Non-oxidative decomposition of methanol into hydrogen in a rotating gliding arc plasma reactor

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ABSTRACT
A direct current rotating gliding arc (RGA) reactor co-driven by a magnetic field and tangential flow has been developed for the non-oxidative decomposition of methanol into hydrogen and other valuable products. The influence of input CH\textsubscript{3}OH concentration and carrier gas (N\textsubscript{2} and Ar) on the reaction performance of the plasma process has been investigated in terms of the conversion of methanol, product selectivity, and energy efficiency of the process. The maximum CH\textsubscript{3}OH conversion of 92.4\% and hydrogen selectivity of 53.1\% are achieved in the plasma methanol conversion using N\textsubscript{2} as a carrier gas. Optical emission diagnostics has shown the formation of a variety of reactive species (e.g., H, OH, CH, CN, N\textsubscript{2} and C\textsubscript{2}) in the plasma decomposition of methanol. The vibrational and electronically excited species (e.g., N\textsubscript{2} \((\Lambda^{\Sigma_{u}^{+}})\) and Ar\textsuperscript{*}) could be critical in the conversion of CH\textsubscript{3}OH, leading to a higher CH\textsubscript{3}OH conversion in the CH\textsubscript{3}OH/N\textsubscript{2} RGA due to the presence of more reaction pathways. Compared to other non-thermal plasmas, the RGA plasma shows a much better process performance, offering a promising and flexible route for hydrogen production.

Keywords: Rotating gliding arc; Methanol decomposition; Hydrogen production; Optical emission

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1. Introduction

Recently, the development of novel and cost-effective hydrogen production processes has attracted significant interest due to the depletion of fossil fuels and the environmental impact of the usage of fossil fuels. However, technical problems with the handling, storage, and transport of hydrogen largely limit its widespread use, particularly in portable fuel cells which have been considered as a promising alternative to the traditional battery technology [1]. The development of portable hydrogen generation systems could provide a source of clean hydrogen for portable fuel cells [2]. Methanol has been considered as an excellent H₂-containing source for portable hydrogen production due to its high hydrogen to carbon ratio, easy transportation, and low boiling point [3-8]. Catalytic steam reforming of methanol has been extensively investigated for hydrogen production [9]. However, this process still faces technical challenges that limit its use in a commercial-scale system. Although significant efforts have been devoted to find active, stable, and cost-effective catalysts for producing hydrogen from methanol, rapid deactivation of catalysts and the requirement of high temperature in the reforming process incur high energy and operational costs and consequently limit its industrial applications, particularly in on-board hydrogen production systems [10].

Non-thermal plasma technology provides an attractive alternative to the conventional catalytic route for methanol conversion at a relatively low temperature [1-8, 11, 12]. In non-thermal plasmas, the overall gas temperature can be as low as room temperature, while the electrons are highly energetic, with a typical electron temperature of 1-10 eV, which is sufficient to break down most chemical bonds of gas molecules and produce chemically reactive species including the excited
atoms, ions and molecules for the initiation and propagation of chemical reactions [12]. High reaction rate and fast attainment of steady state in the plasma processes allows rapid start-up and shutdown of the plasma process, providing highly flexibility to be integrated into portable hydrogen production systems [11, 12]. Different non-thermal plasma systems have been developed for methanol conversion into hydrogen to maximize hydrogen production and energy efficiency of the plasma process, such as microhollow cathode discharge (MHCD) [2], microwave discharge [5-8], and dielectric barrier discharge (DBD) [13]. However, the relatively low power level of these plasma systems makes it difficult to achieve high, efficient conversion of methanol at a high gas flow rate, restricting the potential scale-up of this process [14]. For instance, Futamura et al. reported a methanol conversion of only 8-26% can be obtained at a feed N₂ flow rate of 100 ml/min and an input CH₃OH concentration of 1% in the plasma decomposition of methanol using a DBD [15].

Gliding arc discharge (GAD) has been considered as a transitional plasma with a relatively high electron density and high flexibility to work in a wide range of reactant flow rates and plasma power levels (up to several kW) [11, 16-18]. In a traditional GAD reactor that consists of two divergent knife-shaped electrodes, high flow rate (e.g., 10-20 l/min) is generally required to push the arc moving along the electrodes, generating a discharge zone for chemical reactions. As a consequence, the fast gas speed and limited two-dimensional plasma reaction area confined by the flat electrodes lead to a low retention time of reactants, thereby limiting the conversions of reactants and the energy efficiency of the plasma process [14, 19].

A direct current (DC) rotating gliding arc (RGA) co-driven by a magnetic field and tangential flow has been developed for hydrogen production from methane conversion in our previous work [19]. Compared to the traditional gliding arc system with knife-shaped electrodes, the RGA reactor
can generate a synergetic effect resulting from the combination of swirling flow and Lorentz force, which can make the arc rotate rapidly and steadily without extinction (with a rotational speed of up to 100 rotations per second) with a wide range of gas flow rate (e.g., 0.05-40 l/min), creating a three-dimensional stable plasma area with the increased retention time of the reactants in plasma chemical reactions. Our previous study showed that this RGA system significantly improved the performance of plasma methane conversion with a maximum CH₄ conversion of 91.8%, a hydrogen selectivity of 80.7% and a maximum energy yield of H₂ of 22.6 g/kWh [19].

In this study, an RGA plasma reactor has been developed for the non-oxidative decomposition of methanol into hydrogen. N₂ and Ar have been commonly used as the carrier gases in the plasma processes for energy conversion and fuel production [2, 5, 20]. Significant efforts have been devoted to investigating the effect of different operating parameters (e.g., input power, flow rate, etc.) on the performance of plasma chemical reactions, whereas less attention has been paid to understand the role of different carrier gases in the plasma chemical processes. This is of primary importance because different carrier gases will generate different reactive species and significantly affect the plasma chemical reactions in different ways, especially the methanol decomposition process [19, 21]. In this work, the effect of input CH₃OH concentration and carrier gas (N₂ and Ar) on the reaction performance (e.g., conversion of methanol, selectivity of gas products, and energy efficiency) of the methanol conversion process has been investigated in an RGA plasma reactor. Optical emission spectroscopy (OES) has been used to give new insights into the formation of reactive species in the plasma chemical reactions. In addition, the possible reaction pathways in the plasma methanol decomposition process using different carrier gases have been discussed. Finally, a comparison of the methanol conversion process using different plasma systems has been carried out.
2. Experimental

2.1 Experimental setup and gas analysis

Fig. 1 shows the schematic diagram of the experimental set-up. A con-shaped stainless steel electrode (anode) is placed inside a circular stainless steel cylinder which acts as a cathode. A more detailed description of the RGA reactor can be found in our previous work [19]. The carrier gas (N₂ or Ar) was injected through three tangential inlets at the bottom of the reactor to form a swirling flow in the reactor. A magnet was placed outside the reactor to generate a magnetic field for the stabilization and acceleration of the arc. With the combined effect of swirling flow and Lorentz force, the arc moves upward and finally rotates rapidly around the inner electrode, forming a stable plasma volume for chemical reactions.

![Fig. 1 – Schematic diagram of the experimental setup](image)

Methanol was controlled and injected into the gas tube using a high-resolution syringe pump
In this way, the total feed flow rate (0.6 mol/min) of the mixed stream and input CH$_3$OH concentration (5-35 mol %) could be controlled. The mixed stream was then heated to 100 °C in a stainless steel pipe with an inner diameter of 4 mm (40 cm in length) equipped with a temperature controller system, to generate a steady-state vapor before flowing into the RGA reactor. The quartz cover of the plasma reactor was also heated to 100 °C to prevent any vapor condensation on the inner wall of the reactor. The plasma reactor was connected to a DC power supply (380 V/10 kV) with a 40-kΩ resistance connected in the circuit to limit and stabilize the breakdown current. A two-stage condenser was placed at the exit of the plasma reactor to collect the condensable vapors in the effluent: the first-stage condenser pipe was equipped with an ice water circulation system, while the second-stage liquid trap was placed inside the ice water container.

The gaseous products were measured by a gas chromatography (GC9790A, Fuli Analytical Instrument) equipped with a thermal conductivity detector (TCD) for the detection of H$_2$, O$_2$, and N$_2$ and a flame ionization detector (FID) for the analysis of CO, CO$_2$, and hydrocarbons. The condensed liquid was measured by a gas chromatography – mass spectrometry (JEOL, JMS-Q1050GC). We found the condensed liquid was mainly methanol with trace amounts of ethanol, propanol and ethylene glycol. Thus, the volume of the condensed liquid can be roughly regarded as the volume of the unreacted methanol after the plasma reaction [4, 6, 22-24]. The emission spectra of the plasmas were recorded by a 750-mm monochromator (PI-Acton 2750, grating: 1800 grooves/mm) equipped with an intensified charge-coupled device (ICCD, PI-MAX 2, 512×512 pixel). An optical fiber was placed at the exit of the RGA reactor to collect the plasma radiation.
2.2 Definition of parameters

For the plasma methanol decomposition process, the conversion of CH$_3$OH is defined as:

$$X(\text{CH}_3\text{OH})(\%) = \frac{\text{moles of CH}_3\text{OH converted}}{\text{moles of CH}_3\text{OH input}} \times 100\%$$  \hspace{1cm} (1)

The selectivities ($S$) of the products can be calculated:

$$S(\text{H}_2)(\%) = \frac{\text{moles of H}_2 \text{ produced}}{2 \times \text{moles of CH}_3\text{OH converted}} \times 100\%$$  \hspace{1cm} (2)

$$S(\text{CO})(\%) = \frac{\text{moles of CO produced}}{\text{moles of CH}_3\text{OH converted}} \times 100\%$$  \hspace{1cm} (3)

$$S(\text{CO}_2)(\%) = \frac{\text{moles of CO}_2 \text{ produced}}{\text{moles of CH}_3\text{OH converted}} \times 100\%$$  \hspace{1cm} (4)

$$S(\text{C}_n\text{H}_m)(\%) = \frac{m \times \text{moles of C}_n\text{H}_m \text{ produced}}{\text{moles of CH}_3\text{OH converted}} \times 100\%$$  \hspace{1cm} (5)

The energy yield of H$_2$ is defined as:

$$EY(\text{H}_2) \text{ (g/kWh)} = \frac{\text{grams of H}_2 \text{ produced per min.}}{\text{power(W)} \times 60/3600000} \times 100\%$$  \hspace{1cm} (6)

The energy conversion efficiency ($ECE$) of the process is calculated based on the change of the lower heating values ($LHV$) of the fuels before and after the reaction.

$$ECE(\%) = \frac{\sum p_i \times LHV_i}{\text{power(W)} \times 60/1000 + \text{moles of CH}_3\text{OH converted per min} \times \text{LHV}_{\text{CH}_3\text{OH}}} \times 100\%$$  \hspace{1cm} (7)

Where $p_i$ refers to the moles of produced fuel $i$ (i: H$_2$, CO, CH$_4$, C$_2$H$_4$, and C$_2$H$_2$) per minute.

($LHV_{\text{H}_2} = 241.6 \text{ kJ/mol}$, $LHV_{\text{CO}} = 283.0 \text{ kJ/mol}$, $LHV_{\text{CH}_4} = 803.7 \text{ kJ/mol}$, $LHV_{\text{C}_2\text{H}_4} = 1331.5 \text{ kJ/mol}$, $LHV_{\text{C}_2\text{H}_2} = 1265.376 \text{ kJ/mol}$, $LHV_{\text{CH}_3\text{OH}} = 638.5 \text{ kJ/mol}$)

3. Results and discussion

3.1 Plasma decomposition of methanol
H₂ and CO were the major gaseous products in the non-oxidative decomposition of methanol using the RGA plasma, while trace amounts of CO₂, CH₄, C₂H₂, and C₂H₄ (total selectivity: 1.1-3.8%) were also formed. C₂H₆ was only detected with a selectivity of 0.5% in the conversion of 5% methanol using the argon RGA plasma. Note that C₂H₆ was identified as the main C₂ hydrocarbons in plasma processing of hydrocarbons using dielectric barrier discharges [25, 26]. However, previous work has also shown the shift of the distribution of C₂ hydrocarbon from C₂H₆ to C₂H₂ and C₂H₄ in the dry reforming of methane and carbon dioxide using an AC gliding arc plasma [11]. No C₃ or higher hydrocarbons gases were detected in this experiment. In the plasma partial oxidation or steam reforming of methanol, significant undesired gaseous byproducts were often generated with high selectivity, such as HCHO (45-60% selectivity) [27] and CO₂ (11.8-95% selectivity) [13, 24], the plasma non-oxidative methanol decomposition process using an RGA reactor could produce much cleaner gas products of which the syngas is the main one.

The effect of input CH₃OH concentration on the discharge power of the CH₃OH/N₂ and CH₃OH/Ar RGA plasmas is shown in Fig. 2. As we can see, the discharge power (149.8-349.4 W) of the CH₃OH/N₂ plasma is much higher than that of the CH₃OH/Ar plasma (105.2-271.6 W) at the same CH₃OH concentration. In both plasma chemical reactions, the discharge power initially increases with the increase of the input CH₃OH concentration to 20%, over which the discharge power is saturated when further increasing the CH₃OH concentration to 35%.

Fig. 3 shows the effect of input CH₃OH concentration on the conversion of CH₃OH. Increasing the CH₃OH concentration leads to a significant decrease of the CH₃OH conversion, even though the discharge power of the plasmas is initially increased with methanol concentration. The conversion of CH₃OH is higher in the CH₃OH/N₂ plasma than that in the CH₃OH/Ar RGA at the same methanol concentration, since the higher discharge power is generated in the CH₃OH/N₂ plasma.
with more reaction pathways due to the formation of a variety of excited species such as vibrational excited N\(_2\) and electronically excited N\(_2\).

Fig. 2 – Effect of input CH\(_3\)OH concentration on the discharge power

![Discharge power vs. Input CH\(_3\)OH concentration](image)

Fig. 3 – Effect of input CH\(_3\)OH concentration on CH\(_3\)OH conversion

![CH\(_3\)OH conversion vs. Input CH\(_3\)OH concentration](image)

Fig. 4 shows the influence of the CH\(_3\)OH concentration on the selectivity of H\(_2\) and CO and the
H₂/CO molar ratio. The selectivity of H₂ and CO produced in the CH₃OH/N₂ RGA is significantly higher than that in the CH₃OH/Ar plasma, especially at a high methanol concentration (> 20%). The effect of the CH₃OH concentration on the selectivity of H₂ and CO shows a similar evolution in both plasma chemical processes: the selectivity of syngas increases almost linearly as the CH₃OH concentration initially increases from 5 to 15 %, and then plateaus to an almost constant value when further increasing the methanol concentration.

![Graph showing the effect of input CH₃OH concentration on H₂ selectivity, CO selectivity, and H₂/CO molar ratio.](image)

**Fig. 4 – Effect of input CH₃OH concentration on (a) H₂ selectivity and CO selectivity; and (b) H₂/CO molar ratio**

It is expected that N-containing products (e.g., NH₃ and HCN) were produced in the plasma methanol decomposition process in the CH₃OH/N₂ plasma, as evidenced from the present of NH and CN bands in the emission spectra of the CH₃OH/N₂ plasma.

From the stoichiometry of methanol decomposition reaction, a H₂/CO molar ratio of 2 would
be expected. In this study, the H₂/CO ratio is slightly below 2 for most operating conditions. We can see that increasing the CH₃OH concentration from 5 to 10% leads to a noticeable drop of the H₂/CO ratio from 2.51 to 2.07 in the CH₃OH/N₂ plasma, while the H₂/CO molar ratio in the CH₃OH/Ar RGA increases from 1.52 to 2.00. This might be attributed to the formation of different byproducts in both plasma systems. As the methanol concentration increases from 10% to 35%, the H₂/CO molar ratio in the CH₃OH/N₂ plasma slightly decreases, whilst this parameter in the CH₃OH/Ar plasma is almost constant.

Fig. 5 shows the effect of CH₃OH concentration on the selectivities of gaseous byproducts. The selectivity of the gas products (CO₂, CH₄, C₂H₂, and C₂H₄) in the CH₃OH/N₂ plasma decreases in the order: CH₄ > C₂H₂ > C₂H₄ ≈ CO₂, whilst in the CH₃OH/Ar gliding arc, the selectivity of these gases follows the order CO₂ > CH₄ > C₂H₂ > C₂H₄. CO₂ was formed with significantly higher selectivity in the CH₃OH/Ar RGA compared to the CH₃OH/N₂ plasma. Increasing the concentration of CH₃OH from 5 to 35% significantly decreases the CO₂ selectivity from 46.30 to 1.15% in the CH₃OH/Ar plasma. In contrast, the selectivity of CO₂ is almost independent on the input concentration of CH₃OH in the CH₃OH/N₂ plasma and remains low (0.2%).

In the plasma methanol conversion process, CO₂ is more likely to be formed from the reaction of CO with OH radicals (Eq. (8)) [7].

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$$  \hspace{1cm} (8)

Strong OH bands were observed in the spectra of the CH₃OH/Ar plasma, whereas no OH bands were detected in the spectra of the CH₃OH/N₂ RGA (see Fig. 9 and Fig. 10), which suggests that more CO₂ could be produced via Eq. (8) when Ar is used as a carrier gas, leading to a higher CO₂ selectivity. In addition, CO₂ could also be formed from the Boudouard reaction of CO:

$$2\text{CO} \rightarrow \text{CO}_2 + \text{C}$$  \hspace{1cm} (9)
Very low selectivity of CO\textsubscript{2} (0.2\%) was obtained in the CH\textsubscript{3}OH/N\textsubscript{2} RGA, which reveals that this reaction (Eq. (9)) might be inhibited in the plasma methanol conversion process using N\textsubscript{2} as a carrier gas.

**Fig. 5** – Effect of input CH\textsubscript{3}OH concentration on the selectivity of gaseous byproducts (a) CO\textsubscript{2}, (b) CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, and C\textsubscript{2}H\textsubscript{4}
The effect of CH$_3$OH concentration on the energy conversion efficiency and energy yield of H$_2$ is presented in Fig. 6. Both parameters follow the similar evolution of the selectivity of H$_2$ and CO with the increase of the CH$_3$OH concentration (Fig. 4). At a CH$_3$OH concentration of higher than 20%, both the energy conversion efficiency and energy yield of H$_2$ are higher in the CH$_3$OH/N$_2$ RGA than those in the CH$_3$OH/Ar RGA.

We find that the selectivities of gas products are almost constant as the methanol concentration varies between 15% and 35%, except the CO$_2$ selectivity in the argon plasma process, as shown in Figs. 4 and 5. This phenomenon suggests that there might be no significant changes of the dominant reaction routes in the plasma methanol conversion process. Fig. 7 shows the production of gaseous products increases linearly with increasing the converted methanol at the CH$_3$OH concentration of 15-35% in the CH$_3$OH/N$_2$ plasma. Similar evolution behavior of the gas products (except CO$_2$) can be found in the Ar plasma-assisted methanol conversion process (Fig. 8). Note that the CO$_2$ formation decreases linearly with increasing the methanol converted, indicating that there is a
significant change in the formation of CO$_2$. Both reactions can be globally represented by

$$\text{CH}_3\text{OH}/\text{N}_2 \text{ RGA plasma}$$

$$1 \text{ CH}_3\text{OH} \rightarrow 0.9993 \text{ H}_2 + 0.5801 \text{ CO} + 0.0026 \text{ CO}_2 + 0.0182 \text{ CH}_4 + 0.0073 \text{ C}_2\text{H}_2 + 0.0013 \text{ C}_2\text{H}_4 + \ldots.$$

(10)

$$\text{CH}_3\text{OH}/\text{N}_2 \text{ RGA plasma}$$

$$1 \text{ CH}_3\text{OH} \rightarrow 0.7648 \text{ H}_2 + 0.4113 \text{ CO} + \text{(variable) CO}_2 + 0.0130 \text{ CH}_4 + 0.0055 \text{ C}_2\text{H}_2 + 0.0008 \text{ C}_2\text{H}_4 + \ldots.$$

(11)

Fig. 7 – Production of gaseous products as a function of methanol converted in the CH$_3$OH/N$_2$ RGA at the CH$_3$OH concentration of 15-35%
Fig. 8 – Production of gaseous products as a function of methanol converted in the CH$_3$OH/Ar RGA at the CH$_3$OH concentration of 15-35%.

3.2 Optical diagnostics of plasma chemical processes

Optical emission diagnostics has been carried out to understand the formation of reactive species and to give new insights into the possible reaction mechanisms in the plasma methanol conversion processes. Fig. 9 shows typical emission spectra of the CH$_3$OH/N$_2$ RGA. The spectra are clearly dominated by numerous strong CN ($B^2\Sigma \rightarrow X^2\Sigma$, $\Delta v = 1, 0, -1$) violet bands at an exposure time of 500 $\mu$s. In addition, C I line (193.09 nm), N$_2$ second positive system ($C^3\Pi_u \rightarrow B^3\Pi_g$), NH ($A^3\Pi \rightarrow X^3\Sigma$) at 336.0 nm, C$_2$ swan system ($d^3\Pi_g \rightarrow a^3\Pi_u$, $\Delta v = 1, 0$), and CN violet system of $\Delta v = -2$ can be observed using a long exposure time of 25 ms, as plotted in Fig. 9.

Different emission spectra were detected in the CH$_3$OH/Ar plasma (Fig. 10) to those in the CH$_3$OH/N$_2$ RGA. Besides the CN bands due to gas impurity, numerous C$_2$ swan bands ($\Delta v = 1, 0, -1$) and weak CO fourth positive system ($A^3\Delta \rightarrow X^2\Pi$, $\Delta v = 6-10$) can be observed. In addition, OH ($A^2\Sigma^+ \rightarrow X^2\Pi$, $\Delta v = 0$) and CH ($A^2\Delta \rightarrow X^2\Pi$, $\Delta v = 0$) bands, as well as H Balmer lines (H$_\alpha$, H$_\beta$, and H$_\delta$) can be clearly seen in the spectra. In contrast, these bands (OH, CH, and C$_2$) and H atomic lines cannot be found in the spectra of the CH$_3$OH/N$_2$ RGA. C I spectral lines at 193.09 nm and
247.87 nm, together with numerous argon atomic lines are also visible in the CH$_3$OH/Ar plasma. Fe spectra lines from the electrode materials are detected in both plasma systems. An overview of these atomic lines and molecular bands that detected in the CH$_3$OH/N$_2$ and CH$_3$OH/Ar plasmas is presented in Table 1.

Vibrational temperature represents the chemical reactivity of vibrational excited species, and provides insight into the relative rates of vibration-vibration and vibration-translation energy exchange processes [28]. The vibrational temperature of CN in the CH$_3$OH/N$_2$ RGA was determined from a group of CN ($B^2\Sigma \rightarrow X^2\Sigma$, $\Delta v=0$) violet bands using a Boltzmann plot [29]. The results show that increasing the input concentration of CH$_3$OH from 5 to 35% results in a quasi-linear drop of the vibrational temperature from 14300 ± 800 K to 8930 ± 1300 K in the CH$_3$OH/N$_2$ plasma, since CH$_3$OH could quench the vibrational levels of CN [30]. It is interesting to note that the vibrational temperature in the CH$_3$OH/N$_2$ plasma is considerably higher than that of other typical non-thermal plasmas, such as DBD in N$_2$ or Ar (2000-5000 K) [31-34] and glow discharge in N$_2$ (2000-4000 K) [35]. In addition, the vibrational temperature in the CH$_3$OH/N$_2$ RGA plasma is also found higher than that of a pure N$_2$ RGA plasma (4000 K) [36] and an air/water gliding arc with knife-shaped electrodes (3900-4500 K) [37], showing higher vibrational levels of
Fig. 9 – Typical emission spectra of the CH$_3$OH/N$_2$ plasma (CH$_3$OH concentration= 5%, exposure time= 500 μs; for enlarged area: exposure time= 25 ms)

Fig. 10 – Typical emission spectra of the CH$_3$OH/Ar plasma (CH$_3$OH concentration= 5%, exposure time= 25 ms)

Table 1 – Overview of the atomic lines and molecular bands in the spectra of the CH$_3$OH/N$_2$ and CH$_3$OH/Ar plasmas

<table>
<thead>
<tr>
<th>Species</th>
<th>Transition</th>
<th>Wavelength (nm)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>CH$_3$OH/N$_2$</td>
</tr>
<tr>
<td>C I</td>
<td>$2s^22p^3\rightarrow2s^22p3s$</td>
<td>193.09</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>$C^3\Pi_u \rightarrow B^3\Pi_g$</td>
<td>312-316, 337.1</td>
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<tr>
<td>NH</td>
<td>$A^3\Pi \rightarrow X^3\Sigma^+$, (0, 0)</td>
<td>336.0</td>
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<tr>
<td>CN</td>
<td>$B^2\Sigma \rightarrow X^2\Sigma$</td>
<td>$\Delta v = 1, 0, -1$</td>
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<td></td>
<td></td>
<td>$\Delta v = -2$</td>
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<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>$d^3\Pi_g \rightarrow a^3\Pi_u$</td>
<td>$\Delta v = 1, 0$</td>
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<td></td>
<td></td>
<td>$\Delta v = -1$</td>
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<tr>
<td>CO</td>
<td>$A^1\Pi \rightarrow X^1\Sigma^+$, $\Delta v = 6-10$</td>
<td>ND</td>
</tr>
<tr>
<td>OH</td>
<td>$A^2\Sigma^+ \rightarrow X^2\Pi$, $\Delta v = 0$</td>
<td>ND</td>
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<tr>
<td>H</td>
<td>Balmer system</td>
<td>$\delta$</td>
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<td>$\beta$</td>
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<td></td>
<td></td>
<td>$\alpha$</td>
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<tr>
<td>CH</td>
<td>$A^2\Delta \rightarrow X^2\Pi$, $\Delta v = 0$</td>
<td>ND</td>
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<td></td>
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<td>2nd order: 835-880</td>
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<tr>
<td>Ar</td>
<td>-</td>
<td>ND</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>314.43, 334.23, 334.98</td>
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</table>

<sup>a</sup> ND: Not detected

The vibrational temperature of CN in the CH<sub>3</sub>OH/Ar plasma was also obtained using the aforementioned method by adding 5 mol % N<sub>2</sub> into the CH<sub>3</sub>OH/Ar plasma, and the corresponding vibrational temperature is in the range of 6600 ± 900 to 8100 ± 400 K, which is also much lower than that in the CH<sub>3</sub>OH/N<sub>2</sub> plasma.

The electron density of the CH<sub>3</sub>OH/Ar plasma can be determined from the Stark broadening of the Ar atomic line at 696.5 nm. The detailed method can be found in previous works [38, 39]. The estimated electron density of the 5% CH<sub>3</sub>OH/Ar RGA is (1.53 ± 0.14)×10<sup>16</sup> cm<sup>-3</sup>. This value is about an order of magnitude lower than that of the AC gliding arc with knife-shaped electrodes [11].
In this study, the electron density obtained in the CH$_3$OH/Ar and CH$_3$OH/N$_2$ RGA plasmas is significantly higher (several orders of magnitude) than that of typical non-thermal plasmas, such as DBD (10$^{10}$-10$^{13}$ cm$^{-3}$) and corona discharge (10$^{9}$-10$^{13}$ cm$^{-3}$) [11, 40].

3.3 Reaction Mechanisms

The possible dominant reaction pathways in the RGA decomposition of methanol are schematically shown in Fig. 11. At a high concentration of CH$_3$OH (e.g., 20-35%), electron impact dissociation of methanol via different reaction channels (Eq. (12)-(18)) plays a dominant role in the decomposition of CH$_3$OH into a variety of radicals or intermediates [41-43], with subsequent radical recombination reactions to form higher hydrocarbons or further dissociation of radicals and intermediates [25].

\[
\begin{align*}
\text{CH}_3\text{OH} + e & \rightarrow \text{CH}_3 + \text{OH} + e \quad (12) \\
\text{CH}_3\text{OH} + e & \rightarrow \text{CH}_2\text{OH} + \text{H} + e \quad (13) \\
\text{CH}_3\text{OH} + e & \rightarrow \text{CH}_3\text{O} + \text{H} + e \quad (14) \\
\text{CH}_3\text{OH} + e & \rightarrow \text{CH}_2 + \text{H}_2\text{O} + e \quad (15) \\
\text{CH}_3\text{OH} + e & \rightarrow \text{tran-HCOH} + \text{H}_2 + e \quad (16) \\
\text{CH}_3\text{OH} + e & \rightarrow \text{cis-HCOH} + \text{H}_2 + e \quad (17) \\
\text{CH}_3\text{OH} + e & \rightarrow \text{CH}_2\text{O} + \text{H}_2 + e \quad (18)
\end{align*}
\]
In the CH$_3$OH/N$_2$ and CH$_3$OH/Ar gliding arc plasmas, initially formed highly energetic electrons interact with the carrier gas (N$_2$ or Ar) to produce a cascade of processes yielding a variety of chemically reactive species including electronically excited metastable N$_2$($\Lambda^3Σ_u^+$), vibrationally excited N$_2$(X$^2Σ_g^+$, $ν$), and electronically excited Ar* species [44-47]. These excited species are believed to make a significant contribution to the dissociation of methanol (Eq. (19)-(21)) into a variety of radicals and intermediates (e.g., CH$_3$, OH, CH$_2$O, CH$_2$OH), especially at a low concentration of methanol (e.g., 5%) [44, 45].

\begin{align*}
\text{CH}_3\text{OH} + \text{N}_2 (\Lambda^3Σ_u^+) & \rightarrow \text{radicals and intermediates} + \text{N}_2 & (19) \\
\text{CH}_3\text{OH} + \text{N}_2 (X^2Σ_g^+, ν) & \rightarrow \text{radicals and intermediates} + \text{N}_2 (X^2Σ_g^+, ν') & (20) \\
\text{CH}_3\text{OH} + \text{Ar}^* & \rightarrow \text{radicals and intermediates} + \text{Ar} & (21)
\end{align*}

Previous plasma modeling work has demonstrated that quenching reactions with metastable nitrogen N$_2$($\Lambda^3Σ_u^+$) appear to be important in the destruction of ethylene (10-10000 ppm) besides the reactions with radicals in an atmospheric pressure air DBD, while the direct electron impact
dissociation reactions are negligible for the destruction of ethylene [47]. Diamy et al. have also shown that metastable N\textsubscript{2} species are critical in the initial decomposition of methane in a CH\textsubscript{4}/N\textsubscript{2} glow discharge [30, 48]. In addition, Pintassilgo et al. have demonstrated that the vibrational excited N\textsubscript{2} could contribute much to the decomposition of CH\textsubscript{4} in a 2% CH\textsubscript{4}/N\textsubscript{2} afterglow plasma [44, 45].

We can find that more reaction channels for the conversion of methanol exist in the CH\textsubscript{3}OH/N\textsubscript{2} plasma due to the formation of more excited species compared to the CH\textsubscript{3}OH/Ar plasma, which can also explain the higher conversion of methanol obtained in the plasma reaction using N\textsubscript{2} as a carrier gas.

CH\textsubscript{2}O is a key intermediate from the initial decomposition of methanol (Eq. (16)-(21)). CH\textsubscript{2}O is unstable in non-thermal plasmas and can be further decomposed to form H\textsubscript{2} and CO through the dissociation with electrons and excited species (e.g., N\textsubscript{2} (A\textsuperscript{3}Σ\textsubscript{u}\textsuperscript{+}), N\textsubscript{2} (X\textsuperscript{2}Σ\textsubscript{g}\textsuperscript{+}, ν), Ar\textsuperscript{*}),

\begin{equation}
\text{CH}_2\text{O} + e, \ N_2 (A), \ N_2 (X, v) \rightarrow \text{CHO} + H + e, \ N_2, \ N_2 (X, v')
\end{equation}

\begin{equation}
\text{CHO} + e, \ N_2 (A), \ N_2 (X, v) \rightarrow \text{CO} + H + e, \ N_2, \ N_2 (X, v')
\end{equation}

\begin{equation}
H + H \rightarrow H_2
\end{equation}

H\textsubscript{2} can also be generated from the direct dissociation of methanol (e.g., Eq. 16-21) or the recombination of H radicals from methanol decomposition (e.g., Eq. (24)).

In addition, the H and OH radicals that present in the plasma bulk may also contribute to the conversion of CH\textsubscript{2}O and CHO through the following reactions, generating CO, H\textsubscript{2}, and H\textsubscript{2}O [49].

\begin{equation}
\text{CH}_2\text{O} + H \rightarrow \text{CHO} + H_2
\end{equation}

\begin{equation}
\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O}
\end{equation}

\begin{equation}
\text{CHO} + H \rightarrow H_2 + \text{CO}
\end{equation}

\begin{equation}
\text{CHO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O}
\end{equation}

Very low selectivities of hydrocarbons (mainly CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4}) have been obtained in the
CH$_3$OH/N$_2$ (2.7-3.8%) and CH$_3$OH/Ar (1.1-2.6%) plasmas. The initially generated CH$_3$ and CH$_2$ radicals are the key species to form these hydrocarbons (CH$_4$, C$_2$H$_2$, and C$_2$H$_4$) through further dissociation or recombination reactions. For instance, CH$_4$ can be formed from the recombination of CH$_3$ and H, which can explain why the selectivity of CH$_4$ is one order of magnitude higher than that of C$_2$ hydrocarbons.

Carbon can be mainly formed from the Boudouard reaction (Eq. (9)), which also leads to the formation of CO$_2$. CO$_2$ might also be formed via water gas shift reaction (Eq. (29)).

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (29)$$

### 3.4 Comparison of different plasma technologies for hydrogen production from methanol

Table 2 shows a comparison of the performance (e.g., methanol conversion rate, selectivity of syngas, and energy yield of H$_2$) of plasma methanol conversion using different processes and plasma systems.

In the steam reforming of methanol using a pulsed gliding arc reactor, a high energy yield of H$_2$ was achieved with a relatively low conversion of methanol [3]. Note the energy cost for the production of steam has not been considered in the calculation of energy yield of H$_2$. The combination of plasma with catalysts (e.g., Cu/Al$_2$O$_3$ and Cu/ZnO) was also used to enhance the conversion of CH$_3$OH in the steam reforming of methanol by a DBD [13, 24]. However, the energy efficiency of the plasma-catalytic process is much lower in a DBD plasma reactor compared to that using a gliding arc.
Table 2 – Comparison of the performance of RGA plasmas with other non-thermal plasmas for hydrogen production from methanol conversion

<table>
<thead>
<tr>
<th>Plasma type</th>
<th>Process</th>
<th>Carrier gas</th>
<th>Reactants</th>
<th>Power supply/ Discharge power</th>
<th>CH₂OH conversion (%)</th>
<th>S(H₂) (%)</th>
<th>S(CO) (%)</th>
<th>H₂/ CO</th>
<th>EY(H₂) (g/kWh)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulsed GAD</td>
<td>SR +</td>
<td>Ar 2 l/min</td>
<td>H₂O + 5-85% CH₃OH: 2-20 ml/min</td>
<td>AC, 250 Hz, 25 kV, 0.3-0.45W</td>
<td>3-33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>~50-176</td>
<td>[3]</td>
</tr>
<tr>
<td>DBD + Cu/Al₂O₃ catalyst</td>
<td>SR</td>
<td>Ar 10 ml/min</td>
<td>H₂O + 50% CH₃OH: CH₂OH: 0.0165 ml/min</td>
<td>AC, 18.5 kHz, ~12.5-21.5 W</td>
<td>15-80</td>
<td>~16-45</td>
<td>-</td>
<td>-</td>
<td>~0.5-16</td>
<td>[13]</td>
</tr>
<tr>
<td>DBD + Cu/ZnO catalyst</td>
<td>SR</td>
<td>N₂</td>
<td>H₂O + 50% CH₃OH: CH₂OH: 0.008 ml/min</td>
<td>AC, 50 kHz, 0.4-0.47 W</td>
<td>6-54.4</td>
<td>~3-14</td>
<td>-</td>
<td>-</td>
<td></td>
<td>[24]</td>
</tr>
<tr>
<td>MHCD DEC</td>
<td>SR +</td>
<td>N₂ 10.5-23.7 ml/min</td>
<td>4.7-56.7% CH₃OH</td>
<td>DC, ~0.8-1.3 W</td>
<td>7.4-47.0</td>
<td>55-80</td>
<td>50-80</td>
<td>1.5-2.8</td>
<td>1.2-10.8</td>
<td>[2]</td>
</tr>
<tr>
<td>GAD DEC</td>
<td>SR +</td>
<td>Ar 43.3-86.6 ml/min</td>
<td>17.4-37.8% CH₃OH</td>
<td>AC, &lt; 300W</td>
<td>51.8-62.2</td>
<td>43.4-49.5</td>
<td>81.4-81.9</td>
<td>1.14-1.2</td>
<td>~6.9</td>
<td>[4]</td>
</tr>
<tr>
<td>Corona DEC</td>
<td>SR +</td>
<td>Ar 40 ml/min</td>
<td>20-75% CH₃OH</td>
<td>AC, 2 kHz, 0.8 kV, 12 W</td>
<td>10-80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>~4.5</td>
<td>[22]</td>
</tr>
<tr>
<td>DBD DEC</td>
<td>SR +</td>
<td>N₂ 100 ml/min</td>
<td>1% CH₃OH</td>
<td>AC, 50 Hz, 0.21-1.99 W</td>
<td>8-26</td>
<td>12-21.7</td>
<td>11.7-20.0</td>
<td>1.96-2.70</td>
<td>~0.05-0.63</td>
<td>[15]</td>
</tr>
<tr>
<td>RGA DEC</td>
<td>SR +</td>
<td>Ar 7.9-11.5 l/min</td>
<td>5-35% CH₃OH</td>
<td>DC, 10 kV, 105.2-271.6 W</td>
<td>36.1-87.5</td>
<td>14.8-44.3</td>
<td>19.5-45.6</td>
<td>1.52-2.00</td>
<td>8.95-25.40</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N₂ 8.8-12.8 l/min</td>
<td>DC, 10 kV, 149.8-349.4 W</td>
<td>43.0-92.4</td>
<td>24.4-53.1</td>
<td>19.4-60.3</td>
<td>1.76-2.51</td>
<td>10.94-34.54</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a SR: Steam reforming of methanol  
b DEC: Non-oxidative decomposition of methanol  
c The energy yield of H₂ (1 g/kWh) corresponds to the energy cost of 31.67 kJ/mol H₂

In Table 2, we can see that non-oxidative decomposition of methanol offers relatively higher selectivities of H₂ and CO, as well as higher H₂/CO molar ratio, compared with steam reforming of methanol processes due to limited water gas shift reaction. Compared to other plasma systems (e.g.
the RGA plasma shows a significantly higher conversion of methanol, a relatively high selectivity of syngas, and a highest energy yield of hydrogen in plasma decomposition of methanol process. It is also interesting to note that the RGA plasmas can provide a feed flow rate, or processing capacity, of several orders of magnitude higher (e.g., 7.9-11.5 l/min) than that using other non-thermal plasma systems (e.g., 10.5-100 ml/min in a DBD reactor), whilst allowing for the conversion of a wider range of reactant concentration, both of which are beneficial to the industrial applications.

4. Conclusions

In this study, non-oxidative decomposition of methanol for hydrogen production has been carried out in the atmospheric pressure DC rotating gliding arc plasma reactor. The effect of carrier gas and input CH$_3$OH concentration on the reaction performance of the plasma conversion processes has been evaluated. The use of N$_2$ as a carrier gas in the plasma methanol conversion shows much better performance compared with the CH$_3$OH/Ar gliding arc in terms of the CH$_3$OH conversion, syngas selectivity, energy yield of H$_2$, and energy conversion efficiency of the plasma process. It is found that increasing the input methanol concentration from 5 to 35 % significantly decreases the CH$_3$OH conversion from 92.4 to 43.0 % in the CH$_3$OH/N$_2$ RGA and from 87.5 to 36.1 % in the CH$_3$OH/Ar RGA. Optical emission diagnostics of the plasma process clearly shows the generation of a variety of reactive species in both plasmas. The estimated electron density of the 5% CH$_3$OH/Ar plasmas is $(1.53 \pm 0.14) \times 10^{16}$ cm$^{-3}$, which is significantly higher than that of other typical non-thermal plasmas, such as DBD ($10^{10}$-$10^{13}$ cm$^{-3}$) and corona discharges ($10^{9}$-$10^{13}$ cm$^{-3}$), indicating a high processing capacity of the RGA plasma. The vibrational and electronically excited species (e.g., N$_2$
\( (A^3\Sigma^+_u), N_2(X^2\Sigma^+_g, v), Ar^* \) are expected to play an important role in the methanol decomposition process. We find that the RGA plasma can provide a feed flow rate, or processing capacity, of several orders of magnitude higher (e.g., 7.9-11.5 l/min) than that using other non-thermal plasma systems (e.g., 10.5-100 ml/min in a DBD reactor), whilst allowing for the conversion of a wider range of reactant concentration, both of which are beneficial to the industrial applications.

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