any additional capacity the off-taker of CO<sub>2</sub> does not require can be permanently stored underground.

#### **7.1.2 BD3 CCS Project Background**

BD3 CCS Facility of the SaskPower Boundary Dam Power Station is located in the southeast corner of Saskatchewan near the border with the USA, named after the Boundary Dam Reservoir, which is the surface water source for power plants cooling. The region is endowed with 300-year supply of lignite coal that is affordable, abundant, and accessible and has been fueling power plants in Saskatchewan for nearly a century. New Canadian greenhouse gas regulations on CO<sub>2</sub> emissions from fossil fuel power generation came into effect on 1 July 2015. Essentially, the regulations require existing and new coal-

fired power generation facilities to operate with the same emissions as natural gas-fired plants: 420 tonnes CO<sub>2</sub>/GWh. In addition to the performance standard under the Regulation, the current Pan-Canadian Regulation for reducing carbon emission charges a carbon tax at a price of \$40 on fossil fuel consumption. Prior to modification, Boundary Dam's Unit #3 emitted 1110 tonnes CO<sub>2</sub>/GWh, but at a 90% capture rate, the plant will, at full capacity, operate with emission at 140 tonnes CO<sub>2</sub>/GWh—essentially four times less carbon emissions than a natural gas facility. However, According to SaskPower, the federal government's carbon pricing is having an impact on SaskPower, with emissions payments going up to an estimated \$180 million in 2022 from \$56 million in 2020. The investment in the BD3 power unit's retrofit and carbon capture plant was C\$1.467 billion, of which the carbon capture plant accounted for about 50%. That gave 30 years of prolonged life to a power unit which could produce 115-120 MW clean base load power 24 hours a day (Jonathan and Crawford, 2013).

### 7.1.3. Technology selection of BD3 CCS Project

SaskPower pursued various technology options for carbon capture from oxyfuel combustion to amine solvent absorption that ultimately led to the decision to select the commercially unproven CANSOLV amine solvent carbon dioxide capture process. SaskPower then coupled that technology with Shell Cansolv's proven sulphur dioxide capture process to simplify the capture plant operation and to further reduce emissions. By the end of 2009, Shell Cansolv's CO<sub>2</sub> amine absorption capture process was the leading technology option due, in part, to its proven record of deployment of very similar SO<sub>2</sub> capture technology in coal-fired power plants and other industrial facilities at various global locations. This assured SaskPower of a lower risk of scale-up by selecting the CANSOLV technology for CO<sub>2</sub>. SaskPower had forged ahead with the design and construction of the BD3 ICCS retrofit well in advance of GHG Regulations being enacted in Canada, which came into effect on 1 July 2015. This was a strategic and environmentally-responsible decision to ensure the continued use of lignite coal reserves in Saskatchewan that could last 250–500 years.

After it is piped to the adjacent capture plant, the emissions are put through a flue gas cooler to bring the temperature down from 199°C to around 89°C, which helps enhance the adsorption of the CO<sub>2</sub> and SO<sub>2</sub>. SaskPower enhances this process by adding a polymer heat exchanger which pre-heats the condenser water used for steam generation in the power plant. The cooler also condenses out the moisture that comes from the lignite–poor-quality coal–burned at the plant. This moisture is not wasted; it is diverted to the cooling tower.

In the tower, the gas first passes through a pre-scrubber that further cools the gas and removes contaminants; then bubbles up through the scrubber, where liquid amines absorb the SO<sub>2</sub>. Moreover, the gas is introduced to the caustic polisher section reusing residual caustic generated in the CO<sub>2</sub> capture

system to remove the remaining SO<sub>2</sub>. The captured CO<sub>2</sub> comes out of the stripper at 16 psi and is passed through an eight-stage compressor to ramp it up to around 2,500 psi, producing supercritical CO<sub>2</sub>. A carbon dioxide stripper, made of stainless steel, which weighs roughly 250 tonnes, *44 metres Tall* and 26 feet in diameter. The rectangular absorber tower with ceramic tiles inside is even taller, at 54M X11, according to online information.

#### 7.1.4 Design and Construction process and considerations

The BD3 capture facility is fully integrated with its host power plant from which it draws its steam and power needs. The BD3 facility includes CO<sub>2</sub> capture, compression, and transport infrastructure. CO<sub>2</sub> produced at the BD3 operation is mainly utilized and stored at nearby enhanced oil recovery (EOR) operations near Weyburn, Saskatchewan, while also providing CO<sub>2</sub> for injection and permanent geological storage at a depth of 3,400 m in a deep saline aquifer at Aquistore Project at the SaskPower Carbon Storage and Research Centre, located near the Boundary Dam Power Station, an onsite CO<sub>2</sub> measurement, monitoring and verification (MMV) project, managed by the Petroleum Technology Research Centre in Regina, Saskatchewan. Key factors contributed to the decision to retrofit BD3 to convert it to clean coal power include the value that would be realized over the next 30 years of operating the retrofitted power plant from the sale of three valuable by-products: carbon dioxide, sulphuric acid and fly ash. This would help to offset the cost of capture. The latter two by-products provide the off-taker market with essential materials for the production of fertilizer and cement, respectively. A 2010 study comparing the cost of building a new NGCC with the retrofit with CCS showed the levelized electricity cost was equal while the clean coal would have one 3<sup>rd</sup> emission of natural gas. This would satisfy SaskPower's core mission to deliver steady power to its customers, while capturing CO<sub>2</sub>, which would mitigate the environmental impact of coal use, with the associated generation of a revenue stream to offset the cost of capture.

#### 7.1.5 Operational Status and Performances Updates

The carbon capture facility at Boundary Dam was designed to be capable of capturing **3,200 metric tons** of CO<sub>2</sub> daily, or 1 million metric tons annually. The current performance status of the project, which through a full-scale flue gas post-combustion capture process, produces 115 megawatts (MW) of clean power, captures 90% of CO<sub>2</sub>, 100% of SO<sub>2</sub>, and lowers NO<sub>x</sub> and PM emissions, and recovers vapourized water from the flue gas to meet half (34 M/H) of the cooling water demand. SaskPower reports that the parasitic energy requirements are 21%, lower than the typical 24% to 40% reported for other CCS schemes (Giannaris et al., 2021).



BD3 CCS Facility has achieved a significant milestone recently with a total of cumulative five million tonnes captured since start-up (Stephene, 2015). As of the end of 2022, 5,001,707 tonnes of CO<sub>2</sub> have been captured and prevented from entering the atmosphere, and the majority has been stored on oilfield through EOR, with about 10 per cent permanently sequestered deep underground. The BD3 CCS facility is on track to achieve an 800,000-tonne target for the fiscal year of 2022-23 (Total capture for the 2022 calendar year was 749,035 tonnes).

During the fourth quarter of 2022 (1 October – 31 December), the CCS facility was available 79% of the time, capturing 192,703 tonnes of CO<sub>2</sub>. While online, the facility had a daily average capture rate of 2,631 tonnes in Q4, with a peak one-day capture of 2,874 tonnes. A two-week planned maintenance outage in Q4 allowed SaskPower to undertake scheduled work to enable the facility to run smoothly until the next planned outage in May 2023 (Preston et al., 2018).

## **7.2 Research and design experience of Qilu Petrochemical-Shengli OilField 1 million tons/year CCUS project capture and transport unit**

### **7.2.1 Project Purpose and Project Scope**

Qilu Petrochemical-Shengli Oil Field project is China's first million-tonne CCUS (Carbon Capture, Utilization, and Storage) project and is the largest CCUS full industry chain demonstration base and benchmark project in China. It sets a precedent for the construction of million-tonne CCUS projects in China, and it lays a solid foundation for the large-scale industrial application of CCUS projects. The project is of great significance to constructing the "artificial carbon cycle" model, which will significantly improve China's carbon emission capacity and effectively push forward the achievement of China's "double carbon" target. When completed, the project can reduce CO<sub>2</sub> emissions by 1 million tons each year. This is equivalent to planting nearly 9 million trees each year, stopping nearly 600,000 economy cars from being driven each year, and an additional 2.965 million tons of fuel is expected to be added over the next 15 years. The project is composed of CO<sub>2</sub> capture and CO<sub>2</sub> transportation in Qilu Petrochemical. After being captured in Qilu Petrochemical Company, CO<sub>2</sub> is transported to Shengli Oilfield for oil drive, and sequestered in a green way, realising the integrated application of CO<sub>2</sub> capture, oil drive and storage.

### **7.2.2 Introduction of construction scale and capture process**

#### **7.2.2.1 Gas source and component**

The raw gas is supplied by the exhaust gas of the gas installation of the Qilu Petrochemical Company

Second Fertilizer Plant, which has a large handling capacity, low inlet pressure and high CO<sub>2</sub> purity. The component of the raw gas, the liquefied and refined gas, are shown in Table 7.1, and the physical properties are shown in Table 7.2.

**Table 7.1 Gas composition list ( design value )**

Number	Component	Content( mol%)	
		Raw gas components	liquefaction purification
1	H <sub>2</sub>	0.5%	0.012%
2	N <sub>2</sub>	7.3796%	0.6289%
3	CO	0.403%	0.0363%
4	CO <sub>2</sub>	91.62%	99.2931%
5	CH <sub>4</sub>	0.002%	0.0003%
6	Ar	0.07%	0.0095%
7	H <sub>2</sub> S	0.0004%	0.0004%
8	COS	0	0
9	methanol	0.015%	0.0191%
10	water	0.01%	0.0001%

**Table 7.2 Physical parameters (0.1013MPa(g), 25°C)**

Physical parameters	Index
Average molecular weight	42.55
Cp/Cv	1.291
Viscosity (cP)	0.01501
Thermal conductivity (W/m·K)	0.01786
Compressibility factor	0.9950
Density (kg/m <sup>3</sup> )	1.747

### 7.2.2.2 Construction scale and design principles

The project is based on the exhaust gas of the gas installation of the Qilu Petrochemical Company Second Fertilizer Plant to demonstrate CO<sub>2</sub> capture technology, with the designed CO<sub>2</sub> production capacity of 1 million tons/year. Taking the variation in waste gas composition into account, the installation is intended to run smoothly within 60~105% of the rated production capacity, with the maximum load of the installation intended to be 105% of the normal load. The installation has an annual continuous operating time of 8,000 hours. Currently, the project team has fully integrated with the owner unit, taking the steam, electricity, recycled water, and other supporting facilities necessary for the 1 million tons/year CO<sub>2</sub> capture into account adequately. The project makes full use of the reserved supporting facilities and land for the CO<sub>2</sub> capture project to reduce reduce the impact on production and engineering investment of Qilu Petrochemical and lay the foundation for the good operation of the CO<sub>2</sub> capture project. The project requires water, electricity and steam to be connected to the main project.

### 7.2.3 Product programs

#### 7.2.3.1 Product Categories

The raw gas is supplied by the exhaust gas of the gas installation of the Qilu Petrochemical Company Second Fertilizer Plant, whose main components are CO<sub>2</sub> and N<sub>2</sub>. The Qilu Petrochemical Company Second Fertilizer Plant captures, compresses, dries and liquefies CO<sub>2</sub>, eventually obtaining liquid CO<sub>2</sub> with a purity greater than 99% (mol%). Liquid CO<sub>2</sub> products are transported to Shengli Oilfield via pipelines for oil drive and sequestration.

#### 7.2.3.2 Actual indicators of product quality

The raw gas is dried and liquefied under pressure to obtain liquid CO<sub>2</sub> products with a pressure of 1.9 MPa and a temperature of -27 °C. The main component of the product gas is shown in Table 7.3. The product gas meets the purity requirements for on-site geological sequestration.

**Table 7.3 Gas composition after liquefaction**

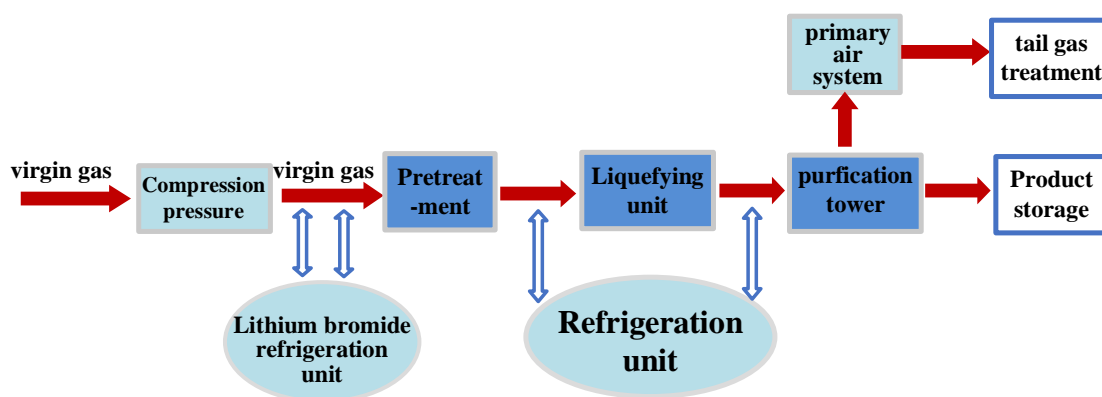
composition		CO <sub>2</sub>	H <sub>2</sub> S	H <sub>2</sub> O
Molar	molecular percentage,	≥0.99	≤0.001	≤10ppm
	mol%			

### 7.2.4 Process Description

#### 7.2.4.1 CO<sub>2</sub> capture process

The process of "compression-condensation-purification" is adopted to recover CO<sub>2</sub>. The raw gas is first pressurised by a compressor unit, then passes through a lithium bromide refrigeration unit to recover waste heat for cooling, and then sequentially enters the drying dehydration and liquefaction purification system. The raw gas is condensed and liquefied at low temperatures to obtain a liquid CO<sub>2</sub> product. The liquid CO<sub>2</sub> product is ready to be stored in tanks once it has been qualified.

In accordance with its function, the production process can be divided into compression units, liquid purification units, refrigeration units, tank storage units, loading unit and conveying units. The process flow of CO<sub>2</sub> recycling is shown in Figure 7.1.



**Figure 7.1 Carbon dioxide recycling process flow chart**

#### 7.2.4.1.1 Compression unit

Compressor is an essential piece of equipment to keep the system running, and its stability is the key factor affecting the normal operation of the system. Currently, centrifugal compressor, reciprocating compressor and screw compressor are the more commonly used types of compressors. The capacity of the unit is key to compressor selection, while the gas composition and final pressure also have a certain influence on compressor selection. Centrifugal compressors are mostly driven by steam, and they are adapted for use in high-flow conditions. Currently, screw compressors and reciprocating compressors are often used to handle the small and medium flow. The project has low gas pressure and high gas volume, so the MCL706 centrifugal compressor is chosen. Horizontal split welded casing is selected, and the speed regulation mode is variable speed when used. The flow ranges from 60% ~ 105%. The shaft power of the centrifugal compressor is large. Taking the utility conditions at the project site into consideration, steam turbine is used as the drive mechanism of the centrifugal compressor for this project.

#### 7.2.4.1.2 Liquid purification units

The project has a high concentration of CO<sub>2</sub>, so low temperature distillation technology, indicated in Figure. 7.2, is chosen to liquefy and purify CO<sub>2</sub>. The selective removal of impurities without the use of chemicals results in dry liquid CO<sub>2</sub>.

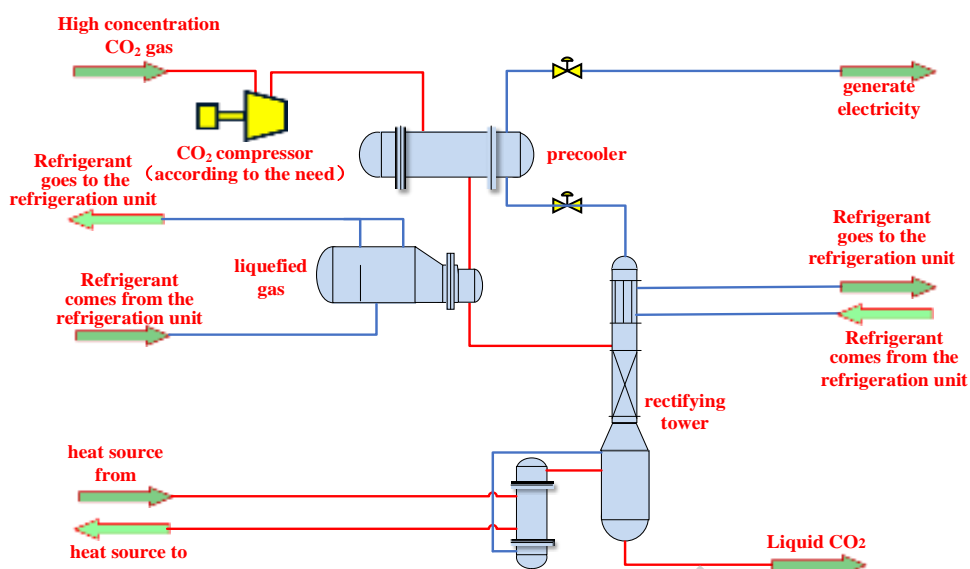


Figure 7.2 Low-temperature distillation process flow chart

### (1) Dry Dehydration System

The CO<sub>2</sub> raw gas passes through the compression unit and then enters the drying tower for dehydration treatment. The dehydration process is based on a double tower + pre-sorption tower technology.

Commonly used solid desiccants consist of molecular sieve, lithium oxide, activated carbon, alumina, silica gel and compound desiccant. Molecular sieve has poor absorption ability. Lithium oxide has good water absorption properties, but it is corrosive and has a high heat release when absorbing water which affects its cooling capacity. Silica gel has the advantages of good adsorption performance, economic and practical, but it is easy to break after the adsorption of a significant amount of water. Alumina has poor adsorption capacity, only 50% of silica gel, its regeneration temperature is high, and its regeneration time is long. Composite desiccant is unstable and deliquescent, but its adsorption performance is good.

The CO<sub>2</sub> raw gas is dehydrated using molecular sieves as adsorption carriers, and the water content after dehydration is decreased to less than 10 ppm. When used as a solid desiccant, a molecular sieve carries out gas adsorption by adsorption; that is, water molecules are adsorbed on the surface of the solid. A molecular sieve has a capillary or cylindrical surface, and therefore its adsorption force is more concentrated. When the diameter of the capillary pores approaches that of the adsorbed molecules, Capillary coagulation means that the cohesion starts to concentrate when the diameter of the capillary pores approaches that of the adsorbed molecules. Because of the high cohesion, water can be drawn out from the airflow and condensed into a liquid phase in the capillary pores when the temperature is higher than the boiling point. The advantages and disadvantages of commonly used solid desiccants are shown in Table 7.4 below.

**Table 7.4 Comparison of advantages and disadvantages of common solid desiccants**

Refrigeration circle	Merit	Defect
Lithium oxide desiccant	big amount of water absorption	Corrosive, large heat release when absorbing water, affecting cooling capacity
silica-gel drier	Good adsorption value performance, economical and practical	Easy to crack, high regeneration temperature, long time, limited use times ( usually 10-30 times, the first regeneration after the drying effect is almost the same as the original finished product, and the second regeneration effect is reduced to 90 %, after 10-30 times of regeneration, the drying effect is reduced to the original 80 %, generally no desiccant regeneration
Molecular sieve	Strong adsorption, high temperature can still accommodate water molecules, pore size can be controlled by different processes	Relatively low dehydration capacity
Alumina drier	Large water absorption, fast drying speed	Aluminum oxide adsorption capacity is weak, and high regeneration temperature ( usually 250-350 °C ), long time ( 3-5h )
Composite desiccant	Good moisture absorption	Unstable, easy to deliquesce

## (2) Liquefaction system

After pressurised dehydration, the product gas is cooled to less than  $-20\text{ }^{\circ}\text{C}$  by a horizontal shell and tube liquefier. Three horizontal shell and tube liquefiers are put into use. The shell medium is propylene, while the tube medium is  $\text{CO}_2$ . The raw  $\text{CO}_2$  gas is condensed into liquid  $\text{CO}_2$  due to the evaporation of liquid propylene.  $\text{CO}_2$  is completely liquefied and then sent to the purification system for deeper purification.

## (3) Purification system

Purify the product gas from the liquefaction system. MellapakPlus TM structured filler is Sulzer's latest generation of structured filler, which effectively increases the handling capacity of the filler. The ripple direction of the upper and lower parts of each filler unit gradually approaches the vertical direction. This can not only reduce the pressure drop and shear force caused by the interaction between vapor and liquid phase, but also reduce the possibility of liquid flooding so as to eliminate local bottlenecks. MellapakPlus TM structured filler also offers significant advantages, such as high mechanical strength and strong corrosion resistance. The new MellapakPlus TM filler design allows for a significant reduction in tower diameter to reduce the customer's upfront investment costs.

## (4) Expander

The expansion generator unit recovers the pressure energy of the exhaust gas, and the electricity generated is integrated into the plant grid. The low-temperature exhaust gas, after the expansion is heat exchanged with the raw gas.

Principle of the expansion generator unit: exhaust gas enters the expansion generator unit to be expanded and cooled, and the power output of the expansion generator unit is passed through the

gearbox and transmitted to the generator to generate electricity. An emergency shut-off valve is provided at the inlet of the expansion generator unit. When the unit interlocks and shuts down, the emergency shut-off valve immediately cuts off the gas supply to the expansion generator unit. At the same time, the bypass control valve is opened to bring the gas supply directly into the subsequent process to ensure system balance and stability.

#### (5) Fresh air system

Three fans are put into use, and the flow of each fan is 20000Nm<sup>3</sup>/h. The non-condensable exhaust gas discharged from the expansion generator exchanges heat with air and then enters the exhaust buffer tank. Then it is transported to the RCO unit for exhaust gas treatment.

#### 7.2.4.1.3 Refrigeration units

The main advantages of propylene refrigeration units and lithium bromide refrigeration units are low noise, energy saving and environmental friendliness. In this project, a combination of a centrifugal propylene refrigeration unit and a lithium bromide refrigeration unit is put into use.

The propylene refrigeration unit provides the necessary cryogenic conditions for the condensation and liquefaction of CO<sub>2</sub>. The project is processed on a large scale with a turbine-driven centrifugal refrigeration unit.

The lithium bromide aqueous solution absorbs heat by the low boiling point vaporisation of water in a high vacuum state for the purpose of refrigeration. The refrigerant cycle is the cycle of lithium bromide aqueous solution in the machine from dilute to concentrated and concentrated to dilute, refrigerant water from liquid to vapor and from vapor to liquid. The two cycles are carried out simultaneously. The lithium bromide refrigeration unit produces cryogenic cooling water by the waste heat of the final stage outlet of the CO<sub>2</sub> raw gas compressor. The compressed CO<sub>2</sub> raw gas is further cooled to 8 °C using cryogenic cooling water and then transported to subsequent liquefaction and purification installation.

#### 7.2.4.1.4 Spherical tank area and loading units

The CO<sub>2</sub> raw gas is processed by the liquefaction and purification installation to obtain liquid CO<sub>2</sub> product, which is respectively stored in the corresponding spherical tanks and then conveyed by a loading crane. The main equipment of the spherical tanks area and loading units is shown in Table 7.5 below.

**Table 7.5 Main equipment of spherical tank area and loading unit**

equipment name	quantity	major parameter
Carbon dioxide spherical tank	2	Volume 4000m <sup>3</sup> , material 07MnNiMoDR, design temperature-45 ~ 50°C, design pressure 2.2MPa

equipment name	quantity	major parameter
Carbon dioxide loading pump	2	Flow 30 ~ 120m <sup>3</sup> /h, head 50m
Carbon dioxide loading crane tube	14	DN50/DN50-304

#### 7.2.4.1.5 Integrated optimisation of the capture process

The CO<sub>2</sub> capture process of this project adopts two energy-saving processes: the recovery of waste heat by the additional refrigeration unit and the recovery of exhaust pressure energy by the expansion generator. The recovery of waste heat by the additional refrigeration unit can reduce the operating load and electricity consumption of the ice machine and reduce carbon emission. The expansion generator unit recovers the pressure energy of the exhaust gas, and the electricity generated is integrated into the plant grid. The low-temperature exhaust gas, after expansion, can exchange heat with the raw gas to maintain system balance and stability. After the energy-saving process is put into use, the combined energy consumption of capture is 63.263 kg standard oil/tCO<sub>2</sub>. In light of the "Standard for Calculation of Energy Consumption for Petrochemical Design" ( GB/T50441-2016 ), the energy consumption is converted to 2.649 GJ/tCO<sub>2</sub>. Table 7.6 shows the consumption of utilities for capture and compression drying in each scheme:

**Table 7.6 Utility consumption**

No.	Name	Unit	Specification	Unit consumption/t products	Time consume	Energy conversion value ( kg standard oil )	Energy consumption ( kg standard oil/t )
1	Electricity	kWh	6000/380V	13.428	1180	0.22	2.954
2	Circulating water	t	0.45MPa	86.373	7590	0.06	5.182
3	Medium-pressure superheated steam	t	4.0MPaG	0.624	54.6	88	54.912
4	Instrument air	Nm <sup>3</sup>	0.7MPaG	3.414	300	0.038	0.130
5	Medium nitrogen gas	/	1.3MPa	0.569	50	0.15	0.085
6	Footing	/	/	/	/	/	63.263

### 7.3 Research and design experience of a 150 kt/a CO<sub>2</sub> capture and purification project

#### 7.3.1 Project purpose and scope

The Guohua Jinjie Power Plant CO<sub>2</sub> capture project relies on the Shenhua Jin Guohua 600 MW sub-critical coal-fired unit to investigate advanced chemical absorption and CO<sub>2</sub> capture processes to capture and store post-combustion CO<sub>2</sub> in a brine layer. The project includes a 150,000 ton/year CO<sub>2</sub> capture



system that utilizes a CO<sub>2</sub> capture system built by Shenhua Coal to Oil Company. A storage unit (located in Erdos, Inner Mongolia) was used for geological storage. The successful implementation of this project will help optimize the entire process of post-combustion CO<sub>2</sub> capture and brine storage, mastering various key technologies to achieve near-zero emissions from coal-fired power plants.

### 7.3.2 Introduction of construction scale and capture technology

#### 7.3.2.1 Source and composition of the flue gas

The flue gas is introduced from the flue at the outlet of the desulfurization absorption tower of the King Street Power Plant. The composition of the flue gas is shown in Table 7.7.

**Table 7.7 Flue gas composition (design value)**

Component	Molecular weight	Mole fraction / (mol%)
CO <sub>2</sub>	44.011	11.1
O <sub>2</sub>	31.999	6.1
N <sub>2</sub>	28.014	70.7
SO <sub>2</sub>	64.065	35 mg/Nm <sup>3</sup>
SO <sub>3</sub>	80.064	/
Dust concentration	—	<10 mg/Nm <sup>3</sup>
HCl	36.461	0.0001
HF	20.006	0.0001
H <sub>2</sub> O	18.015	12.1
NO <sub>x</sub>	—	50 mg/Nm <sup>3</sup>

#### 7.3.2.2 CO<sub>2</sub> stream

The flue gas of the project was introduced from the outlet of the desulfurization absorption tower, and the main components of the flue gas are CO<sub>2</sub> and N<sub>2</sub>. After trapping, compression, drying and liquefaction, liquid CO<sub>2</sub> with 99.5% (V%) purity was obtained at Shenhua Jinjie Power Plant and then transported to the storage site of Shenhua CCS project in Ulanmulun Town, Ijinhuluo Banner, Ordos City, Inner Mongolia for geological storage. After pressurizing, drying, and liquefying, the pressure of the product was 2.2 MPag and the temperature was -20°C. The main components in the product are shown in Table 7.8, and the purity of CO<sub>2</sub> in the product gas meet the requirements for geological storage on site.

**Table 7.8 Composition of the liquefied gas**

Components	Mole percent, mol%
CO <sub>2</sub>	0.995
N <sub>2</sub>	0.004
O <sub>2</sub>	0.001
H <sub>2</sub> O	<10 ppm

### 7.3.2.3 Process description

For the characteristics of low partial pressure and complex composition of CO<sub>2</sub> in the flue gas of coal-fired power plants, the project integrated and applied design technologies such as a new high-efficiency CO<sub>2</sub> absorber, plastic packed absorption tower, flue gas pretreatment process, low-energy CO<sub>2</sub> capture mechanical vapour recompression (MVR) heat pump, and super gravity reactor. The flow chart of the capture link is shown in Figure 7.3. Depending on the function, the production process can be divided into capture purification, compression, drying, liquefaction and storage units. The refinery site was reserved for the project.

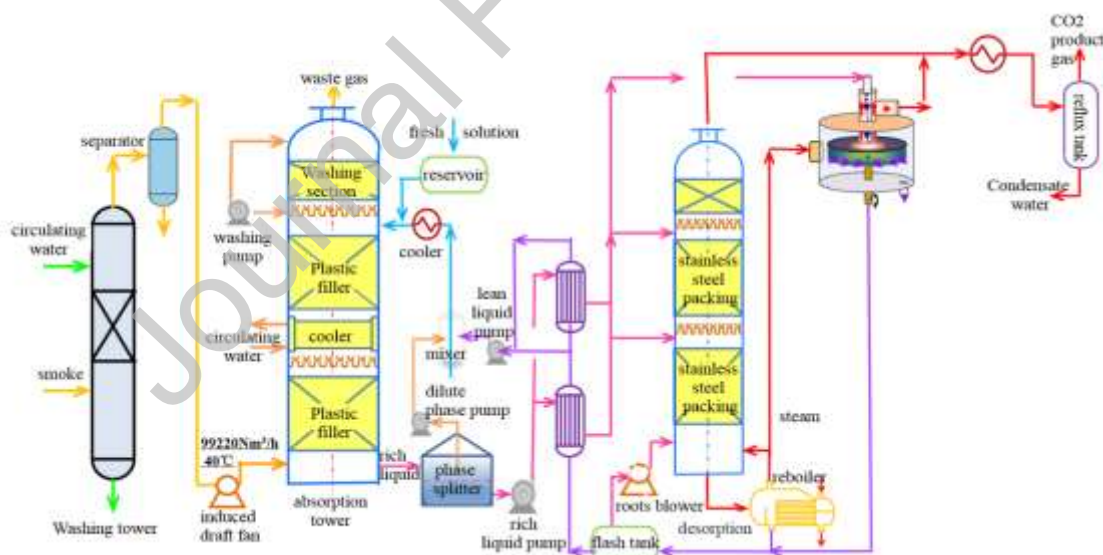


Figure 7.3 Flow chart showing the low energy CO<sub>2</sub> capture process.

#### 7.3.2.3.1 Integrated optimization of the capture process

As shown in Figure 7.3, the CO<sub>2</sub> capture project employed three energy-efficient processes, including interstage cooling, split desorption, and an MVR heat pump. The intercooling process improved the

absorption load and reduced regeneration energy consumption by cooling the semi-rich liquor from the absorption tower. The rich-liquid split desorption process also recovered waste heat from the regeneration gas by direct heat exchange between the cold rich liquid and the regeneration tower top regeneration gas. In addition, the MVR heat pump process can recover latent heat from the flash vapour by flashing and heating the lean hot liquids back to the regeneration tower. Regeneration energy consumption was reduced by 20% from 2.9 GJ/ton CO<sub>2</sub> to 2.34 GJ/ton CO<sub>2</sub> and 0.58 GJ/ton CO<sub>2</sub>/ton CO<sub>2</sub>.

#### 7.3.2.3.2 Process characteristics

(1) Using new high-efficiency CO<sub>2</sub> capture absorbers (including composite amine absorbers, phase change absorbers and ionic liquids), the energy consumption of the new absorbers was reduced by more than 30% compared to the regeneration of traditional MEA solvents. At the same time, the loss of absorber was less than 1.0 kg/t CO<sub>2</sub>, and the corrosion rate of the absorption tower and desorption tower was less than 0.076 mm/a.

(2) Using flue gas pretreatment technology, the flue gas was pretreated by alkali washing and free water separation before it entered the capture system to reduce the loss of solvent at the back end and maintain the system water balance.

(3) The project process integrated energy-saving processes such as MVR heat pump, inter-stage cooling, and split-desorption, forming a new technology of CO<sub>2</sub> absorption with low cost and low energy consumption, achieving CO<sub>2</sub> capture rate  $\geq 90\%$ , CO<sub>2</sub> purity  $> 99\%$ , and regeneration energy consumption  $\leq 2.4$  GJ/ton CO<sub>2</sub>.

(4) Compared with the traditional stainless steel packed absorption tower, the cost of inexpensive plastic-packed absorption tower was reduced by more than 30%.

### 7.3.3 Materials consumption

The raw materials, utilities, and main consumption quota are shown in Table 7.9.

**Table 7.9 Raw materials, utilities, and major consumption quotas**

Serial number	Description & specification	Unit	Quantity	Remark
1	Design scale: product gas (dry gas)	Nm <sup>3</sup> /h	87217	/
	Flue gas (dry gas)	Nm <sup>3</sup> /h	100000	/
2	Amine solvent	t	~80	400 m <sup>3</sup> for original start-up solution
	Chemicals Corrosion inhibitor	t	~1	
	Antioxidant	t	~0.6	
3	Chemicals Amine solvent	t/a	~150	Annual operation demand
	Corrosion inhibitor	t/a	~3.75	

4	Public works	Antioxidant	t/a	~3.75	
		Sodium hydroxide	t/a	~100	
		Circulating water	t/h	~2594	
		Electric	kwh	~4942.75	
		0.3MPag steam	t/h	~23.76	1.0 MPag steam for drying skid, and 0.63 MPag steam for amine recovery
		1.0MPa steam	t/h	~1.5	
		0.63 MPag steam	t/h	~5	
	Desalted water	t/h	~4.5		
5	Rate of expenditure	Circulating water	t/tCO <sub>2</sub>	~115	/
		Electric	kW /tCO <sub>2</sub>	~263	/
		Steam	t/tCO <sub>2</sub>	~1.27	/
		Amine solvent	kg/tCO <sub>2</sub>	≤1.0	/
		Corrosion inhibitor	kg/tCO <sub>2</sub>	≤0.025	/
		Antioxidants	kg/tCO <sub>2</sub>	≤0.025	/
		Sodium hydroxide	kg/tCO <sub>2</sub>	≤0.67	/
	Desalted water	kg/tCO <sub>2</sub>	~240	/	

### 7.3.4 Comprehensive energy consumption analysis

In the normal production process, the main electrical equipment in the station included compressors, pump equipment, drying skid silica gel regeneration, indoor and plant lighting, and pipeline electric tracing heat. Steam was mainly used for solution regeneration and intermittent amine recovery heaters. Desalinated water was mainly used for the preparation of chemicals and process system make-up water. Circulating water was mainly used for lean liquid cooling, regenerative cooling and compressor inter-stage cooling. The utility consumption of the capture, compression and drying components in each scenario is shown in Table 7.10.

**Table 7.10 Consumption of public works**

Project	Unit	Quantity						
		Capture and purification	Compressing components	Drying section	Liquefying part	Storage and loading	Total	
<b>Public works</b>	Circulation water	t/h	~1800	~190	~30	~574	--	2594
	Electrical	kW	~2007.75	~1700	175	~1042	~18	4942.75
	Steam	t/h	~21	--	--	--	--	21
	Desalinated water	t/h	~4.5	--	--	--	--	4.5

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Makeup of the circulating water	of t/h	~33	~4	~1	~12	--	50
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The project used a compatible design that integrates the physical properties of the composite amine absorber, ionic liquid and phase change absorber. In the design, the calculated total capture power was higher than the actual operating value based on the consideration of full adaptability. The energy consumption was the same for each part of the back-end, starting from compression.

### 7.3.5 Estimation of total investment

The construction investment consisted of engineering costs, other engineering construction costs and basic reserve costs. Among them, the engineering cost was 992,322,000 yuan, the engineering secondary cost, including management, design, supervision, protection, seismic assessment and environmental assessment cost was 234,235,000 yuan, and the basic reserve cost was 613,280,000 yuan, totalling 128,788,500 yuan. The project cost was 9,923,220,000 RMB, including 6,995,540,000 RMB for equipment purchase, 1,122,290,000 RMB for main materials, 6,656,680,000 RMB for installation and 113,911,000 RMB for construction. Other expenses: Other costs totalled RMB 2,432,350,000, including construction site acquisition and clearing fees, project construction management fees, project construction technical service fees, complete set of start-up and test freight fees, production preparation fees, and large transportation measures. The basic reserve cost was calculated as 5% of the sum of construction cost and other costs, totaling 6,132,800 yuan. The project consisted of all own funds and was interest-free during the construction period. The total investment reported and approved was the sum of construction investment and interest and working capital during the construction period. The total investment reported and approved was 13,839,800 yuan.

## 8. Conclusions and outlook

Carbon capture from flue gas, the primary CO<sub>2</sub> source, is pivotal for achieving net-zero global CO<sub>2</sub> emissions. Post-combustion carbon capture, the most mature and widely utilized technology, presents significant viability and feasibility for existing power plants, requiring no substantial renovation or infrastructure upgrades. The primary post-combustion CO<sub>2</sub> capture technologies encompass absorption

separation (physical and chemical), adsorption separation (physical and chemical), and membrane separation. Over 60% of post-combustion technologies employ absorption-based methods. Particularly, the chemical absorption method, typified by MEA absorption, is highly promising for industrial applications due to its suitability for handling large air volumes and its operational simplicity. It primarily consists of two critical processes: the chemical absorption of CO<sub>2</sub> in the absorption tower and the thermal regeneration of the absorbent in the desorption tower. Nonetheless, CO<sub>2</sub> capture from flue gas sources still faces considerable challenges impeding further development and commercialization. Accordingly, more extensive studies are required to explore the commercial prospects of the pre-combustion CO<sub>2</sub> capture process. Since the late 1990s, large-scale direct air capture (DAC) has been proposed as an additional method for mitigating rising atmospheric CO<sub>2</sub> concentrations. Despite the ambient CO<sub>2</sub> concentrations being extremely low, several DAC approaches have been put forward, utilizing adsorption and absorption technologies. Nevertheless, the topic remains under development. Ensuring efficient operation with reasonable energy consumption is a prerequisite for the practical application of DAC. This review discusses in detail a clear and complete performance evaluation method, focusing on energy consumption and energy efficiency.

Chemical absorption with amine solvents currently serves as a relatively mature post-combustion CO<sub>2</sub> capture method, with practical applications in large fixed emission sources, such as coal/gas-fired power plant flue gas. However, it is still in the industrial demonstration stage due to the absence of large-scale industrial or commercial applications. Replacing conventional aqueous amine solutions with organic solvents or ionic liquids could provide significant benefits. Additionally, life cycle assessment can be employed to evaluate the environmental and economic impacts of carbon capture and storage. Alkali-metal-based carbonates of K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> are proven as promising candidates for CO<sub>2</sub> capture, while the practical applications of pure carbonates were restricted by their poor capacities and kinetics. As a result, the proper design of efficient K<sub>2</sub>CO<sub>3</sub>- and Na<sub>2</sub>CO<sub>3</sub>-based sorbents is of significant importance in broadening their application prospects. The most promising method for modification of K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> is to load them on a porous support, where the optimization of the support materials, K<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> loading amounts, and preparation methods are expected to improve the texture properties and surface morphology, enhance the dispersion of active K<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub>, and hence accelerate the CO<sub>2</sub> adsorption. In spite of the extensive studies on this topic, the influence of the abundant impurities in flue gases, such as sulphur- and chlorine-containing species, on the CO<sub>2</sub> capture performance of alkali-metal-based sorbents was rarely studied systematically, which is critical in evaluating their durability and regeneration efficiency in practical applications.

Apart from liquid-based sorbents, solid sorbents are emerging as potential candidates for large-scale CO<sub>2</sub> capture. These can be categorized as low, medium, and high-temperature solid sorbents. CaO has a high capacity for CO<sub>2</sub> capture. Although it can be deactivated during the CO<sub>2</sub> capture process, the spent CaO could be used for cement industries. One of the key challenges of CaO-based carbon capture

is the use of high temperatures (up to 900 °C). MgO is an excellent medium-temperature adsorbent for carbon capture. However, it has very slow reaction kinetics. Key breakthroughs are needed for MgO-based materials development towards its commercial applications.

Furthermore, membrane technology has emerged as a promising alternative for CO<sub>2</sub> capture due to its inherent attributes, such as a smaller footprint, simpler setup and operation, energy savings, and the absence of phase transformation. However, designing a highly permeable membrane remains a significant challenge for efficient CO<sub>2</sub> capture. Other CO<sub>2</sub> capture technologies, including oxy-fuel combustion technology and chemical looping process, have also been reviewed. Techno-economic analysis and process modeling of CO<sub>2</sub> capture technologies are being developed to gain in-depth insights into the CO<sub>2</sub> capture process under various conditions.

The primary factor limiting the commercialization of CO<sub>2</sub> capture technology is its high cost. However, the International Energy Agency (IEA) forecasts that by 2030, the cost of CO<sub>2</sub> capture, such as DAC, is likely to decrease to less than \$100/t with the large-scale application of technology. To meet specific climate targets, it is imperative to explore all CO<sub>2</sub> removal technologies thoroughly, as capturing CO<sub>2</sub> at the source, such as power plants, is insufficient. Novel reaction systems such as RPB and process intensification (integrated with CO<sub>2</sub> conversion) and broad system optimization are required. However, for novel high-efficient systems (e.g., RPB), large-scale demonstration is needed to validate process modelling. Process modelling and simulation (e.g., CFD) of carbon capture systems should be further carried out. However, more research is required to enhance the accuracy of modelling and simulation results. Furthermore, extensive process conditions such as adsorption enthalpies should be considered for post-combustion CO<sub>2</sub> capture modelling.

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#### Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: