Catalyst-free one-step plasma reforming of CH_4 and CO_2 to higher value oxygenates under ambient conditions

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Abstract: Direct conversion of CH_4 and CO_2 to liquid fuels and chemicals is appealing for biogas conversion but challenging due to their inert nature. Herein, we report a promising plasma process for the catalyst-free one-step conversion of CH_4 and CO_2 into higher value oxygenates. Artificial neutral network (ANN) models were developed to analyze the process parameters and key discharge indicators that affect reaction performance. This provided new insights into optimizing the plasma gas conversion process with multiple parameters.

Keywords: Non-thermal plasma; Dry reforming of methane; Biogas utilization; Oxygenates; Methanol synthesis.

1. Introduction

The dry reforming of methane (CH_4, DRM) with carbon dioxide (CO_2) for producing higher-value liquid fuels and chemicals has gained considerable attention due to the negative environmental impact of greenhouse gases. The conversion of biogas into transportable liquids could provide access to a broad range of waste, particularly in remote locations. However, a single-step direct conversion of CH_4 and CO_2 to oxygenates is not thermodynamically feasible, requiring a two-step and indirect route using thermal catalysis, which is energy-intensive and limits scalability. Non-thermal plasma (NTP) offers a promising alternative, allowing thermodynamically unfavorable reactions to occur under ambient conditions. NTP has unique properties to activate inert molecules with strong chemical bonds, such as CO_2 and CH_4, resulting in a range of chemically reactive species. Various types of NTP have been used for DRM, with research focused on syngas production. However, direct conversion of CH_4 and CO_2 to oxygenates using NTP has still received less attention, and reported selectivity for total liquid products in this process is 50-60%, with individual oxygenate selectivity only <15% [1]. Furthermore, there are still knowledge gaps regarding the intrinsic links among processing parameters, plasma properties, and reaction performance, limiting the potential for industrial development.

In this work, we developed a temperature-controlled coaxial DBD reactor for converting CH_4 and CO_2 into oxygenates, with methanol as the primary liquid product. The reaction temperature can be controlled between 5 and 65°C, allowing for an understanding of the low-temperature performance of the plasma process[2]. We investigated the effects of various process parameters and performed diagnostics to determine the mean electron energy and density and the generation of chemically reactive species. We also developed an ANN model to investigate the relative importance of process parameters and optimize the process for producing target oxygenates.

2. Materials and Methodology

2.1 Experimental setup

The experiments were conducted in a temperature-controlled unconventional coaxial DBD reactor with circulating water as the ground electrode and reactor cooling. A stainless-steel rod was used as the high voltage electrode, and the reaction temperature was controlled between 5 and 65 °C by a cooling circulation bath. The reactor length and discharge gap were fixed, and a cooling trap was used to condense liquid products. Gas flow rates were measured using a soap-film flowmeter, and the DBD reactor was connected to a high voltage power supply. The applied voltage and current were measured using a high-voltage probe and current monitor, respectively. An external capacitor was connected to measure the charge formed, and electrical signals were sampled using a digital oscilloscope. The discharge power was calculated using the area of the Lissajous figure. A homemade control software was developed to monitor the discharge power in real-time. The gas temperature in the discharge zone was measured using a fiber optical thermometer, and gas and liquid products were analyzed using gas chromatography and gas chromatography-mass spectrometry. Sampling and measurements began after running the reaction for 4.5 h and lasted 6 h, with each measurement repeated three times.

2.2 Development of ANN model

Two single-layer artificial neural network (ANN) models (ANN_1 and ANN_2) were used to predict the plasma-driven DRM process and evaluate the importance of process parameters and discharge indicators. The ANN models were trained using the TensorFlow module and evaluated using the mean squared error (MSE). The plasma DRM process was evaluated using two non-dimensional indices, I_1 and I_2, which combined normalized conversion of CO_2 and CH_4 or selectivity of major products with energy efficiency.

3. Results and Discussion

A catalyst-free single-step approach has been developed for synthesizing oxygenates through the plasma-driven DRM reaction in a temperature-controlled reactor. By adjusting the process parameters, including the CO_2/CH_4 ratio, discharge power, reaction temperature, and residence time, the product distribution can be finely tuned. The highest methanol selectivity of 43% was achieved at 5 °C and 15 W (Fig. 1), while a lower discharge power (10 W)

was favorable for producing acetic acid at room temperature (20 °C). The selectivity of gaseous products, mainly H_2 and CO, increased with higher discharge power and reaction temperature. We also established the correlation between different process parameters (discharge power, reaction temperature, and residence time) and the key discharge properties, such as mean electron energy (E_e), electron density (n_e), and specific energy input (SEI). A higher discharge power led to a higher mean electron density but a similar mean electron energy, whereas changing the reaction temperature affected both the mean electron energy and electron density. Moreover, combining a low reaction temperature with a high electron energy significantly promoted the electron impact reactions of CO_2 and CH_4.

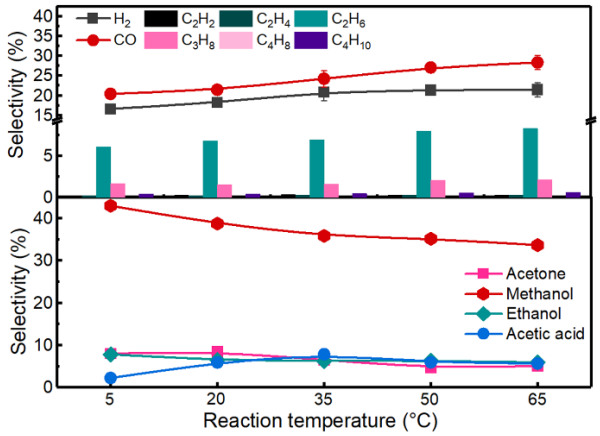

Fig. 1. Effect of different reaction temperatures on the product distribution of gases and oxygenates. (flow rate: 40 mL/min; discharge power: 15 W; CO_2/CH_4 = 1:1)

To gain a better understanding of the factors influencing reforming performance, the possible relationships among the process parameters, discharge parameters, and process performance have been analyzed (Fig. 2). Furthermore, we developed two well-trained ANN (artificial neural network) models. The first model (ANN_1) revealed that discharge power was the most critical process parameter, while the second model (ANN_2) helped to identify the key discharge indicators that affect reaction performance. The results of the ANN models demonstrated that higher conversions of CO_2 and CH_4 with better energy efficiencies can be achieved at 10–20 W and 5–20 °C. Furthermore, methanol production can be optimized with a selectivity of over 40% and an energy efficiency of over 0.8 mol/kWh under suitable conditions (20 W, 5 °C, and 2 s). Overall, this work demonstrates that the direct transformation of CH_4 and CO_2 into oxygenates can be finely tuned and optimized for the selective synthesis of target liquid products, such as methanol. This technology holds great potential to address the challenges of global warming and climate change.

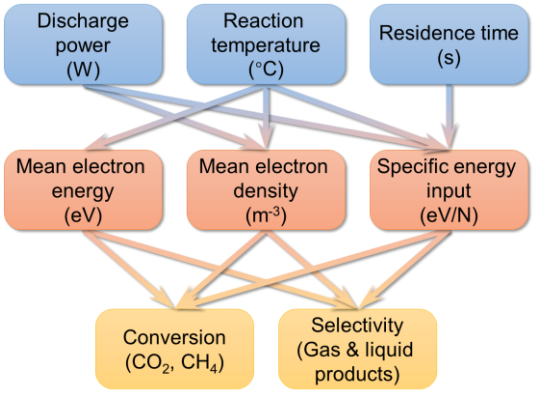

Fig. 2. Scheme of the possible relationship of process parameters (blue), key indicators of plasma-driven DRM reaction (red), and performance (yellow).

4. Significance

For the first time, we demonstrated that the distribution of gaseous products and oxygenates could be tailored by varying process parameters, since as they could influence the key discharge properties, including E_e, n_e and SEI, simultaneously. Lower discharge powers (10-15 W) and reaction temperatures (5-20 °C) were proved to be more favourable for the production of oxygenates, especially for methanol and acetic acid.

5. Acknowledgments

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6. References

[1] L Wang, Y Yi, C Wu, H Guo, X Tu, Angewandte Chemie 129 (44), 13867-13871(2017).
[2] Y Wang, Y Chen, J Harding, H He, A Bogaerts, X Tu, Chemical Engineering Journal 450, 137860 (2022).