Plasma-assisted conversion of methane for hydrogen production in a DC rotating gliding arc discharge reactor

H. Zhang\textsuperscript{1,2}, X. D. Li\textsuperscript{1}, F. S. Zhu\textsuperscript{1} and X. Tu\textsuperscript{2}

\textsuperscript{1} State Key Laboratory of Clean Energy Utilization, Zhejiang University, 38\# Zheda Road, Hangzhou, 310027 Zhejiang, P.R. China
\textsuperscript{2} Department of Electrical Engineering and Electronics, University of Liverpool, Brownlow Hill, Liverpool L69 3GJ, U.K.

Abstract: A direct current (DC) rotating gliding arc (RGA) discharge reactor co-driven by a magnetic field and tangential flow was developed for the conversion of methane into hydrogen at atmospheric pressure. The RGA plasma was shown to occur as a warm plasma, according to the optical emission spectroscopic analysis. Additionally, the effect of load resistance, CH\textsubscript{4}/N\textsubscript{2} ratio, and feed flow rate on the performance of plasma methane conversion has been investigated. The results indicated that this RGA plasma was promising for the production of hydrogen by methane decomposition. Based on this reactor, the maximum CH\textsubscript{4} conversion of 91.8\% and H\textsubscript{2} selectivity of 80.7\% can be achieved at a flow rate of 6 L/min.

Keywords: rotating gliding arc, warm plasma, methane conversion, hydrogen production, optical emission spectroscopy

1. Introduction
Hydrogen energy has been regarded as one of the most promising clean energy sources that can play a key role in various specialized areas, such as fuel cells and internal combustion engines. Currently, thermal catalytic reforming of methane is the most well-developed and economical technique for hydrogen generation [1, 2]. However, due to high capital costs, requirement of high temperature, and large equipment size, the catalytic reforming process is limited in some applications such as mobile systems and small-scale distributed generation of synthesis gas, in which rapid ignition/response is essential [2-4].

Atmospheric pressure gliding arc discharge (GAD) with compact design, fast start and response characteristics, excellent chemical selectivity, high power density, and low energy consumption has been considered as a promising hydrogen production route [5, 6]. Whereas, in a traditional GAD reactor with knife-shaped electrodes that commonly used, the arc evolution of breakdown, elongation, extinction, and re-breakdown in the traditional two dimensional set up leads to an inhomogeneous distribution of reactive species, resulting in an unsatisfactory conversion rate. Rotating gliding arc (RGA) discharge can partly solve this problem by periodically rotating the arc. RGA plasma is considered as a warm plasma that has both thermal and non-thermal properties, indicating a relatively high electron density and electron energy as well as moderate gas temperature, which is beneficial for hydrogen production with high productivity [7], and has been used to produce hydrogen from methane reforming [8-10]. Gutsol et al. compared various plasma systems for fuel conversion and suggested that the warm plasmas were optimal for industrial applications due to the unique characteristics [11]. Lee et al. investigated the partial oxidation of methane using a RGA reactor and reported a methane conversion rate of higher than 95\% [10].

In this study, a DC RGA reactor co-driven by a magnetic field and tangential flow has been developed for hydrogen production from methane conversion in nitrogen. Optical emission spectroscopic (OES) diagnostics has been carried out to understand the key physical properties of the plasma (e.g. vibrational and rotational temperatures). The effect of load resistance, CH\textsubscript{4}/N\textsubscript{2} ratio and feed flow rate on the reaction performance of methane reforming has been investigated in terms of methane conversion rate and selectivity of gas products.

2. Experimental setup and analysis
The experimental system is mainly consisted of a RGA reactor, mass flow controllers (MFCs), a DC power supply, load resistances, and plasma diagnostic systems, as shown in Fig. 1. In the RGA reactor, a cone-shaped inner electrode (height: 100 mm) was placed inside a circular cylinder (inner diameter: 36mm; ground electrode) and connected to a high voltage source. The minimum gap between the two electrodes was 2 mm for the initial ignition of the arc. The reactant gases (N\textsubscript{2} or CH\textsubscript{4}+N\textsubscript{2}) were injected into the bottom of the reactor by three tangential inlets to form a swirling flow field in the reactor. The whole reactor was placed inside a ring magnet to form a magnetic field with a flux density of approximately 2000 G.
3. Results and discussion

3.1 OES analysis of the RGA plasma in pure N₂

The spectra are characterized by the N₂ first positive system (FPS) (B°Πₐ(v′) → A°Σₐ⁺(v'')) , N₂ second positive system (SPS) (C°Πₐ(v′) → B°Π₈(g) (v'')) , and N₂⁺ first negative system (FNS) (B⁺²Σ₈⁺(v′) → X⁺²Σ₈⁺(v'')).

Vibrational temperature $T_{\text{vib}}$ , rotational temperature $T_{\text{rot}}$ , electron temperature $T_{\text{e}}$ and electron density $N_{\text{e}}$ of the RGA N₂ plasma were determined using spectral methods and the Boltzmann equation. The sequence bands $\Delta v = 2$, 1, 0, -1, -2 of N₂ SPS were selected for the calculation of $T_{\text{vib}}$ by the Boltzmann plot method, as described in [12]. $T_{\text{rot}}$ was determined by the best fit of a simulated spectrum to the experimental one using the vibrational band (0–2) of N₂ SPS centered at 380.4 nm. $T_{\text{e}}$ and $N_{\text{e}}$ were calculated via a Boltzmann equation solver [13, 14].

The calculated parameters for the RGA N₂ plasma are summarized and compared with those of thermal and non-thermal plasmas in Table 1. We can find the RGA plasma is unique among thermal and non-thermal plasmas and can be considered as a warm plasma [7]. The plasma has typical non-thermal properties that allow chemically selective processes with low energy consumption to occur, whereas the relatively higher electron density ($10^{13}$ cm$^{-3}$) and gas (rotational) temperature compared to those of non-thermal plasmas are also beneficial for certain chemical processes and high-productivity systems.

3.2. Decomposition of methane to hydrogen and gaseous byproducts

3.2.1. Effects of CH₄/N₂ ratio and resistance

Fig. 2 shows the effect of CH₄/N₂ ratio $R$ on the CH₄ conversion rate, the selectivities of products, and specific energy consumption (SEC, defined as the electricity consumption per liter of H₂ produced) at different resistances. The main products were H₂, C₂H₂, and C₂H₄; C₂H₆, C₃, or C₄ species were not detected by the GC. For the 40-kΩ resistance, methane conversion decreases with increasing $R$. In addition, the gas temperature drops with increasing $R$, reducing the reaction rate of methane decomposition. The highest methane conversion is 91.8%, with $R=0.1$, which is much higher than that of a traditional mini-GAD reactor (maximum, 45%) [15] or a RF plasma reactor (maximum, 75.3%) [16].

Table 1. Typical parameters for the RGA N₂, thermal, and non-thermal plasmas

<table>
<thead>
<tr>
<th>Plasma parameter</th>
<th>Thermal</th>
<th>RGA N₂</th>
<th>Typical non-thermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{\text{e}}$ (cm$^{-3}$)</td>
<td>10$^{15}$-10$^{19}$</td>
<td>1.5-4.9×10$^{13}$</td>
<td>10$^{8}$-10$^{11}$</td>
</tr>
<tr>
<td>$T_{\text{e}}$ (eV)</td>
<td>1-10</td>
<td>0.8-0.9</td>
<td>1-5</td>
</tr>
<tr>
<td>$T_{\text{vib}}$ (eV)</td>
<td>1-10</td>
<td>0.42-0.44</td>
<td>0.2-0.45</td>
</tr>
<tr>
<td>$T_{\text{rot}}$ (K)</td>
<td>10000-100000</td>
<td>1400-2200</td>
<td>300-1500</td>
</tr>
</tbody>
</table>

Overall, the methane conversion and the selectivities of products for the 40-kΩ resistance are higher than those for the 70-kΩ resistance due to the higher electron energy and electron density. It is worth noting that, for the 70-kΩ resistance, the methane conversion first falls from 75.5% to 55.5% as $R$ increases from 0.05 to 0.6 and then increases. A plausible explanation for this behavior is that CH₄ molecules can be dissociated via thermal activation and plasma induced reactions [4]. It has been known in Section 3.1 that, the gas temperature for the 70-kΩ resistance was very high, and decreased with increasing $R$ as well. When $R$ was 0.05-0.6, thermal activation was dominant in the decomposition of CH₄ molecules, and consequently, the methane conversion decreased with increasing $R$ due to the decline of gas temperature. When $R$ reached 0.6, plasma chemistry began to play a significant role, resulting in a slight increase in the methane conversion.
Overall, the methane conversion and the selectivities of products for the 40-kΩ resistance are higher than those for the 70-kΩ resistance due to the higher electron energy and electron density. It is worth noting that, for the 70-kΩ resistance, the methane conversion first falls from 75.5% to 55.5% as $R$ increases from 0.05 to 0.6 and then increases. A plausible explanation for this behavior is that CH$_4$ molecules can be dissociated via thermal activation and plasma induced reactions [4]. It has been known in Section 3.1 that, the gas temperature for the 70-kΩ resistance was very high, and decreased with increasing $R$ as well. When $R$ was 0.05-0.6, thermal activation was dominant in the decomposition of CH$_4$ molecules, and consequently, the methane conversion decreased with increasing $R$ due to the decline of gas temperature. When $R$ reached 0.6, plasma chemistry began to play a significant role, resulting in a slight increase in the methane conversion.

H$_2$ selectivity decreases, whereas C$_2$H$_2$ selectivity increases with $R$ from 0.05 to 0.6 and then plateaus. C$_2$H$_4$ selectivity remains relatively constant at approximately 0.5%. The SECs for different resistances vary with relatively different trends. For the 40-kΩ resistance, the SEC first decreases and then remains relatively constant. For the 70-kΩ resistance, the SEC decreases inversely with $R$, but a slight increase followed by a fall occurs at approximately $R=0.6$. It should be noted that a significant carbon deposition could affect the continuous operation of the RGA reactor when $R$ is greater than 0.5. Therefore, our results suggest that a resistance of 40 kΩ and a CH$_4$/N$_2$ ratio of 0.1 to 0.4 should be selected to achieve a relatively high methane conversion and H$_2$ selectivity as well as a relatively low SEC.

3.2.2. Effect of feed flow rate

The flow rate of the reactants plays a significant role in determining the residence time within the plasma zone and the characteristics of the RGA plasma, thereby affecting the overall performance of the plasma system. Fig. 3 illustrates the effect of the feed flow rate on CH$_4$ conversion, the selectivities of products, and SEC. The methane conversion decreases from 62.1% to 16.4% with an increase in flow rate from 6 to 24 L/min. This behavior can be explained from two perspectives. First, the increase in flow rate decreases the energy density of the plasma zone, leading to a lower mean electron energy; thus, the dehydrogenation of CH$_4$ is weakened. Second, the residence time of reactive gases within the plasma zone declines, which can be determined as the volume of plasma zones divided by flow rate, from 0.595 to 0.149 ms.

H$_2$ is the primary gaseous product. The selectivities of H$_2$, C$_2$H$_2$, and C$_2$H$_4$, first increase to maximum values of 52.9%, 31.7% and 0.9%, respectively, at a flow rate of 20 L/min and then decline with further increasing the flow rate. With the increase in flow rate, the energy density of the plasma zone decreased, which reduces the dehydrogenation ability of the plasma. Thus, the CH$_4$ molecules tended to decompose to CH$_2$ and CH radicals rather than C atoms, and more H$_2$, C$_2$H$_2$, and C$_2$H$_4$ molecules were recombined. Then, as the flow rate continued to increase, the energy density declined and gradually became too low to decompose CH$_4$ molecules to form CH$_2$ or CH radicals. Thus, the selectivities of the products began to decrease. SEC appears to vary inversely with H$_2$ selectivity. According to the results, a feed flow rate of approximately 8 L/min should be considered when operating this plasma system because it yields a high conversion of CH$_4$, as well as a relatively low SEC.

4. Conclusions

Hydrogen production from methane conversion has been carried out in a DC RGA reactor. According to the spectroscopy measurements, the RGA N$_2$ plasma has a relatively high electron density ($10^{13}$ cm$^{-3}$ in magnitude), moderate electron temperature (approximately 10000 K), and relatively high vibrational temperature (approximately 5000 K) and rotational temperature (1400-2200 K), allowing for chemically selective processes with high productivity and low consumption to occur.

The results indicate that this RGA plasma is promising for the production of hydrogen by methane decomposition. For the 40-kΩ resistance, both CH$_4$ conversion and H$_2$ selectivity decreased with an increase in the CH$_4$/N$_2$ ratio, while increasing the gas flow rate decreased the conversion of CH$_4$. The SEC for H$_2$ production varied in the range of 14.3-45.0 kJ/NL for different CH$_4$/N$_2$ ratios or flow rates. The results show that a relatively high CH$_4$ conversion and H$_2$ selectivity, as well as a relatively low SEC can be achieved at a 40-kΩ resistance, a CH$_4$/N$_2$ ratio of 0.1-0.4, and a feed flow rate of 8 L/min.

5. References


### 6. Acknowledgement

This work is supported by the National Natural Science Foundation of China (51076142), the Specialized Research Fund for the Doctoral Program of Higher Education of China (2012010110099).