

Methane up-carbonizing: a way towards clean hydrogen energy?

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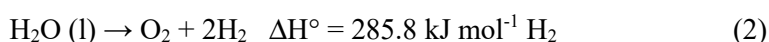
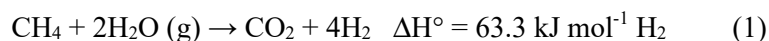
Abstract

A global transition to a hydrogen economy requires widespread adoption of clean hydrogen energy. Methane cracking is one of the most viable technologies for producing clean hydrogen, nearing the ultimate zero-carbon-emissions targets. While major progress has been made in the lab-scale development of high-performance reactors and catalysts for methane pyrolysis, research focusing on industry-relevant scale and process conditions is in its infancy. Herein, recent advances in fundamental and applied research in methane pyrolysis are critically examined, focusing on physico-chemical mechanisms to achieve energy-efficient, low-carbon-emission, scalable processes. The highlighted recent efforts to bridge the gap between laboratory research and industrial applications reveal rapid advances in practical applications based on synergistic chemical engineering, catalysis, and materials science research.

1 Perspectives, challenges, and opportunities for translational research towards commercial
2 applications of methane cracking are discussed aiming at clean hydrogen production.

3 4 5 **1. Status**

6 To achieve the ambitious CO₂ emissions reduction target based on the COP27 Egypt
7 agreement, clean energy sources are vital to decarbonize the industrial and habitable
8 environments. Hydrogen is one of the most promising zero-carbon energy vectors. It is used in
9 fuel-cells to power vehicles and its uses in both industrial processes and domestic heating are
10 rapidly emerging [1,2]. Several technologies for the production of clean hydrogen are currently
11 in development and adoption [3–6]. Based on the environmental impact of the H₂ production
12 approach, the various routes for hydrogen production have been associated with different color
13 codes for easy identification as summarized in Figure 1(a). The present industrial hydrogen
14 production pathway is still dominated by the steam methane reforming (SMR) process using
15 fossil fuels (equations (1)) with unavoidable generation of huge amounts of CO₂. The hydrogen
16 produced via this route is referred to grey hydrogen. In the case where the SMR process is
17 combined with CO₂ capture processes, grey hydrogen turns to blue hydrogen. Presently, carbon
18 capture and storage (CCS) technology is still in its early stages and its environmental and
19 geological impact still needs to be addressed. Water electrolysis powered by renewable energy
20 (equations (2)) is a promising way to produce clean hydrogen and the produced hydrogen is
21 known as green hydrogen. Methane pyrolysis (also known as methane cracking or methane
22 dissociation) is another approach for clean hydrogen production, which ideally produces
23 gaseous H₂ designated as turquoise hydrogen and solid carbon (equations (3)). Based on the
24 energy source used and the feedstock, the hydrogen color can be assigned as pink, aquamarine
25 and brown as well [7].



30 As noted from equation (1)-(3), the energy requirement for turquoise hydrogen produced via
31 the pyrolysis of methane ($\Delta\text{H}^\circ = 37.4 \text{ kJ mol}^{-1} \text{ H}_2$) is much smaller than that of water electrolysis
32 ($\Delta\text{H}^\circ = 285.8 \text{ kJ mol}^{-1} \text{ H}_2$) and the SMR process ($\Delta\text{H}^\circ = 63.3 \text{ kJ mol}^{-1} \text{ H}_2$). It is important to note

1 that the carbon footprint of water electrolysis powdered by non-renewable energy is even larger
2 than that of the SMR process because of the high energy consumption. Al-Qahtani et al. [4]
3 made a comprehensive assessment of a wide range of promising H₂ technologies considering
4 resource depletion, levelized cost of hydrogen and environmental externalities simultaneously
5 (impacts on ecosystem quality and human health) as shown in Figure 1(b). Methane pyrolysis
6 emerges as the most promising technology for a low-carbon and affordable hydrogen
7 production. Parkinson et al. [8] have also compared and evaluated 12 different H₂ production
8 routes as shown in Figure 1(b) and their results suggest that methane pyrolysis may be the most
9 cost-effective technique in the short-term that encourages the construction of infrastructure
10 required to sustain a high penetration of hydrogen in the energy sector. At present, worldwide
11 hydrogen production stands at approximately 120 million tons (Mt) annually, with two-thirds
12 of this volume being pure hydrogen and the remaining one-third mixed with other gases.
13 Nevertheless, to satisfy just 5% of our global energy demands, as per the 2021 data, we would
14 need to produce a staggering 188 million tons (Mt) of hydrogen [9]. Despite the critical need to
15 reduce greenhouse gas emissions, fossil fuels are still expected to have a dominant share of the
16 global energy demand up to 2050 [10]. Methane pyrolysis represents a promising alternative
17 for low-carbon hydrogen production to address the energy transition and the ongoing
18 environmental degradation [11–13].

19 Numerous comprehensive reviews have been published, offering in-depth insights into
20 methane pyrolysis for hydrogen production [12–20]. Significant amount of the analyzed data
21 pertains to the laboratory-scale exploration of high-performance reactors and catalysts in both
22 thermal non-catalytic and catalytic methane cracking processes. Recently, McConnachie et al.
23 [14] and Msheik et al. [21] have provided detailed and up-to-date analyses, particularly focusing
24 on liquid catalysts. However, it is important to note that research focusing on scaling-up and
25 process conditions relevant to industry for diverse methane pyrolysis technologies is in its
26 infancy. This perspective-type article seeks to provide a broad overview of the current state of
27 this field, with a specific emphasis on its present status and an exploration of the fundamental
28 aspects across various methane pyrolysis technologies. Additionally, it outlines the existing
29 limitations and foresees the forthcoming engineering challenges in the practical implementation
30 of this technology. In doing so, it serves as a valuable resource for researchers and practitioners
31 involved in both foundational studies and industrial applications. This perspective-type review
32 is anticipated to be particularly advantageous for individuals interested in the latest research
33 developments in this domain, drawing perspectives from both academic and industrial sectors.

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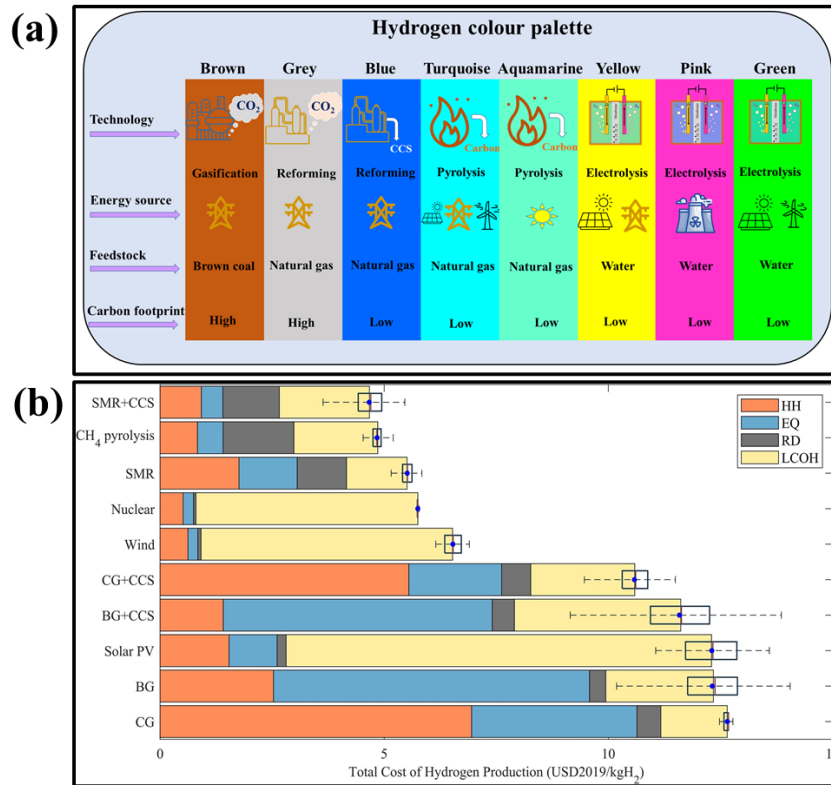
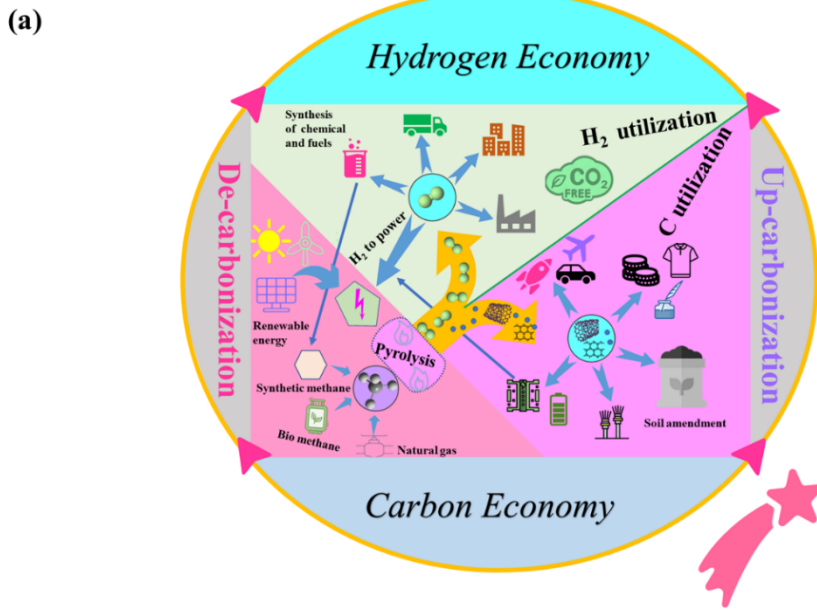


Figure 1. (a) Hydrogen color coding of various approaches for hydrogen production; (b) Total cost of the evaluated H₂ production routes in terms of externalities (HH, EQ, and RD) and LCOH (Reprinted with permission from [3]). HH refers to the monetized human health indicator, EQ stands for the monetized ecosystem quality indicator, RD stands for the monetized resources depletion and LCOH stands for the levelized cost of hydrogen. The other acronyms in Figure 1(b): SMR: Steam methane reforming; CCS: Carbon capture and storage; CG: Coal gasification; BG: Biomass gasification; PV: Photovoltaics.

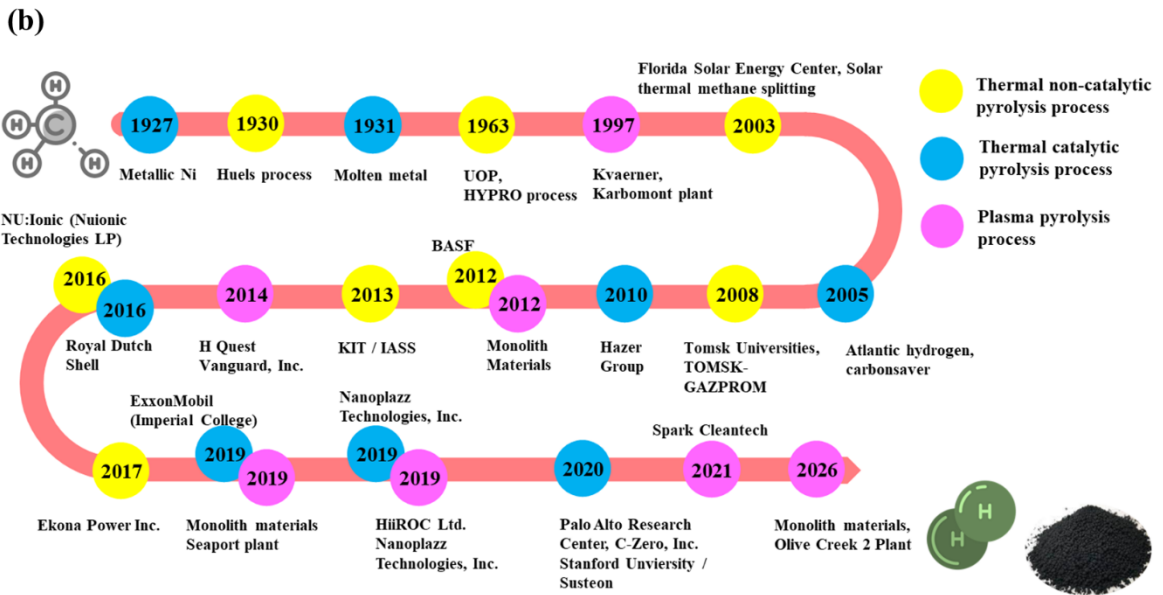
2. Up-to-date progress

Apart from natural gas, the source of methane used can also be biomethane (derived from plant-derived materials) and synthetic methane (derived from CO₂ utilization). In particular, hydrogen production from biomethane can be carbon-negative even using the current electricity energy sources. The H₂ produced by methane cracking can be stored and transported safely over long distances using the liquid organic hydrogen carrier technologies and can then be used as a chemical feedstock or fuel in buildings, transportation, power generation, and industry (Figure 2(a)). Methane pyrolysis research has been going on for over a century and different types of reactors have been considered and studied (Figure 2(b)), but the technology has yet to be commercialized. The major technologies or routes for methane cracking can be generally

1 grouped into three categories [22] as shown in Figure 2(c): thermal non-catalytic pyrolysis,
 2 thermal catalytic pyrolysis, and plasma pyrolysis. In the following, the various routes are
 3 critically examined, focusing on the current status and insights, as well as the challenges and
 4 opportunities for fundamental research and industrial translation.
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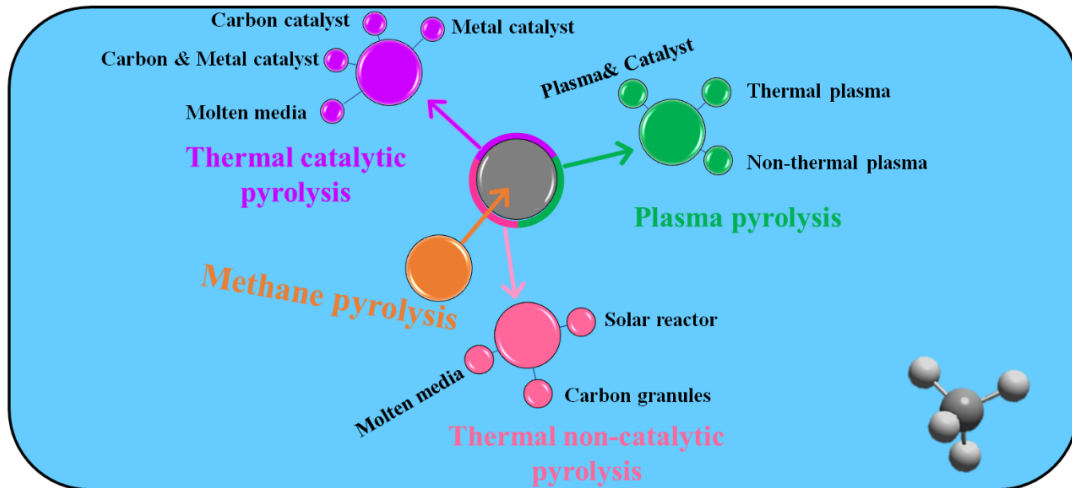


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(c)



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2 Figure 2. (a) Schematic representation of hydrogen and carbon product productions via methane
3 pyrolysis and of their utilizations; (b) Key developments in methane pyrolysis and (c) Common
4 classification of methane pyrolysis routes.

5

6 2.1. Thermal non-catalytic pyrolysis process

7 Methane dissociation is an endothermic reaction that typically occurs at high temperatures. To
8 achieve a reasonable high conversion in a thermal non-catalytic pyrolysis process, more than
9 1200 °C is required to cleave the C-H bonds of CH₄ [23]. A thermal non-catalytic decomposition
10 of natural gas process at temperatures of up to 1400 °C has been developed by a consortium led
11 by BASF [22]. Currently, the ongoing research project is focused on enhancing and scaling up
12 the thermal non-catalytic pyrolysis process, building upon the information provided in a 2021
13 BASF report [24]. The high-temperature requirement of the non-catalytic methane pyrolysis
14 process can also be reached by utilizing concentrated solar energy, which can be considered as
15 a sustainable and promising route for hydrogen production [7,21,25,26]. The solar reactor
16 concepts developed by different research groups have shown significant recent progress [25,27–
17 29]. Although higher methane conversions have been achieved, the issue of carbon deposition
18 clogging the solar reactors remains. This problem also persists in conventional thermal reactors
19 and inhibits the continuous operation of the pyrolysis process. With this problem in mind, better
20 reactor designs to address the coking issue and achieve homogenous heating, are needed. As of
21 the date of this publication, scaling up of the solar processes for methane cracking at high
22 temperatures remains a big challenge. Moreover, a very high sunlight concentration is needed
23 to reach the high temperatures (>1200 °C), which requires large-scale solar power concentrators.
24 The required high temperature in solar systems can be reduced with the addition of catalysts.

1 Thus, custom-designed solar systems which are compatible with the catalysts, are needed. The
2 reduced process temperature also allows for the use of lower-cost materials in the construction
3 of the solar reactor.

4 **2.2. Thermal catalytic pyrolysis process**

5 The reaction temperature required for the decomposition of CH₄ can be significantly reduced
6 in the presence of a catalyst. Catalytic methane decomposition has attracted considerable
7 attention and been extensively investigated over a variety of metal-based and carbonaceous
8 catalysts [15,16,33,18–21,26,30–32]. The catalytic performances towards methane
9 decomposition are determined by the properties of the different catalysts such as supports,
10 promoters, shape, and size. Transitional metals like iron, nickel and cobalt are the most widely
11 studied catalysts because of their availability, high performance, and low cost. Ni shows
12 excellent performance for catalytic methane cracking and is one of the most catalytically active
13 transition metals. Fe-based catalysts tend to be more cost-effective, but they generally operate
14 at higher temperatures compared to than Ni- based catalysts. However, rapid encapsulation of
15 active sites by the produced solid carbon deactivates Ni metal catalysts quickly, particularly at
16 high temperatures. A wide range of supports and promoters have been employed for enhancing
17 the catalytic performance and resistance to deactivation of the metal catalysts [18,34,35]. The
18 most widely used supports are SiO₂, Al₂O₃, MnO, MoO, TiO₂ and MgO. Numerous alternative
19 strategies have been explored to enhance the design of methane decomposition catalysts for
20 more efficient and sustainable hydrogen production. These strategies encompass the
21 incorporation of secondary or tertiary metals, utilization of various synthesis methods, and
22 modifications to the support material, all of which have been extensively examined and
23 discussed in the literature [16,21,36–39]. Guevara et al. [40] investigated the catalytic
24 decomposition of CH₄ using a nickel/MCM-41 catalyst with Ce and observed no major catalytic
25 deactivation after 1400 min, which can be linked to the ordered pore system and large surface
26 area of the MCM-41 support. Although great progress has been achieved for catalytic
27 decomposition of CH₄ via the use of different types of catalysts and the optimization of the
28 process conditions, the accumulation of the carbon produced on the catalyst surface remains
29 the main challenge leading to gradual catalyst deactivation. To maintain the process continuity,
30 the catalysts require periodic removal of the accumulated carbon through a regeneration process:
31 gasification (with CO₂ or steam) or oxidation (with air or oxygen). Once the catalysts are
32 deactivated, the input stream can be directly switched from CH₄ to the regeneration gas, which
33 removes the deposited carbon from the surface of the catalysts, regenerating the catalysts.
34 However, the regeneration cycles can result in a reduction in the performances of the catalysts

1 over time due to the oxidation of the active sites (such as Ni agglomeration) and undesirable
2 CO₂ emissions based on the reported studies [16,21,26]. Since the produced carbon reacts
3 during the regeneration processes, the potentially useful carbon product from pyrolysis is lost.
4 In terms of CO₂ emissions, this catalyst regeneration approach cannot be a promising route
5 towards CO₂-free H₂ production.

6 To address the catalyst deactivation issue, using the carbon itself as a catalyst for methane
7 cracking to combat the issue of carbon poisoning has attracted major attention. Different types
8 of carbon-based materials have been studied as catalysts for the catalytic methane pyrolysis
9 process, including activated carbon, ordered mesoporous carbons, carbon black, carbon
10 nanotubes, activated carbon, graphite and coal chars [15,16,21,26,30,41]. In spite of carbon
11 catalysts showing excellent stability for high-temperature operations, undergoing deactivation
12 is ultimately unavoidable just as with metal-based catalysts.

13 In general, Ni-based catalysts show a better activity while Fe-based and carbon-based
14 catalysts show better stability. Regarding the environmental concerns, there is a compelling
15 case for the adoption of Fe-based and carbon-supported catalysts, with a particular focus on the
16 future utilization of the resulting solid carbon products. Importantly, addressing the challenge
17 of catalyst regeneration without CO₂ formation still represents a major hurdle in advancing the
18 catalytic methane pyrolysis process. Thorough techno-economic analyses are essential to bridge
19 the knowledge gaps that impede the scaling up the thermal catalytic pyrolysis of methane.

20 Recently, focus has been set on using molten media (molten metals and salts) for methane
21 cracking at low reaction temperatures [42–49], these processes represent a promising path for
22 continuous H₂ production. In contrast with the conventional fixed catalyst bed reactor, the
23 methane bubbles dissociate with the high temperature of molten media and the produced carbon
24 particles float on the surface of the molten media, preventing catalyst deactivation and reactor
25 blockages due to carbon clogging. Different types of molten metals or salts have been
26 investigated as a catalytic material or heat transfer medium. The improvement of heat transfer,
27 as a result of the high heat capacity of molten metals or salts, and the enhancement of the
28 residence time of methane gas owing to the liquid viscosity resulted in a high methane
29 conversion as well as granting reactor protection from thermal shocks. A wide variety of metal
30 alloys formed by the low-melting-point metals have been investigated for use as molten media
31 [42] in CH₄ cracking and it has been reported that a Ni_{0.27}–Bi_{0.73} molten alloy achieved the
32 highest methane conversion (95%) among all the studied metal alloys at 1065 °C. In a recent
33 study, they have developed a new Cu_{0.45}Bi_{0.55} alloy and achieved a surprisingly high activity,
34 showing a higher catalytic performance than that of the Ni_{0.27}Bi_{0.73} molten alloy [44]. Recently,

1 Chen et al. introduce a novel and exceptionally effective catalyst obtained through the alteration
2 of a Ni-Bi liquid alloy, with the incorporation of Mo to form a ternary NiMo-Bi liquid alloy
3 catalyst [49]. This catalyst demonstrated a notably low activation energy of 81.2 kilojoules per
4 mole, facilitating methane pyrolysis within the temperature range of 450 to 800 °C. Remarkably,
5 the catalyst displayed both 100% selectivity for hydrogen and impressive stability for up to 120
6 hours at 800 °C.

7 This finding demonstrates new ideas for utilizing catalytically inert and low-cost metals to
8 improve the performance of the molten alloy for methane cracking. Despite the large merits
9 provided by the molten metals for CH₄ cracking over conventional pyrolysis, the metal losses
10 and carbon contamination caused by the metal evaporation due to the high vapor pressure pose
11 big challenges.

12 The marketability and practicality of carbon products generated through molten media depend
13 on morphology, quality, and contamination levels, necessitating additional separation
14 procedures as a final step. Plamer et al. [50] observed a surprisingly high degree of metal
15 contamination from the produced carbon collected after 120 hours of experiments using 27 mol %
16 Ni–73 mol % Bi. To purify the resulting carbon, three distinct methods were evaluated,
17 including vacuum distillation, magnetic extraction, and hydrochloric acid washing. The highest
18 achievable carbon purity reached 97.8 wt%, but only after implementing multiple cleaning and
19 separation processes the metal contamination levels decreased to 0.2-2 wt% [50]. These levels
20 and the associated additional costs required to attain them are likely unacceptable in a
21 commercial production process. Carbon generated through the commercial pyrolysis process
22 should ideally be free of contamination, as even a trace of residual metal content would make
23 it unsuitable for sale or safe disposal. Molten salts with lower vapor pressure and melting points
24 can be a promising alternative to molten metals [14,51]. Separating the molten salts from the
25 contaminated carbon is much easier than from molten metals since the salts are soluble in water.
26 Molten salts generally show low catalytic performance thus coupling molten metals with salts
27 may reach high performances for methane pyrolysis with a robust system against deactivation
28 [21,52]. Despite significant advancements made through various methods to enhance the
29 purification of the resulting carbon, the achieved level of purity still falls short of meeting
30 commercial standards according to the literature [32,53–55]. An area that demands further
31 consideration in the future is the development of effective methods for the continuous removal
32 of carbon particles accumulated on the surface of molten media. It is also important to select
33 appropriate salts and metals that are not prone to introducing contaminants. Methane pyrolysis
34 within molten media represents a relatively new approach, and extensive research is needed to

1 identify suitable combinations and to optimize the process conditions suitable for future
2 industrial applications.

3 Currently, Hazer Group Ltd. is one of the market leaders in catalytic methane
4 decomposition for H₂ production, employing a fluidized bed reactor operating at 850 °C in the
5 presence of iron ore catalysts. The technology is currently still at the pilot scale. Despite its
6 promising potential, thermal catalytic pyrolysis of methane still requires further development
7 to improve H₂ production. Furthermore, the disposal of substantial quantities of catalysts
8 presents a significant challenge for large-scale application. Therefore, extensive investigations
9 must be undertaken to address the knowledge gaps hindering the advancement of large-scale
10 H₂ production through thermal catalytic pyrolysis of methane.

11 12 **2.3. Plasma pyrolysis (thermal/non-thermal) process**

13 Plasma, known as the fourth state of matter, is an ionized gas and consists of a variety of
14 reactive species including energetic electrons, excited atomic and molecular species, photons,
15 reactive radicals, and ions [56]. In general, the plasma used for methane pyrolysis can be
16 categorized as thermal and non-thermal plasmas. In most cases, plasma processes operate in the
17 absence of a catalyst. One of the fundamental parameters that characterizes a plasma is the
18 temperature of the plasma species. The temperatures of the electrons, gas molecules and ions
19 in a thermal plasma are homogeneously distributed. On the other hand, the electrons have a much
20 higher energy compared with the energies of gas molecules in a non-thermal plasma, which can
21 provide efficient and fast heat transfer to accelerate thermodynamically unfavorable chemical
22 reactions. Many plasma systems for methane cracking have been developed and the outstanding
23 merits of the plasma pyrolysis process are the fast switching-on and shutting-off of the systems
24 allowing for flexible utilization of the intermittent and irregular electricity supply of the
25 renewable energy sources such as solar and wind energies [57–60].

26 Thus far, thermal plasma-based methods represent the most highly developed
27 commercialized technology for the production of H₂ and carbon black, which were pioneered
28 by Kvaerner and SINTEF. However, the carbon black quality produced by this technology was
29 deemed inadequate, and as a result, it was discontinued in 2003. Nonetheless, Monolith
30 Materials is still advancing the technology through IP licensing agreements. The plasma torch
31 technology is based on the SINTEF/Kvaerner torch concept but with many modifications and
32 improvements, where producing carbon black is the primary product, and the working
33 temperature is 1000-3000 °C. Monolith Materials has also announced plans to construct a

1 275,000 t/y carbon-free anhydrous ammonia plant in Hallam, Nebraska, USA, to process the
2 hydrogen produced through methane cracking [61]. The ammonia product is aimed at the local
3 fertilizer market. Due to the high operating temperature, thermal plasma processes generally
4 have a high energy consumption, and the energy efficiency is low because of the thermal losses.
5 To achieve an efficient methane conversion, more than 30% of the energy input is needed to
6 exceed the theoretical thermodynamic value [62].

7 Non-thermal plasma processes have gained increasing attention since they can be operated
8 at a low gas temperature while still providing high electron temperatures, improving the energy
9 efficiency and reducing the investment needed for the equipment to cope with the harsh
10 conditions at high temperatures [63–66]. Several types of non-thermal plasma have already
11 been investigated for methane decomposition including microwave (MW) plasma, dielectric
12 barrier discharge (DBD), gliding arc (GA), corona and spark discharges. Gallon et al. reported
13 the production of carbon nanofibers on a NiO/Al₂O₃ catalyst, achieving a 99% hydrogen
14 selectivity during plasma methane activation using a DBD reactor [67]. Heijkers et al. [68]
15 investigated the underlying reaction mechanisms of methane decomposition via chemical
16 kinetics modeling in the case of MW, DBD and GA reactors and discovered that thermal effects
17 have a major role in the methane conversion whereas vibrational–translational non-equilibrium
18 play a minor role. The Gazprom (Russian Federation) company is a typical example that is
19 currently involved in the non-thermal plasma technology for methane pyrolysis. They patented
20 a method of combining a nickel-based catalyst stage with a plasma torch [69]. So far, there has
21 been no published approach to scaling up the laboratory apparatus, and the technology remains
22 at the laboratory scale. Despite significant efforts to develop a non-thermal plasma process for
23 methane cracking with a high energy efficiency, the conversion efficiency of methane via the
24 non-thermal plasma process remains low.

25 One of the major challenges in operating a plasma reactor for hydrogen production is the
26 formation of carbon deposits in the electrode surfaces or the reactor wall over time, which tends
27 to quench the plasma and thus halt the process. Moreover, the majority of investigations in the
28 literature use diluted methane with inert gases such as N₂, Ar, and He. More investigations are
29 needed to run pure methane or methane-rich gas as an input in the case of using non-thermal
30 plasma. Noteworthy, the plasma processes can operate either under low or atmospheric pressure
31 conditions. Therefore, the production of hydrogen at low or atmospheric pressures requires
32 additional energy which will increase the overall cost of the compressed hydrogen storage.

34 3. Summary

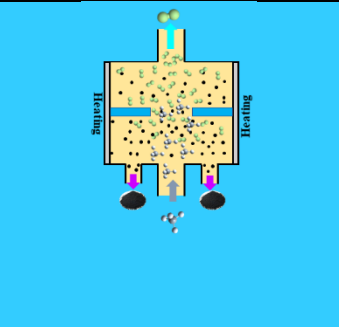
1 **3.1. Technology readiness**

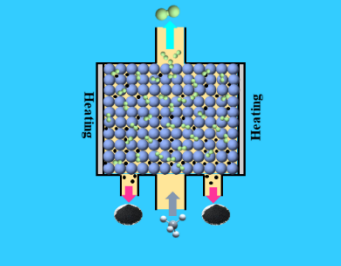
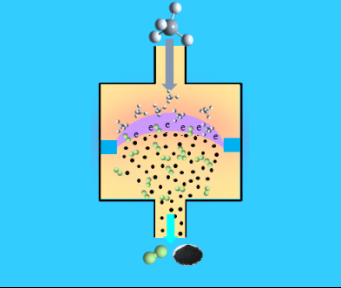
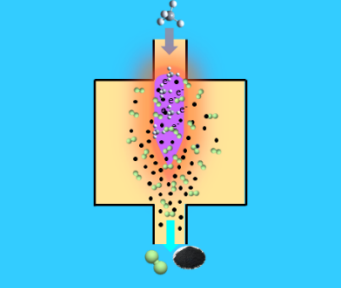
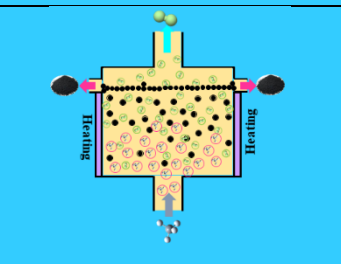
2 According to the currently available information, the technology landscape for methane
 3 cracking is fragmented, with no clear winner. The different methane pyrolysis processes for H₂
 4 production have distinct advantages and drawbacks, which are summarized in Table 1. The
 5 plasma pyrolysis process developed by Kvaerner and Monolith Materials is particularly
 6 promising, with high commercialization potential. Other pyrolysis technologies (thermal non-
 7 catalytic pyrolysis, thermal catalytic pyrolysis, molten metal/salt process) are still at the
 8 laboratory scale or the pilot-scale and it is unlikely that they will reach the commercial-ready
 9 level in the next few years.

10 **3.2. Lower process temperatures needed**

11 The reaction temperature ranges for methane pyrolysis in various pyrolysis processes (molten
 12 media-based, non-catalytic including plasma-based, carbon-based and metal-based catalyzed
 13 reactions) are partially overlapping. Figure 3 (a) presents the methane conversion as a function
 14 of the reaction temperature in different pyrolysis processes. The approximate temperature
 15 ranges acceptable for each reaction type are generally summarized as follows: 550–800 °C for
 16 Ni-based catalyzed reactions, 550–700 °C for Co-based catalyzed reactions, 700-1100 °C for
 17 molten media-based pyrolysis processes, 600–900 °C for Fe-based catalyzed reactions, 750–
 18 1100 °C for carbon-based catalyzed reactions and above 1100 °C for the non-catalytic reactions.
 19 As shown in Figure 3(a), the CH₄ conversion rate can generally reach close to 100% at
 20 temperatures above 1200 °C in the case of thermal non-catalytic and plasma pyrolysis processes,
 21 whereas it seems that methane is difficult to completely convert into hydrogen via the thermal
 22 catalytic pyrolysis process (including the cases using molten media).

23
 24 Table1. Overview of different methane pyrolysis routes

CH ₄ pyrolysis routes	Advantages	Disadvantages	Typical Example	TRL	Typical reactor
Thermal non-catalytic process	-No deactivation -Carbon product with high purity (~100% at high temperature) -High conversion (~100%) -Potential to perform at high pressures	-Inhomogeneity -Low heat efficiency -High temperature	-BASF	4	

Catalytic process	<ul style="list-style-type: none"> -Lower temperature -Material of construction -Scalability -Potential to perform at high pressures 	<ul style="list-style-type: none"> -Carbon products with impurities -Catalyst deactivation -Catalyst cost, inserting 	<ul style="list-style-type: none"> -BASF -Hazer Process 	4 - 6	
Plasma process (thermal)	<ul style="list-style-type: none"> -Fast switch on/off -High conversion -No sensitive cooling -No catalyst needed (in most of the cases) 	<ul style="list-style-type: none"> -Low energy efficiency -High temperature -Broad carbon quality -Low energy efficiency 	<ul style="list-style-type: none"> -Monolith materials -Kvaerner process 	8 - 9	
Plasma process (non-thermal)	<ul style="list-style-type: none"> -Fast switch on/off -No sensitive cooling -Low temperature -High energy efficiency 	<ul style="list-style-type: none"> -Broad carbon quality -Low conversion 	<ul style="list-style-type: none"> -Atlantic Hydrogen -Gazprom 	4	
Molten metal/salt process	<ul style="list-style-type: none"> -No blocking -Catalytic function -Good heat transfer 	<ul style="list-style-type: none"> -Carbon products with impurities -Loss of metals/salts -Corrosion 	<ul style="list-style-type: none"> -TNO-EMBER process -C-Zero 	3 - 4	

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4 3.3. Up-carbonization

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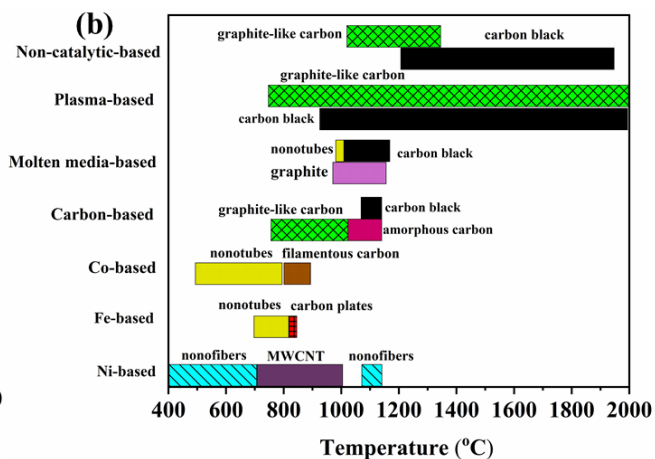
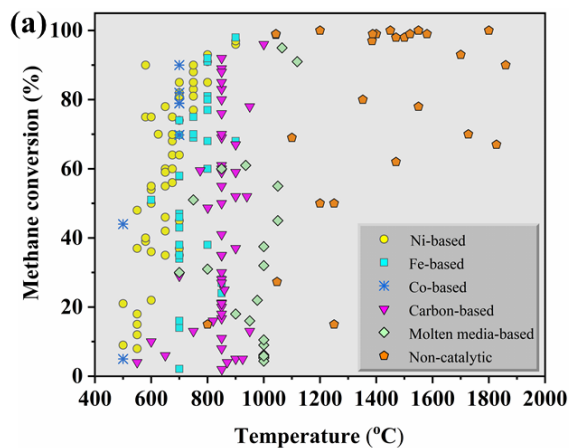
The quality and applications of the carbon produced are also critical for increasing the economic efficiency of the methane pyrolysis process. As noted from Figure 4, the global demand for carbon black was nearly 16.4 million metric tons (MMT) by 2022 and will continue to increase for soil amendment and environmental cleanup [70] in the near future. The continued development of methane pyrolysis technologies that create high-value forms of carbon, such as carbon nanotubes, is also critical for successful commercial implementation since carbon nanotubes are increasingly used in the production of lithium-ion batteries for renewable energy storage. The reaction conditions have a significant influence on the

1 morphology of the carbon produced. Based on published literature results [17,21,35,42], Figure
2 3(b) depicts a simplified representation of the main type of carbon product obtained from the
3 various methane pyrolysis routes (using different types of catalysts) as a function of the reaction
4 temperature. In the thermal catalytic pyrolysis process, metal-based catalysts tend to produce
5 filamentous carbon products such as carbon nanotubes (CNTs) and nanofibers, whereas carbon-
6 based catalysts generate primarily graphite-like carbon or carbon black. Carbon formation in
7 molten media differed significantly from conventional catalytic pyrolysis over solid catalysts.
8 Carbon atoms are solubilized as methane cracking in molten media, which frequently prevents
9 the formation of filamentous carbon products. In some cases, such structures can still be
10 obtained through pyrolysis such as using Ni–Bi/salt (KBr or NaBr) [52]. Thermal non-catalytic
11 and plasma methane cracking techniques yield mostly amorphous carbon or graphite-like
12 carbon, similar to carbon catalyzed methane decomposition. Based on the findings of the
13 literature review and the goal of producing hydrogen [30,63], a thermal non-catalytic or plasma
14 pyrolysis reaction may be a viable route to CH₄ decarbonation because it avoids the limitations
15 and difficulties associated with catalysts, as well as the need for separation and purification
16 units (membrane technology [71,72]) for pure H₂ production.

17 **3.4. Mechanisms**

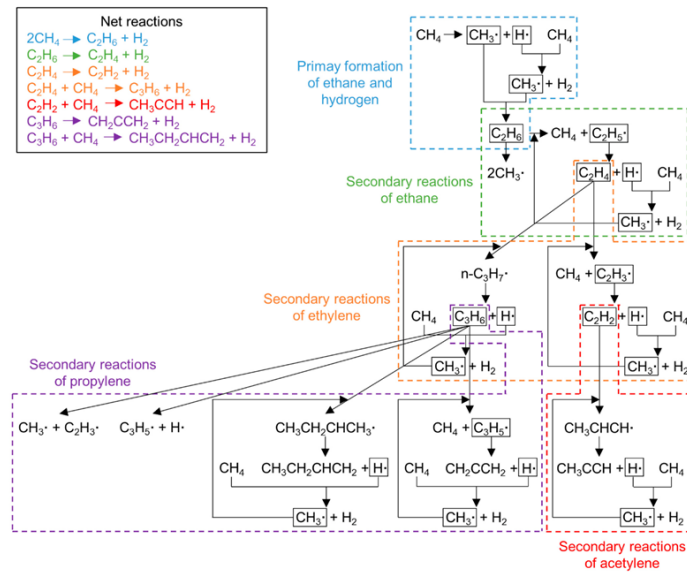
18 Despite being the simplest hydrocarbon, the mechanisms of methane cracking reaction are still
19 unclear. Since the 1960s, researchers have devoted efforts to investigate and postulate reaction
20 mechanisms for thermal non-catalytic methane cracking (Figure 3(e)) [73]. Regardless of
21 whether the produced carbon from the decomposition of CH₄ has a catalytic effect, the
22 mechanisms of the reactions at lower and higher temperatures are quite different. At higher
23 temperatures (> 1200 °C), thermal decomposition of methane occurs very quickly. A free
24 radical mechanism generally explains the formation of H₂ and carbon. However, the carbon
25 formation and the following steps (which result in a higher conversion rate) are not yet fully
26 understood [74]. According to the findings of the literature review [74,75], at lower
27 temperatures (< 1400 °C), methane is decomposed into a methyl radical and a hydrogen atom,
28 whereas at higher temperatures (>1400 °C), methane appears to be dissociated into a hydrogen
29 molecule and methylene. The reaction mechanisms of catalytic decomposition of methane have
30 been studied and discussed in many works [15,16,18,34,73,76]. Dissociative adsorption
31 mechanism and molecular adsorption mechanism are the widely accepted ones at present
32 (Figure 3(d)). Methane is first adsorbed on the catalyst surface and then dissociates in a series
33 of stepwise surface dehydrogenation reactions (the four C-H bonds in the adsorbed CH₄
34 molecule are decomposed gradually) via the molecular adsorption mechanism. The only

1 difference in the case of the dissociative adsorption mechanism is that methane directly
 2 dissociates upon adsorption on the active sites of the catalysts generating chemisorbed H and
 3 methyl radicals. Although various rate-limiting steps for thermal catalytic methane pyrolysis
 4 have been proposed, the reaction mechanism and overall rate-limiting step remain an open
 5 question. The final carbon product's morphology is closely linked to the catalyst's itself
 6 characteristics, which can sometimes influence the overall rate-limiting step. In the case of
 7 plasma pyrolysis of methane, it is well accepted that the collisions of electrons with methane
 8 molecules cause electron impact reactions such as ionization, excitation, dissociation, and so
 9 on. H and CH_x (x = 1, 2, 3) radicals are the major species which could initiate the secondary
 10 reactions. According to the proposed reaction pathway in Figure 3(c), the majority of the CH_x
 11 radicals in the plasma active zone participate in the dissociation reactions that generate
 12 hydrogen radicals and gaseous carbon. The remaining CH_x radicals play an active role in post-
 13 plasma zone reactions to generate C2 hydrocarbons [68,77]. When gaseous carbon nucleates
 14 and aggregates on the electrode surface and reactor wall, solid carbon forms. H radicals generate
 15 H₂ primarily through H recombination. Combining in-situ characterization techniques with
 16 machine learning and modeling could be a promising way to elucidate the reaction mechanism
 17 of methane pyrolysis and identify the rate-determining step, which could lead to the
 18 development of high-performance catalysts and reactors.
 19



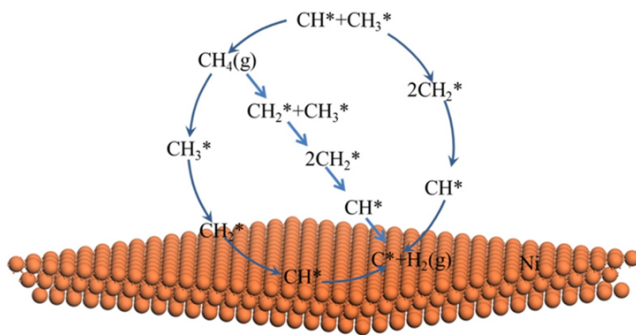
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(c)

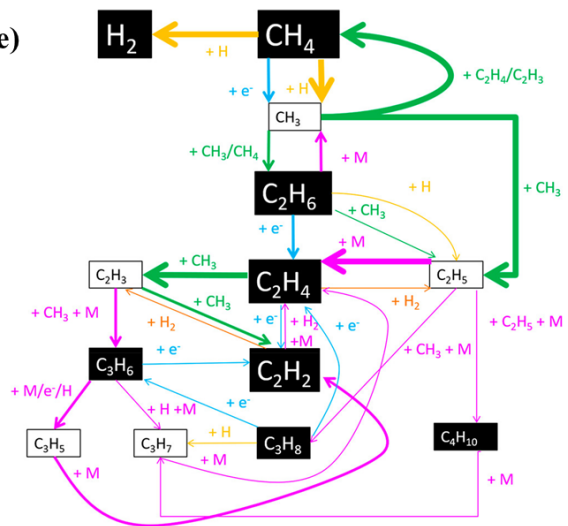


1

(d)



(e)



2

3 Figure 3. The methane conversion (a) and the primary carbon products obtained (b) as a function of
 4 reaction temperature in various pyrolysis processes. The data for the primary carbon products is mainly
 5 based on the information from [16,17,21,35]. Proposed reaction pathways for (c) thermal non-catalytic
 6 (Reprinted with permission from [15]), (d) thermal catalytic and (e) plasma-based (Reprinted with
 7 permission from [68]) methane pyrolysis.

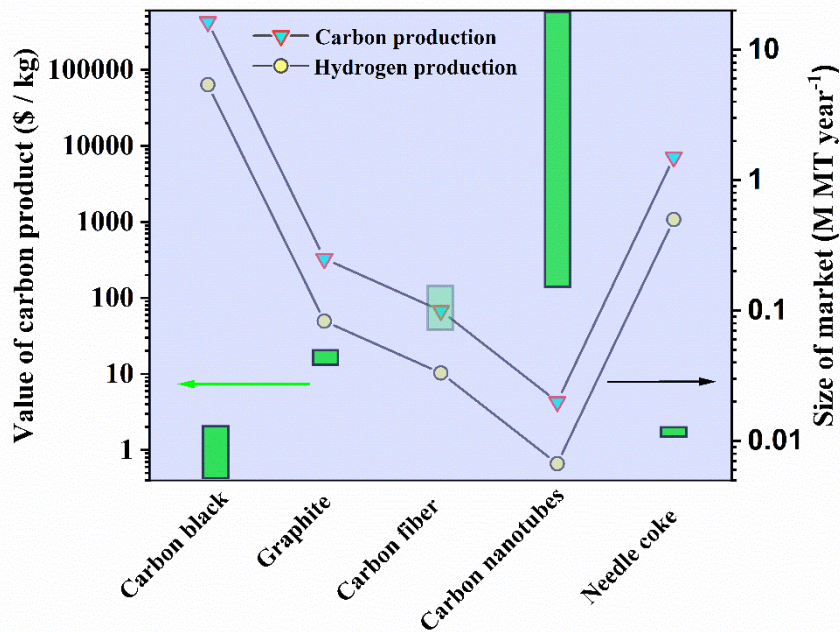


Figure 4 Carbon Products- Value and global market size (million metric tons (MMT)) based on the data from [78].

4. Challenges, research needs, and opportunities

4.1. Urgency and Innovation

Generally, methane pyrolysis has a promising future as a CO₂ free hydrogen production technique. Nonetheless, there are still many challenges and open questions regarding its industrial implementation. At present, methane decomposition is mostly associated with pyrolysis of natural gas for H₂ production. The use of real-world natural gas for large-scale H₂ production should take into account the impact of the impurities such as higher hydrocarbons. CH₄ emissions from natural gas production is an important consideration [79–81] and should not be underestimated when promoting it with technologies like methane pyrolysis to lessen the impact of climate change. Given the impending deadline for achieving the net zero goal, it is imperative to prioritize this technique as a hydrogen production technology for expediting the transition. This recognition becomes even more significant in light of the ambitious decarbonization goals outlined in the 'Egypt Climate Pact.' Further issues such as hydrogen storage, distribution, and end-use might well deserve intensive work on the basis of the green chemistry concept for the development of the hydrogen economy. In addition to temperature, residence time and pressure are also important operating parameters for methane pyrolysis. Special consideration should be given to the impact of high pressure because operating at high

1 pressure could be of special importance in reducing reactor volume at industrial scale, whereas
2 most reported works generally run at atmospheric pressure. Despite extensive efforts having
3 been devoted to investigate the reaction mechanisms of methane cracking, no definitive
4 conclusions on the elementary reactions and the rate-limiting step have been reached, requiring
5 further investigations to get a better understanding of the reaction pathways.

6 *In-situ* characterization techniques offer the unique ability to observe and understand reaction
7 kinetics and the formation of intermediate species in real-time during the methane pyrolysis
8 process. These real-time monitoring methods play an important role in identifying the diverse
9 reaction pathways and intermediate species involved in methane pyrolysis. This knowledge is
10 crucial for the fine-tuning of reaction parameters and the design of efficient and durable
11 catalytic materials that can selectively enhance the desired pathways, thereby enhancing the
12 overall efficiency of hydrogen production. Numerical simulations also provide a powerful tool
13 for predicting the behavior of the methane pyrolysis systems under a broad range of process
14 conditions, some of which may be impractical or even impossible to explore through
15 experimentation. Such simulations can effectively streamline the selection of potential catalysts
16 and operating conditions, thereby expediting the discovery of novel catalysts and process
17 enhancements. This focused approach enhances the chances for successful experimental
18 validation and cost-effectiveness of the practical process development. Furthermore, the
19 formulation and implementation of advanced mathematical models for methane pyrolysis is
20 crucial. These models enable the comprehensive optimization of the entire production process,
21 including reactor design, operating parameters, and integration with other systems such as
22 renewable energy sources or carbon capture technologies [82,83]. This approach also facilitates
23 the scaling up of laboratory-scale processes to industrial levels, a critical step for ensuring the
24 efficient and cost-effective H₂ production. Collectively, *In-situ* characterization and numerical
25 approaches are expected to substantially contribute to the development and advancement of
26 next-generation H₂ production processes that are more energy efficient, economically viable,
27 and environmentally sustainable.

28 The sale of the different solid carbon products produced from methane cracking can offset
29 a significant portion of the cost of hydrogen. Figure 4 depicts the value and global market size
30 for various types of potentially valuable carbon products derived from methane cracking using
31 data from [78]. It is crucial to remember that carbon product cost can vary greatly depending
32 on carbon characteristics and purity. Applying methane cracking in novel molten media
33 reactors with solar energy or plasma integration could represent promising ways for CO₂ free
34 hydrogen production taking the advantages of different pyrolysis processes (Figure 5(a) and

1 (b)). Presently, the separation and purification of high-value carbon products from catalysts are
2 commonly achieved through acid treatment [84], despite its evident environmental
3 disadvantages. Exploring alternative catalysts, such as perovskite-type materials, for methane
4 pyrolysis offers a potential solution. This approach presents the advantage of generating metal
5 oxide-carbon composite materials that can be directly utilized in energy-storage applications,
6 such as batteries and solid oxide cells (SOCs), without the need for additional separation
7 processes [85,86]. This direct utilization is illustrated in Figure 5(c). By employing these novel
8 catalysts, the potential for mitigating environmental concerns and streamlining the production
9 of valuable carbon products is evident. New materials and process design are also critical for
10 the development novel technology separate the value carbon products and “regenerate” the
11 metal-based catalysts.

12 **4.2. Engineering challenges and opportunities towards industrialization of methane** 13 **pyrolysis**

14 Moving from laboratory-scale experiments to commercial-scale production poses a
15 significant engineering hurdle. Ensuring that the process is both scalable and cost-effective at a
16 larger scale necessitates meticulous engineering and optimization efforts. Several notable
17 engineering obstacles must be tackled to achieve successful commercial deployment. High-
18 temperature methane pyrolysis presents considerable technical complexities, underscoring the
19 critical importance of achieving efficient heat transfer. It is imperative that heat is transferred
20 to the reactor efficiently to initiate and sustain the pyrolysis reactions. Designing a reactor
21 system capable of withstanding these extreme conditions while ensuring the efficient delivery
22 of heat represents a major challenge. The use of a fluidized-bed reactor, which allows for the
23 continuous addition and withdrawal of catalyst particles, is pivotal for industrial operation.
24 Additionally, the dynamic movement of these particles facilitates efficient heat and mass
25 transfer between the gas and the solid catalysts. Another promising reactor concept, particularly
26 from an industrial perspective, is the moving-bed reactor, which has been developed by various
27 partners in a funded collaborative project (Germany)[87]. In the moving-bed reactor, methane
28 is introduced from the bottom of the reactor, while carbon catalysts are added from the top
29 section. The solid carbon generated through methane pyrolysis accumulates on the carbon
30 catalysts and is consistently eliminated from the bottom of the reactor. The moving-bed reactor
31 offers significant advantages. This type of reactor enables excellent heat transfer between the
32 gas and the solid catalyst without back-mixing, providing precise control over residence time
33 for both phases [88]. The counterflow operation allows for energy integration within the reactor,
34 while the outstanding heat transfer between the gas and solid particles ensures a thermally

1 efficient process. However, despite the potential for efficient heat transfer in these advanced
2 reactor designs, managing the produced solid carbon remains a formidable process engineering
3 challenge. This solid carbon tends to accumulate on the reactor walls over time, eventually
4 leading to reactor clogging.

5 In recent years, there has been a growing interest in the utilization of liquid bubble column
6 reactors employing molten metals, molten salts, molten metal alloys, or their combinations as
7 both heat transfer and reaction media [14,21]. This approach is gaining prominence due to its
8 distinct advantage of enabling the continuous separation of carbon products from the molten
9 media, unlike traditional solid catalyst configurations. This feature greatly simplifies the
10 management of carbon products and helps prevent reactor clogging, as solid carbon is
11 consistently removed from the molten medium. It is important to note that while this technology
12 holds significant promise, it is currently limited to laboratory-scale experiments. Addressing
13 certain critical design parameters will be pivotal in its development. Specifically, minimizing
14 the loss of molten metals or salts due to evaporation and devising effective containment
15 strategies within the reactor are key considerations that need attention in the coming years.
16 Additionally, reactors filled with molten metals or molten salts must be engineered to withstand
17 the highly corrosive environment at high temperatures.

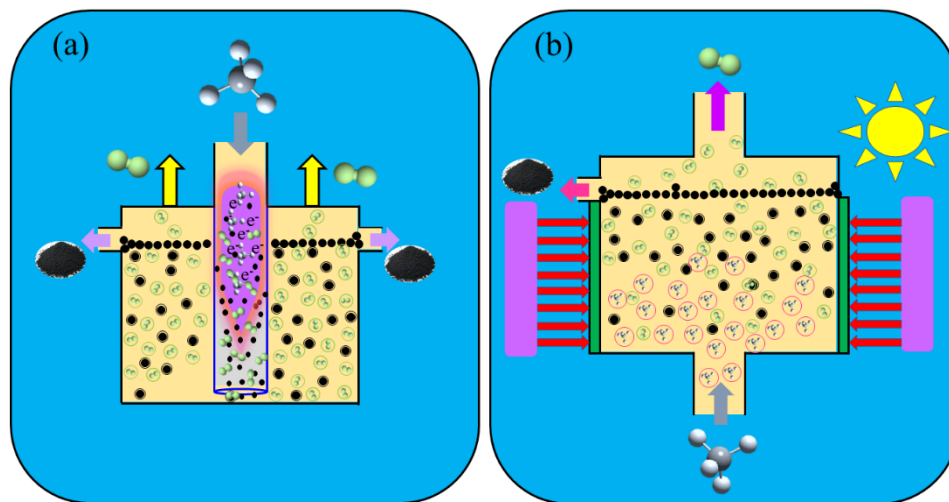
18 The reactor employed in methane pyrolysis should possess the ability to endure extreme
19 conditions, including high temperature and pressure [14,15,17]. These conditions can result in
20 material degradation and corrosion. Consequently, a significant engineering challenge lies in
21 the development of reactor materials and designs that can effectively withstand these harsh
22 conditions while ensuring long-term reliability. Efficient heat recovery is paramount to enhance
23 energy efficiency and reduce operating costs. Engineers must, therefore, concentrate their
24 efforts on creating streamlined heat recovery systems that can recover and reuse the heat
25 generated during the process seamlessly integrated into the overall process design. Effectively
26 managing carbon removal, storage, or utilization presents a central challenge in this context.
27 Given that various methane pyrolysis processes for hydrogen production have own advantages
28 and drawbacks, a viable strategy should combine the best features of different pyrolysis
29 processes. By leveraging the strengths of various pyrolysis methods, it becomes realistic to
30 develop cost-effective and energy-efficient processes primed for commercialization.

31 In the pursuit of overcoming these engineering challenges and advancing methane pyrolysis
32 toward industrialization, interdisciplinary collaboration is indispensable. Chemists, materials
33 scientists, mechanical engineers, and process engineers must work collaboratively to synergize

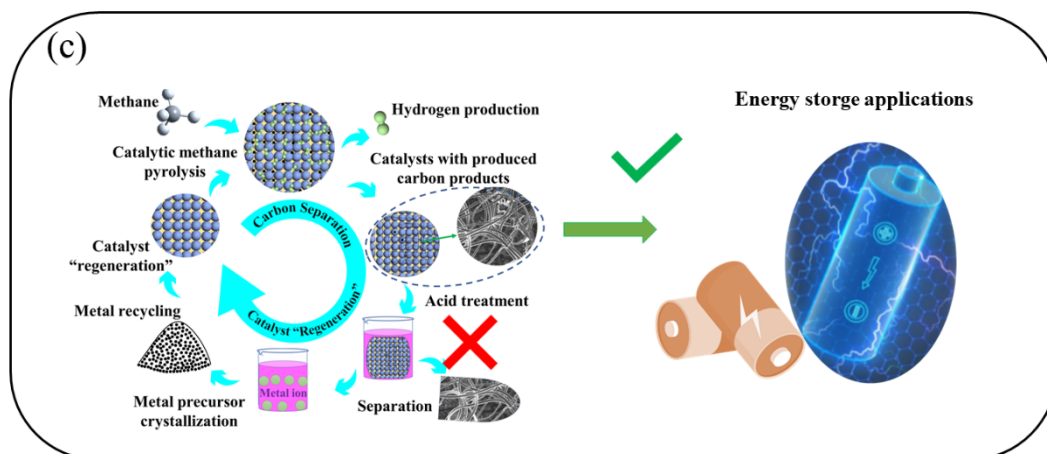
1 their expertise. Research and development endeavors aimed at enhancing efficiency, reliability,
2 and cost-effectiveness in methane pyrolysis are paramount for its successful deployment in
3 commercial settings. This, in turn, could play a significant role in nearing a more sustainable
4 energy future.

6 4.3. De-carbonization-connecting industry sectors

7 Methane pyrolysis has the potential to connect many industrial sectors, such as the iron and
8 steel industry and direct carbon fuel cell with CO₂ capture, in order to reduce the carbon
9 footprint of the related processes [89,90]. Although many challenges remain, CO₂ free
10 hydrogen production via methane cracking is an attractive technology that has yet to realize its
11 full commercial potential. The use of existing commercial natural gas network is the most
12 appealing aspect for organizations involved in the energy business, demonstrating a significant
13 economic advantage. Large corporations such as BASF and Monolith Materials are currently
14 showing an increasing interest in methane cracking as a promising tool for producing hydrogen,
15 which will hasten the commercialization of the methan pyrolysis process.



18



1
2
3 Figure 5. Schematic diagram on integrating novel molten media reactors with plasma (a) and solar
4 energy (b) for methane cracking and (c) Illustration of metal oxide-carbon composite materials
5 generated from thermal catalytic methane pyrolysis for energy-storage applications.
6
7

8 5. Concluding remarks

9

10 The benefits of transitioning to a hydrogen economy are commonly accepted and actively
11 pursued. Clean hydrogen production is critical to achieving a low-carbon-emissions hydrogen
12 economy. Methane pyrolysis emerges as one of the most promising routes for producing
13 affordable and CO₂-free hydrogen, in keeping with the urgent timetable required for climate
14 action. Based on the goal for low-carbon hydrogen production, a thermal non-catalytic or
15 plasma pyrolysis process for methane cracking appears to be the two of the highest potential
16 approaches since they eliminate the need for purification and separation steps for pure H₂
17 production. The sale of the carbon products for potential applications will further lead to a
18 significantly lower H₂ production cost. The development of in-situ characterization techniques,
19 in conjunction with computational simulations and modeling, will greatly improve our
20 understanding of methane cracking mechanisms, allowing for more efficient engineering
21 approaches and material design for low-cost and CO₂-free H₂ production. Further research in
22 catalysis, finding new applications and uses of the produced carbon, improved CH₄ conversion
23 and reactor design can make the methane cracking process competitive with SMR. Substantial
24 efforts are still required to integrate the benefits of various pyrolysis processes and design the
25 next-generation catalysts to meet the requirements under industrial conditions. Despite the long
26 road ahead to commercial maturity, methane cracking currently holds one of the most promising

1 routes for near-term CO₂-free hydrogen production on a large scale to keep up with the urgent
2 climate action using existing natural gas infrastructure.

3 4 **Competing interests**

5 The authors declare no competing interests.

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18 19 20 **Authorship contribution statement**

21 **Guoxing Chen:** Conceptualization, Methodology, Validation, Funding acquisition, Writing –
22 original draft. **Xiao Yu:** Methodology, Validation, Writing – review & editing. **Kostya (Ken)**
23 **Ostrikov:** Methodology, Validation, Writing – review & editing. **Bowen Liu:** Writing – review
24 & editing. **Jonathan Harding:** Writing – review & editing. **Gert Homm:** Funding acquisition,
25 Writing – review & editing. **Heng Guo:** Validation, Writing – review & editing. **Stephan**
26 **Andreas Schunk:** Writing – review & editing. **Ying Zhou:** Funding acquisition, Supervision,
27 Writing – review & editing. **Xin Tu:** Funding acquisition, Supervision, Writing – review &
28 editing. **Anke Weidenkaff:** Funding acquisition, Supervision, Writing – review & editing.

1 **References**

- 2 [1] M. Hermesmann, T.E. Müller, Green, Turquoise, Blue, or Grey? Environmentally
3 friendly Hydrogen Production in Transforming Energy Systems, *Prog. Energy Combust.*
4 *Sci.* 90 (2022) 100996. <https://doi.org/10.1016/J.PECS.2022.100996>.
- 5 [2] D.M. Amaya-Dueñas, G. Chen, A. Weidenkaff, N. Sata, F. Han, I. Biswas, R. Costa,
6 K.A. Friedrich, A -site deficient chromite with in situ Ni exsolution as a fuel electrode
7 for solid oxide cells (SOCs), *J. Mater. Chem. A.* 9 (2021) 5685–5701.
8 <https://doi.org/10.1039/D0TA07090D>.
- 9 [3] T.G. Wi, Y.J. Park, U. Lee, Y.B. Kang, Methane pyrolysis rate measurement using
10 electromagnetic levitation techniques for turquoise hydrogen production: Liquid In, Ga,
11 Bi, Sn, and Cu as catalysts, *Chem. Eng. J.* 460 (2023) 141558.
12 <https://doi.org/10.1016/J.CEJ.2023.141558>.
- 13 [4] A. Al-Qahtani, B. Parkinson, K. Hellgardt, N. Shah, G. Guillen-Gosalbez, Uncovering
14 the true cost of hydrogen production routes using life cycle monetisation, *Appl. Energy.*
15 281 (2021) 115958. <https://doi.org/10.1016/J.APENERGY.2020.115958>.
- 16 [5] S. Dermühl, U. Riedel, A comparison of the most promising low-carbon hydrogen
17 production technologies, *Fuel.* 340 (2023) 127478.
18 <https://doi.org/10.1016/J.FUEL.2023.127478>.
- 19 [6] V. Kindra, I. Maksimov, M. Oparin, O. Zlyvko, A. Rogalev, Hydrogen Technologies: A
20 Critical Review and Feasibility Study, *Energies.* 16 (2023) 5482.
21 <https://doi.org/10.3390/EN16145482>.
- 22 [7] A. Boretti, There are hydrogen production pathways with better than green hydrogen
23 economic and environmental costs, *Int. J. Hydrogen Energy.* 46 (2021) 23988–23995.
24 <https://doi.org/10.1016/J.IJHYDENE.2021.04.182>.
- 25 [8] B. Parkinson, P. Balcombe, J.F. Speirs, A.D. Hawkes, K. Hellgardt, Levelized cost of
26 CO₂ mitigation from hydrogen production routes, *Energy Environ. Sci.* 12 (2019) 19–40.
27 <https://doi.org/10.1039/C8EE02079E>.
- 28 [9] Global Hydrogen Review 2022, [https://www.Iea.Org/Reports/Global-Hydrogen-](https://www.iea.org/reports/global-hydrogen-review-2022)
29 [Review-2022. https://doi.org/10.1787/a15b8442-en](https://doi.org/10.1787/a15b8442-en).
- 30 [10] C. DE Mondial L, World Energy Scenarios WORLD ENERGY COUNCIL.
- 31 [11] G. Chen, X. Tu, G. Himm, A. Weidenkaff, Plasma pyrolysis for a sustainable hydrogen
32 economy, *Nat. Rev. Mater.* 2022 75. 7 (2022) 333–334. [https://doi.org/10.1038/s41578-](https://doi.org/10.1038/s41578-022-00439-8)
33 [022-00439-8](https://doi.org/10.1038/s41578-022-00439-8).
- 34 [12] N. Sánchez-Bastardo, R. Schlögl, H. Ruland, Methane Pyrolysis for CO₂-Free H₂

- 1 Production: A Green Process to Overcome Renewable Energies Unsteadiness, *Chemie*
2 *Ing. Tech.* 92 (2020) 1596–1609. <https://doi.org/10.1002/CITE.202000029>.
- 3 [13] S.R. Patlolla, K. Katsu, A. Sharafian, K. Wei, O.E. Herrera, W. Mérida, A review of
4 methane pyrolysis technologies for hydrogen production, *Renew. Sustain. Energy Rev.*
5 181 (2023) 113323. <https://doi.org/10.1016/J.RSER.2023.113323>.
- 6 [14] M. McConnachie, M. Konarova, S. Smart, Literature review of the catalytic pyrolysis of
7 methane for hydrogen and carbon production, *Int. J. Hydrogen Energy.* 48 (2023) 25660–
8 25682. <https://doi.org/10.1016/J.IJHYDENE.2023.03.123>.
- 9 [15] N. Sánchez-Bastardo, R. Schlögl, H. Ruland, Methane Pyrolysis for Zero-Emission
10 Hydrogen Production: A Potential Bridge Technology from Fossil Fuels to a Renewable
11 and Sustainable Hydrogen Economy, *Ind. Eng. Chem. Res.* 60 (2021) 11855–11881.
12 <https://doi.org/10.1021/ACS.IECR.1C01679>.
- 13 [16] Z. Fan, W. Weng, J. Zhou, D. Gu, W. Xiao, Catalytic decomposition of methane to
14 produce hydrogen: A review, *J. Energy Chem.* 58 (2021) 415–430.
15 <https://doi.org/10.1016/J.JECHEM.2020.10.049>.
- 16 [17] T. Keipi, K.E.S. Tolvanen, H. Tolvanen, J. Kontinen, Thermo-catalytic decomposition
17 of methane: The effect of reaction parameters on process design and the utilization
18 possibilities of the produced carbon, *Energy Convers. Manag.* 126 (2016) 923–934.
19 <https://doi.org/10.1016/J.ENCONMAN.2016.08.060>.
- 20 [18] U.P.M. Ashik, W.M.A. Wan Daud, H.F. Abbas, Production of greenhouse gas free
21 hydrogen by thermocatalytic decomposition of methane – A review, *Renew. Sustain.*
22 *Energy Rev.* 44 (2015) 221–256. <https://doi.org/10.1016/J.RSER.2014.12.025>.
- 23 [19] A. Gamal, K. Eid, M.H. El-Naas, D. Kumar, A. Kumar, Catalytic Methane
24 Decomposition to Carbon Nanostructures and CO_x-Free Hydrogen: A Mini-Review,
25 *Nanomater.* 11 (2021) 1226. <https://doi.org/10.3390/NANO11051226>.
- 26 [20] T.I. Korányi, M. Németh, A. Beck, A. Horváth, Recent Advances in Methane Pyrolysis:
27 Turquoise Hydrogen with Solid Carbon Production, *Energies.* 15 (2022) 6342.
28 <https://doi.org/10.3390/EN15176342>.
- 29 [21] M. Msheik, S. Rodat, S. Abanades, Methane Cracking for Hydrogen Production: A
30 Review of Catalytic and Molten Media Pyrolysis, *Energies.* 14 (2021) 3107.
31 <https://doi.org/10.3390/EN14113107>.
- 32 [22] S. Schneider, S. Bajohr, F. Graf, T. Kolb, State of the Art of Hydrogen Production via
33 Pyrolysis of Natural Gas, *ChemBioEng Rev.* 7 (2020) 150–158.
34 <https://doi.org/10.1002/CBEN.202000014>.

- 1 [23] H.F. Abbas, W.M.A. Wan Daud, Hydrogen production by methane decomposition: A
2 review, *Int. J. Hydrogen Energy*. 35 (2010) 1160–1190.
3 <https://doi.org/10.1016/J.IJHYDENE.2009.11.036>.
- 4 [24] BASF Report. *Innov. Process. Clim. Chem.* 2021. Available Online
5 <https://Report.Basf.Com/2021/En/Sharehold>. (Accessed 14 Sept. 2023).
- 6 [25] S. Rodat, S. Abanades, J.L. Sans, G. Flamant, A pilot-scale solar reactor for the
7 production of hydrogen and carbon black from methane splitting, *Int. J. Hydrogen*
8 *Energy*. 35 (2010) 7748–7758. <https://doi.org/10.1016/J.IJHYDENE.2010.05.057>.
- 9 [26] A. Banu, Y. Bicer, Review on CO_x-free hydrogen from methane cracking: Catalysts,
10 solar energy integration and applications, *Energy Convers. Manag.* X. 12 (2021) 100117.
11 <https://doi.org/10.1016/J.ECMX.2021.100117>.
- 12 [27] D. Paxman, S. Trottier, M. Nikoo, M. Secanell, G. Ordorica-Garcia, Initial Experimental
13 and Theoretical Investigation of Solar Molten Media Methane Cracking for Hydrogen
14 Production, *Energy Procedia*. 49 (2014) 2027–2036.
15 <https://doi.org/10.1016/J.EGYPRO.2014.03.215>.
- 16 [28] S. Abanades, H. Kimura, H. Otsuka, A drop-tube particle-entrained flow solar reactor
17 applied to thermal methane splitting for hydrogen production, *Fuel*. 153 (2015) 56–66.
18 <https://doi.org/10.1016/J.FUEL.2015.02.103>.
- 19 [29] S. Abanades, H. Kimura, H. Otsuka, Hydrogen production from thermo-catalytic
20 decomposition of methane using carbon black catalysts in an indirectly-irradiated tubular
21 packed-bed solar reactor, *Int. J. Hydrogen Energy*. 39 (2014) 18770–18783.
22 <https://doi.org/10.1016/J.IJHYDENE.2014.09.058>.
- 23 [30] M. Yousefi, S. Donne, Technical challenges for developing thermal methane cracking in
24 small or medium scales to produce pure hydrogen - A review, *Int. J. Hydrogen Energy*.
25 47 (2022) 699–727. <https://doi.org/10.1016/J.IJHYDENE.2021.10.100>.
- 26 [31] M. Hamdan, L. Halawy, N. Abdel Karim Aramouni, M.N. Ahmad, J. Zeaiter, Analytical
27 review of the catalytic cracking of methane, *Fuel*. 324 (2022) 124455.
28 <https://doi.org/10.1016/J.FUEL.2022.124455>.
- 29 [32] M. McConnachie, M. Konarova, S. Smart, Literature review of the catalytic pyrolysis of
30 methane for hydrogen and carbon production, *Int. J. Hydrogen Energy*. (2023).
31 <https://doi.org/10.1016/J.IJHYDENE.2023.03.123>.
- 32 [33] A.I. Alharthi, Nickel-iron catalyst for decomposition of methane to hydrogen and
33 filamentous carbon: Effect of calcination and reaction temperatures, *Alexandria Eng. J.*
34 67 (2023) 129–141. <https://doi.org/10.1016/J.AEJ.2022.12.036>.

- 1 [34] U.P.M. Ashik, W.M.A. Wan Daud, J. ichiro Hayashi, A review on methane
2 transformation to hydrogen and nanocarbon: Relevance of catalyst characteristics and
3 experimental parameters on yield, *Renew. Sustain. Energy Rev.* 76 (2017) 743–767.
4 <https://doi.org/10.1016/J.RSER.2017.03.088>.
- 5 [35] Y. Li, D. Li, G. Wang, Methane decomposition to CO_x-free hydrogen and nano-carbon
6 material on group 8–10 base metal catalysts: A review, *Catal. Today.* 162 (2011) 1–48.
7 <https://doi.org/10.1016/J.CATTOD.2010.12.042>.
- 8 [36] K.R. Parmar, K.K. Pant, S. Roy, Blue hydrogen and carbon nanotube production via
9 direct catalytic decomposition of methane in fluidized bed reactor: Capture and
10 extraction of carbon in the form of CNTs, *Energy Convers. Manag.* 232 (2021) 113893.
11 <https://doi.org/10.1016/J.ENCONMAN.2021.113893>.
- 12 [37] T.I. Korányi, M. Németh, A. Beck, A. Horváth, Recent Advances in Methane Pyrolysis:
13 Turquoise Hydrogen with Solid Carbon Production, *Energies.* 15 (2022) 6342.
14 <https://doi.org/10.3390/EN15176342>.
- 15 [38] A.L. Dipu, Methane decomposition into CO_x-free hydrogen over a Ni-based catalyst: An
16 overview, *Int. J. Energy Res.* 45 (2021) 9858–9877. <https://doi.org/10.1002/ER.6541>.
- 17 [39] H.A. Ahmed, A.E. Awadallah, A.A. Aboul-Enein, S.M. Solyman, N.A.K. Aboul-Gheit,
18 Non-oxidative Decomposition of CH₄ Over CeO₂ and CeO₂–SiO₂ Supported Bimetallic
19 Ni–Mo Catalysts, *Catal. Letters.* 152 (2022) 2789–2800.
20 <https://doi.org/10.1007/S10562-021-03844-W/FIGURES/10>.
- 21 [40] J.C. Guevara, J.A. Wang, L.F. Chen, M.A. Valenzuela, P. Salas, A. García-Ruiz, J.A.
22 Toledo, M.A. Cortes-Jácome, C. Angeles-Chavez, O. Novaro, Ni/Ce-MCM-41
23 mesostructured catalysts for simultaneous production of hydrogen and nanocarbon via
24 methane decomposition, *Int. J. Hydrogen Energy.* 35 (2010) 3509–3521.
25 <https://doi.org/10.1016/J.IJHYDENE.2010.01.068>.
- 26 [41] M. Dadsetan, M.F. Khan, M. Salakhi, E.R. Bobicki, M.J. Thomson, CO₂-free hydrogen
27 production via microwave-driven methane pyrolysis, *Int. J. Hydrogen Energy.* 48 (2023)
28 14565–14576. <https://doi.org/10.1016/J.IJHYDENE.2022.12.353>.
- 29 [42] D.C. Upham, V. Agarwal, A. Khechfe, Z.R. Snodgrass, M.J. Gordon, H. Metiu, E.W.
30 McFarland, Catalytic molten metals for the direct conversion of methane to hydrogen
31 and separable carbon, *Science.* 358 (2017) 917–921.
32 https://doi.org/10.1126/SCIENCE.AAO5023/SUPPL_FILE/AAO5023S2.MP4.
- 33 [43] D. Scheiblehner, D. Neuschitzer, S. Wibner, A. Sprung, H. Antrekowitsch, Hydrogen
34 production by methane pyrolysis in molten binary copper alloys, *Int. J. Hydrogen Energy.*

- 1 48 (2023) 6233-6243. <https://doi.org/10.1016/J.IJHYDENE.2022.08.115>.
- 2 [44] C. Palmer, M. Tarazkar, H.H. Kristoffersen, J. Gelinas, M.J. Gordon, E.W. McFarland,
3 H. Metiu, Methane Pyrolysis with a Molten Cu-Bi Alloy Catalyst, *ACS Catal.* 9 (2019)
4 8337–8345. <https://doi.org/10.1021/ACSCATAL.9B01833>
- 5 [45] C.F. Patzschke, B. Parkinson, J.J. Willis, P. Nandi, A.M. Love, S. Raman, K. Hellgardt,
6 Co-Mn catalysts for H₂ production via methane pyrolysis in molten salts, *Chem. Eng. J.*
7 414 (2021) 128730. <https://doi.org/10.1016/J.CEJ.2021.128730>.
- 8 [46] T. Geißler, A. Abánades, A. Heinzl, K. Mehravaran, G. Müller, R.K. Rathnam, C.
9 Rubbia, D. Salmieri, L. Stoppel, S. Stückrad, A. Weisenburger, H. Wenninger, T. Wetzl,
10 Hydrogen production via methane pyrolysis in a liquid metal bubble column reactor with
11 a packed bed, *Chem. Eng. J.* 299 (2016) 192–200.
12 <https://doi.org/10.1016/J.CEJ.2016.04.066>.
- 13 [47] Y.G. Noh, Y.J. Lee, J. Kim, Y.K. Kim, J.S. Ha, S.S. Kalanur, H. Seo, Enhanced
14 efficiency in CO₂-free hydrogen production from methane in a molten liquid alloy bubble
15 column reactor with zirconia beads, *Chem. Eng. J.* 428 (2022) 131095.
16 <https://doi.org/10.1016/J.CEJ.2021.131095>.
- 17 [48] B. de Caprariis, M. Damizia, E. Busillo, P. De Filippis, Advances in molten media
18 technologies for methane pyrolysis, *Adv. Chem. Eng.* 61 (2023) 319–356.
19 <https://doi.org/10.1016/BS.ACHE.2023.03.001>.
- 20 [49] L. Chen, Z. Song, S. Zhang, C.-K. Chang, Y.-C. Chuang, X. Peng, C. Dun, J.J. Urban, J.
21 Guo, J.-L. Chen, D. Prendergast, M. Salmeron, G.A. Somorjai, J. Su, J.A. Paulson,
22 Ternary NiMo-Bi liquid alloy catalyst for efficient hydrogen production from methane
23 pyrolysis, *Science*. 381 (2023) 857–861. <https://doi.org/10.1126/SCIENCE.ADH8872>.
- 24 [50] C. Palmer, E. Bunyan, J. Gelinas, M.J. Gordon, H. Metiu, E.W. McFarland, CO₂-free
25 hydrogen production by catalytic pyrolysis of hydrocarbon feedstocks in molten Ni-Bi,
26 *Energy and Fuels*. 34 (2020) 16073–16080.
27 <https://doi.org/10.1021/ACS.ENERGYFUELS.0C03080>.
- 28 [51] C. Palmer, M. Tarazkar, M.J. Gordon, H. Metiu, E.W. Mcfarland, Methane pyrolysis in
29 low-cost, alkali-halide molten salts at high temperatures, *Sustain. Energy Fuels*. 5 (2021)
30 6107–6123. <https://doi.org/10.1039/D1SE01408K>.
- 31 [52] N. Rahimi, D. Kang, J. Gelinas, A. Menon, M.J. Gordon, H. Metiu, E.W. McFarland,
32 Solid carbon production and recovery from high temperature methane pyrolysis in
33 bubble columns containing molten metals and molten salts, *Carbon*. 151 (2019) 181–191.
34 <https://doi.org/10.1016/J.CARBON.2019.05.041>.

- 1 [53] D. Kang, C. Palmer, D. Mannini, N. Rahimi, M.J. Gordon, H. Metiu, E.W. McFarland,
2 Catalytic Methane Pyrolysis in Molten Alkali Chloride Salts Containing Iron, *ACS Catal.*
3 10 (2020) 7032–7042. <https://doi.org/10.1021/ACSCATAL.0C01262>.
- 4 [54] B. Parkinson, C.F. Patzschke, D. Nikolis, S. Raman, D.C. Dankworth, K. Hellgardt,
5 Methane pyrolysis in monovalent alkali halide salts: Kinetics and pyrolytic carbon
6 properties, *Int. J. Hydrogen Energy.* 46 (2021) 6225–6238.
7 <https://doi.org/10.1016/J.IJHYDENE.2020.11.150>.
- 8 [55] D. Kang, N. Rahimi, M.J. Gordon, H. Metiu, E.W. McFarland, Catalytic methane
9 pyrolysis in molten MnCl₂-KCl, *Appl. Catal. B Environ.* 254 (2019) 659–666.
10 <https://doi.org/10.1016/J.APCATB.2019.05.026>.
- 11 [56] G. Chen, R. Snyders, N. Britun, CO₂ conversion using catalyst-free and catalyst-assisted
12 plasma-processes: Recent progress and understanding, *J. CO₂ Util.* 49 (2021) 101557.
13 <https://doi.org/10.1016/J.JCOU.2021.101557>.
- 14 [57] L. Fulcheri, V.J. Rohani, E. Wyse, N. Hardman, E. Dames, An energy-efficient plasma
15 methane pyrolysis process for high yields of carbon black and hydrogen, *Int. J. Hydrogen*
16 *Energy.* 48 (2023) 2920–2928. <https://doi.org/10.1016/J.IJHYDENE.2022.10.144>.
- 17 [58] S. Kreuznacht, M. Purcel, S. Böddeker, P. Awakowicz, W. Xia, M. Muhler, M. Böke, A.
18 von Keudell, Comparison of the performance of a microwave plasma torch and a gliding
19 arc plasma for hydrogen production via methane pyrolysis, *Plasma Process. Polym.* 20
20 (2023) 2200132. <https://doi.org/10.1002/PPAP.202200132>.
- 21 [59] Y.H. Lee, J.H. Oh, S. Choi, Evaluation of process conditions for methane pyrolysis
22 applying the triple thermal plasma system, *Int. J. Hydrogen Energy.* 48 (2023) 27127–
23 27136. <https://doi.org/10.1016/J.IJHYDENE.2023.03.427>.
- 24 [60] M. Wnukowski, Methane Pyrolysis with the Use of Plasma: Review of Plasma Reactors
25 and Process Products, *Energies.* 16 (2023) 6441. <https://doi.org/10.3390/EN16186441>.
- 26 [61] R. Jensen, C. van der Eijk, A.N. Wærnes, Production of Sustainable Hydrogen and
27 Carbon for the Metallurgical Industry, *Mater. Proc.* 5 (2021) 67.
28 <https://doi.org/10.3390/MATERPROC2021005067>.
- 29 [62] J.R. Fincke, R.P. Anderson, T.A. Hyde, B.A. Detering, Plasma Pyrolysis of Methane to
30 Hydrogen and Carbon Black, *Ind. Eng. Chem. Res.* 41 (2002) 1425–1435.
31 <https://doi.org/10.1021/IE010722E>.
- 32 [63] A. Magazova, S. Böddeker, N. Bibinov, D.W. Agar, Systematic Simulation Strategy of
33 Plasma Methane Pyrolysis for CO₂-Free H₂, *Chemie Ing. Tech.* 94 (2022) 690–700.
34 <https://doi.org/10.1002/CITE.202100181>.

- 1 [64] F. Kerscher, A. Stary, S. Gleis, A. Ulrich, H. Klein, H. Spliethoff, Low-carbon hydrogen
2 production via electron beam plasma methane pyrolysis: Techno-economic analysis and
3 carbon footprint assessment, *Int. J. Hydrogen Energy*. 46 (2021) 19897–19912.
4 <https://doi.org/10.1016/J.IJHYDENE.2021.03.114>.
- 5 [65] R. Zhou, Y. Zhao, R. Zhou, T. Zhang, P. Cullen, Y. Zheng, L. Dai, K. Ostrikov, C.
6 Yadong Zhao, Plasma-electrified up-carbonization for low-carbon clean energy, *Carbon*
7 *Energy*. (2022). <https://doi.org/10.1002/CEY2.260>.
- 8 [66] Y. Wang, W. Yang, S. Xu, S. Zhao, G. Chen, A. Weidenkaff, C. Hardacre, X. Fan, J.
9 Huang, X. Tu, Shielding Protection by Mesoporous Catalysts for Improving Plasma-
10 Catalytic Ambient Ammonia Synthesis, *J. Am. Chem. Soc.* 144 (2022) 12020–12031.
11 <https://doi.org/10.1021/JACS.2C01950>.
- 12 [67] H.J. Gallon, X. Tu, M. V. Twigg, J.C. Whitehead, Plasma-assisted methane reduction of
13 a NiO catalyst—Low temperature activation of methane and formation of carbon
14 nanofibres, *Appl. Catal. B Environ.* 106 (2011) 616–620.
15 <https://doi.org/10.1016/J.APCATB.2011.06.023>.
- 16 [68] S. Heijkers, M. Aghaei, A. Bogaerts, Plasma-Based CH₄ Conversion into Higher
17 Hydrocarbons and H₂: Modeling to Reveal the Reaction Mechanisms of Different
18 Plasma Sources, *J. Phys. Chem. C*. 124 (2020) 7016–7030.
19 <https://doi.org/10.1021/ACS.JPCC.0C00082>.
- 20 [69] A. G. Zherlitsyn et al., Patent RU2522636 C1, 2014.
- 21 [70] N.Z. Muradov, T.N. Veziroğlu, From hydrocarbon to hydrogen–carbon to hydrogen
22 economy, *Int. J. Hydrogen Energy*. 30 (2005) 225–237.
23 <https://doi.org/10.1016/J.IJHYDENE.2004.03.033>.
- 24 [71] G. Chen, A. Feldhoff, A. Weidenkaff, C. Li, S. Liu, X. Zhu, J. Sunarso, K. Huang, X.Y.
25 Wu, A.F. Ghoniem, W. Yang, J. Xue, H. Wang, Z. Shao, J.H. Duffy, K.S. Brinkman, X.
26 Tan, Y. Zhang, H. Jiang, R. Costa, K.A. Friedrich, R. Kriegel, Roadmap for Sustainable
27 Mixed Ionic-Electronic Conducting Membranes, *Adv. Funct. Mater.* 32 (2022) 2105702.
28 <https://doi.org/10.1002/ADFM.202105702>.
- 29 [72] G. Chen, M. Widenmeyer, X. Yu, N. Han, X. Tan, G. Homm, S. Liu, A. Weidenkaff,
30 Perspectives on achievements and challenges of oxygen transport dual-functional
31 membrane reactors, *J. Am. Ceram. Soc.* (2023). <https://doi.org/10.1111/JACE.19411>.
- 32 [73] C.-J. Chen, M.H. Back, R.A. Back, The thermal decomposition of methane. II.
33 Secondary reactions, autocatalysis and carbon formation; non-Arrhenius behaviour in
34 the reaction of CH₃ with ethane, *Can. J. Chem.* 54 (1976) 3175–3184.

- 1 <https://doi.org/10.1139/V76-452>.
- 2 [74] A. Holmen, O. Olsvik, O.A. Rokstad, Pyrolysis of natural gas: chemistry and process
3 concepts, *Fuel Process. Technol.* 42 (1995) 249–267. [https://doi.org/10.1016/0378-](https://doi.org/10.1016/0378-3820(94)00109-7)
4 [3820\(94\)00109-7](https://doi.org/10.1016/0378-3820(94)00109-7).
- 5 [75] M.S. Khan, B.L. Crynes, Survey of Recent Methane Pyrolysis Literature A survey of
6 methane pyrolysis data is presented and discussed, *Ind. Eng. Chem.* 62 (1970) 54–59.
7 <https://doi.org/10.1021/IE50730A005>.
- 8 [76] F. Bimbela, J. Luis Pinilla, A. Arisoy, J. Azubuiké Onwudili, A. Monzón amonzon, M.
9 Azuara, N. Latorre, J.I. Villacampa, V. Sebastian, F. Cazaña, E. Romeo, A. Monzón,
10 Use of Ni Catalysts Supported on Biomorphic Carbon Derived From Lignocellulosic
11 Biomass Residues in the Decomposition of Methane, *Front. Energy Res. |*
12 *Www.Frontiersin.Org.* 7 (2019) 34. <https://doi.org/10.3389/fenrg.2019.00034>.
- 13 [77] N.N. Morgan, M. ElSabbagh, Hydrogen Production from Methane Through Pulsed DC
14 Plasma, *Plasma Chem. Plasma Process.* 37 (2017) 1375–1392.
15 <https://doi.org/10.1007/S11090-017-9829-3/FIGURES/13>.
- 16 [78] R.A. Dagle, V. Dagle, M.D. Bearden, J.D. Holladay, T.R. Krause, S. Ahmed, An
17 Overview of Natural Gas Conversion Technologies for Co-Production of Hydrogen and
18 Value-Added Solid Carbon Products, (2017). <https://doi.org/10.2172/1411934>.
- 19 [79] A.R. Brandt, G.A. Heath, E.A. Kort, F. O’Sullivan, G. Pétron, S.M. Jordaan, P. Tans, J.
20 Wilcox, A.M. Gopstein, D. Arent, S. Wofsy, N.J. Brown, R. Bradley, G.D. Stucky, D.
21 Eardley, R. Harriss, Methane leaks from North American natural gas systems, *Science.*
22 343 (2014) 733–735. <https://doi.org/10.1126/SCIENCE.1247045>.
- 23 [80] R.A. Alvarez, D. Zavala-Araiza, D.R. Lyon, D.T. Allen, Z.R. Barkley, A.R. Brandt, K.J.
24 Davis, S.C. Herndon, D.J. Jacob, A. Karion, E.A. Kort, B.K. Lamb, T. Lauvaux, J.D.
25 Maasackers, A.J. Marchese, M. Omara, S.W. Pacala, J. Peischl, A.L. Robinson, P.B.
26 Shepson, C. Sweeney, A. Townsend-Small, S.C. Wofsy, S.P. Hamburg, Assessment of
27 Methane Emissions from the U.S. Oil and Gas Supply Chain, *Science.* 361 (2018) 186.
28 <https://doi.org/10.1126/SCIENCE.AAR7204>.
- 29 [81] M. Keller, Comment on “Methane Pyrolysis for Zero-Emission Hydrogen Production:
30 A Potential Bridge Technology from Fossil Fuels to a Renewable and Sustainable
31 Hydrogen Economy,” *Ind. Eng. Chem. Res.* 60 (2021) 17792–17794.
32 <https://doi.org/10.1021/ACS.IECR.1C03926>.
- 33 [82] S. Park, M. Kim, Y. Koo, D. Kang, Y. Kim, J. Park, C. Ryu, Numerical modeling of
34 methane pyrolysis in a bubble column of molten catalysts for clean hydrogen production,

- 1 Int. J. Hydrogen Energy. 48 (2023) 7385–7399.
2 <https://doi.org/10.1016/J.IJHYDENE.2022.11.068>.
- 3 [83] L.J.J. Catalan, E. Rezaei, Modelling the hydrodynamics and kinetics of methane
4 decomposition in catalytic liquid metal bubble reactors for hydrogen production, Int. J.
5 Hydrogen Energy. 47 (2022) 7547–7568.
6 <https://doi.org/10.1016/J.IJHYDENE.2021.12.089>.
- 7 [84] I. Wang, R.A. Dagle, T.S. Khan, J.A. Lopez-Ruiz, L. Kovarik, Y. Jiang, M. Xu, Y. Wang,
8 C. Jiang, S.D. Davidson, P. Tavadze, L. Li, J. Hu, Catalytic decomposition of methane
9 into hydrogen and high-value carbons: combined experimental and DFT computational
10 study, Catal. Sci. Technol. 11 (2021) 4911–4921. <https://doi.org/10.1039/D1CY00287B>.
- 11 [85] X. Yu, G. Chen, M. Widenmeyer, I. Kinski, X. Liu, U. Kunz, D. Schüpfer, L. Molina-
12 Luna, X. Tu, G. Homm, A. Weidenkaff, Catalytic recycling of medical plastic wastes
13 over $\text{La}_{0.6}\text{Ca}_{0.4}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ pre-catalysts for co-production of H_2 and high-value added
14 carbon nanomaterials, Appl. Catal. B Environ. 334 (2023) 122838.
15 <https://doi.org/10.1016/J.APCATB.2023.122838>.
- 16 [86] Y. Ji, C. Palmer, E.E. Foley, R. Giovine, E. Yoshida, E. Sebti, A.R. Patterson, E.
17 McFarland, R.J. Clément, Valorizing the carbon byproduct of methane pyrolysis in
18 batteries, Carbon. 204 (2023) 26–35. <https://doi.org/10.1016/J.CARBON.2022.12.044>.
- 19 [87] Bode, A.; Anderlohr, C.; Bernnat, J.; Flick, D.; Glenk, F.; Klinger, D.; Kolios, G.; Scheiff,
20 F.; Wechsung, A.; Hensmann, M.; Möhring, S.; Stubbe, G.; Lizandara, C.; Lange de
21 Oliveira, A.; Schunk, S. A.; Göke, V.; Hunfeld, J.; Mihailowitsch, D.; Pleintinger, S.;
22 Posselt, H.; Weikl, M. C.; Zander, H.-J.; Antweiler, N.; Büker, K.; Eckbauer, M.; Krüger,
23 M.; Marek, P.; Rodermund, K.; Janhsen, U.; Mittelstädt, H.; Möllers, C.; Agar, D. W.;
24 Munera-Parra, A. A. Feste und fluide Produkte aus Gas – FfPaG; Schlussbericht BMBF
25 FKZ 033RC1301 A-G: März, 2018.
- 26 [88] M. Shirzad, M. Karimi, J.A.C. Silva, A.E. Rodrigues, Moving Bed Reactors: Challenges
27 and Progress of Experimental and Theoretical Studies in a Century of Research, Ind. Eng.
28 Chem. Res. 58 (2019) 9179–9198. <https://doi.org/10.1021/ACS.IECR.9B01136>.
- 29 [89] A. Bhaskar, M. Assadi, H.N. Somehsaraei, Can methane pyrolysis based hydrogen
30 production lead to the decarbonisation of iron and steel industry?, Energy Convers.
31 Manag. X. 10 (2021) 100079. <https://doi.org/10.1016/J.ECMX.2021.100079>.
- 32 [90] A. Banu, Y. Bicer, Integration of methane cracking and direct carbon fuel cell with CO_2
33 capture for hydrogen carrier production, Int. J. Hydrogen Energy. 47 (2022) 19502–
34 19516. <https://doi.org/10.1016/J.IJHYDENE.2022.04.187>.

