Dry reforming of methane using a rotating gliding arc reactor

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Abstract: Dry reforming of methane was investigated using a rotating gliding arc reactor driven by a homemade dual-stage pulsed DC power supply. Arc rotation and upward displacement along the conical cathode and along the axis of the coaxial tubular reactor were enabled via the combined action of a 6-point tangential gas injector and static magnetic field. The total flow rate and CO_2/CH_4 ratio were fixed at 4.7 slpm and 1.5, respectively, for two peak currents of 0.75 and 1.50 A. Gas conversions were measured on-line using a mass spectrometer and off-line using a gas chromatograph. For the larger peak current, the average conversions of carbon and hydrogen were 7.1 and 7.9 %, respectively. A negligible amount of acetylene as by-product was obtained, which implies a good selectivity for carbon monoxide and hydrogen.

Keywords: Dry reforming, rotating gliding arc, warm plasma.

1. General

Greenhouse gases (GHG), primarily released into the atmosphere from the combustion of fossil fuels, have increased steadily since the beginning of the first industrial revolution, enhancing the natural greenhouse effect. It is well accepted that the anthropogenic carbon emissions are responsible for the observed large scale effects such as atmospheric temperature increase and ocean acidification, which impact the environment, human health and economy [1–3].

Carbon dioxide (CO_2) and methane (CH_4) are two industrially relevant GHG, and dry reforming of methane (DRM) is a reaction that recycles the two gases to produce syngas (eq. 1), a mix of carbon monoxide (CO) and hydrogen (H_2). Syngas is a building block for the Fischer-Tropsch process, a chemical process to produce liquid hydrocarbons. Currently, syngas is produced industrially by reforming processes such as partial oxidation of methane (eq. 2) and steam reforming (eq. 3). In all cases, CH_4 needs an oxidizing agent for its conversion to syngas. Although DRM is thermodynamically the most unfavourable reaction, it is considered more environmentally friendly due to the use of CO_2 as oxidizing agent [4]. Moreover, no separation of CO_2 from the feed gas is needed in the DRM process, so that sources with large amounts of CO_2 can be taken for this purpose [5].

$$CH_4 + CO_2 \leftrightharpoons 2CO + 2H_2 \quad \Delta H_{298K} = +247 \text{ kJ mol}^{-1} \quad (1)$$
$$CH_4 + \tfrac{1}{2}O_2 \leftrightharpoons CO + H_2 \quad \Delta H_{298K} = -38 \text{ kJ mol}^{-1} \quad (2)$$
$$CH_4 + H_2O \leftrightharpoons CO + 3H_2 \quad \Delta H_{298K} = +205 \text{ kJ mol}^{-1} \quad (3)$$

DRM is a highly energy intensive reaction (eq. 1) and requires temperatures between 700 and 1200 °C and an efficient catalyst to achieve good conversions. However, new technologies such as plasma can assist the conversion process by: (1) providing energy to drive the strongly endothermic reaction, and (2) reducing the activation barrier of CO_2 and CH_4 (i.e., C-H and C-O bond cleavage) and improve the reaction rate [6]

Non-thermal plasma technologies represent an attractive alternative for DRM since expensive high temperature-resistant materials and complex assemblies are not required for reactor construction. Currently used technologies include dielectric barrier discharge (DBD), glow and corona discharges. However, non-thermal plasmas generated by corona discharges and DBDs present high energy cost of syngas (>10 kWh m^{-3}) and low energy efficiency (< 10%) in biogas reforming [7]. On the other hand, warm plasma technologies such as plasma jets and gliding arcs can reach gas temperatures of 730 to 2700 ºC, thus enabling higher reactivity and chemical selectivity [8] while sharing several advantages with non-thermal plasma sources. Sophisticated cooling systems are usually not required due to the moderate power densities of the plasma discharges, the low-current operation limits electrode erosion, and the reactor construction is usually simple. This contribution discusses the use of a laboratory-scale rotating gliding arc (RGA) for the DRM process. The effect of peak current on the conversion efficiency and selectivity is investigated.

2. Experimental setup

The rotating gliding arc (RGA) reactor was adapted from [9] and consists of a vertically-mounted conical live electrode (cathode) mounted inside a hollow anode cylinder that acts as the ground electrode (Fig. 1). Both electrodes are made of stainless steel 316 and the shortest gap between the electrodes is 2.16 mm. This gap increases up to 8.76 mm in the downstream direction. The overall length of the cone cathode is 30.48 mm, with minimum and maximum diameters of 1.52 mm and 14.73 mm, respectively. The angle of the cone cathode is 12.2°. The ground electrode has an inner diameter of 19.05 mm, a wall

thickness of 9.52 mm, and a total length of 482.6 mm. The reactor is terminated with a CF tee enabling gas exhaust on the side port and direct line of sight view along the reactor axis. A mix of gas containing argon Ar (99.998 % purity), CO_2 (99.9 % purity) and CH_4 (99.99 % purity) is injected tangentially through the reactor by six gas injectors mounted at an angle of 20º axially and 30° radially. No external heating was provided to the reactor. The live cone cathode is powered by a homemade dual-stage pulsed DC power supply, consisting of a high-voltage arc igniter and a current driver power supply. A stack of ring magnets mounted around the anode cylinder adds a static axial magnetic field, which resulting Lorentz force acts along the gas drag force [9].

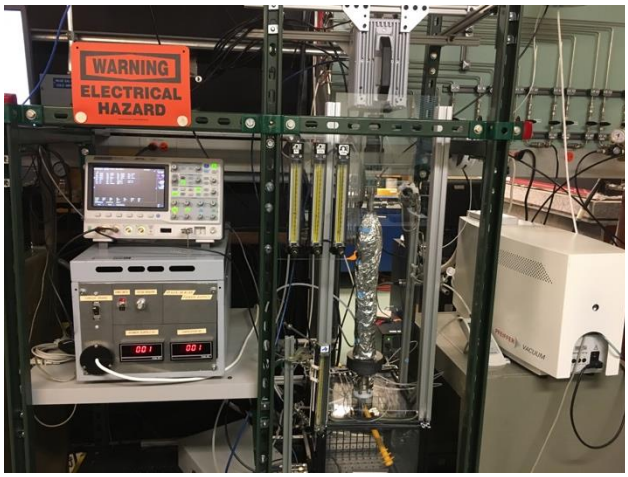

Fig. 1 RGA reactor setup.

The electrical signals are monitored using a high voltage probe (B&K Precision PR55), connected to an oscilloscope (Siglent SDS 2140X). The exhaust gas is analysed on-line by a mass spectrometer (Pfeiffer Ominstar GSD 301), and off-line by a gas chromatograph (Agilent 6890N). The natural volume expansion of the reaction was considered in the MS analysis.

Argon concentration was fixed at 70 % to ensure stable plasma operation. The reaction was carried out at a constant CO_2 to CH_4 volumetric ratio of 1.5, and a total flow rate of 4.7 slpm. The maximum current delivered by the dual-stage pulsed DC power supply was set by changing its internal resistance (1075 Ω, 535 Ω), giving rise to two peak current values of 0.74 and 1.50 A. Fig. 2 shows a typical voltage waveform obtained with a 535 Ω internal resistance. The average pulsing frequency is 25.5 Hz for pulse duration of ~39.2 ms. In comparison, the gas residence time in the plasma zone, estimated as the volume of the plasma zone divided by the volumetric flow rate is ~86 ms. The peak power levels are 595 and 1196 W, respectively, for peak current levels of 0.74 and 1.50 A.

Carbon deposition on the conical cathode and anode wall is observed during reforming. To avoid build-up of soots inside the reactor during long experimental runs, cyclic reforming-cleaning protocols are used. The RGA is operated for 15 min under reforming conditions, followed by 5 min in Ar/CO_2 cleaning periods (the methane flow is stopped during the cleaning period while keeping the other flows are the same level). This cleaning period proven to be sufficient to remove the accumulated solid carbon deposits.

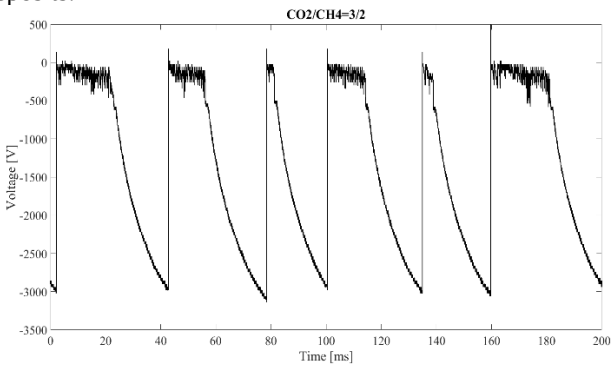

Fig. 2. Characteristic discharge voltage waveform for a power supply internal resistance of 535 Ω.

The performance of the reforming reaction is calculated based on the conversion for carbon and hydrogen:

$$\%H_{converted} = \frac{\dot{n}_{H_{out}}}{\dot{n}_{H_{in}}} \times 100 \quad (4)$$

$$\%C_{converted} = \frac{\dot{n}_{C_{out}}}{\dot{n}_{C_{in}}} \times 100 \quad (5)$$

where:

$$\dot{n}_{H_{out}} = 2\dot{n}_{H_2} + y\,\dot{n}_{C_xH_y} \quad (6)$$

$$\dot{n}_{H_{in}} = 4\dot{n}_{CH_4} \quad (7)$$

$$\dot{n}_{C_{out}} = \dot{n}_{CO} + x\,\dot{n}_{C_xH_y} \quad (8)$$

$$\dot{n}_{C_{out}} = \dot{n}_{CO_2} + \dot{n}_{CH_4} \quad (9)$$

$\dot{n}_i$ is the molar flow rate.

3. Results

The time evolution of the carbon and hydrogen conversion at two different peak RGA current levels are reported in Fig. 3. An increase of conversion is observed when the current is doubled, especially during the second and third cycle, increasing from an average concentration of 4.9 % of carbon to 7.1 %, and from 5.4 % of hydrogen to 7.9 %. When the current increases, the flow of electrons rises, leading to an increase in the electron density and gas temperature in the plasma zone. The increase of current, means a transformation of the kinetic energy from the electrons into thermal energy, which is provided to the gas, helping the highly endothermic reaction. Besides, these electrons can provide enough energy to break down the strong C-O and C-H bonds leading to higher conversions. The main by-product obtained was acetylene (C_2H_2), with an average concentration of 0.06 %. The small amount of acetylene found during the reaction suggests that RGA could be a good plasma source for the production of purer syngas [5,10].

The increased conversions correlate qualitatively with the optical emission spectrometry (OES) results reported in Fig. 4, where the overall emission intensity of the RGA for a peak current of 1.50 A is noticeably higher than the one for 0.74 A. Higher intensity in the emission spectrum is related with higher concentration of active species in the plasma zone. Some of the species identified qualitatively by OES were the C_2 Swan bands in a range from 467.88 nm to 562.62 nm, CH band at 430.16 nm and H_α at 656 nm. These reactive species participate directly in the reforming reaction where CO_2 and CH_4 molecules are ionized, and dissociated to produce ions, and radicals that interact and convert mainly into CO and H_2.

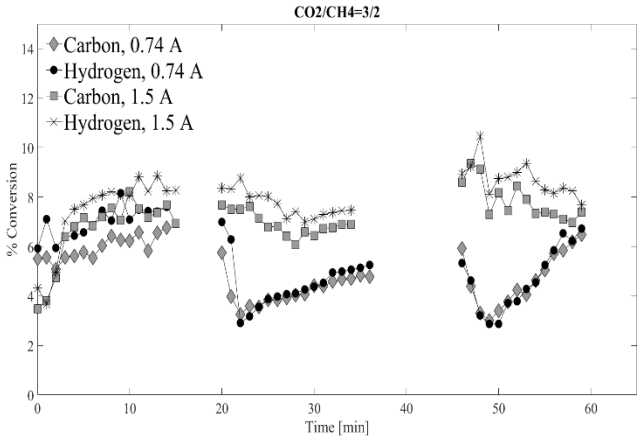

Fig. 3. Time evolution of the carbon and hydrogen conversion for RGA peak currents of 0.74 and 1.50 A.

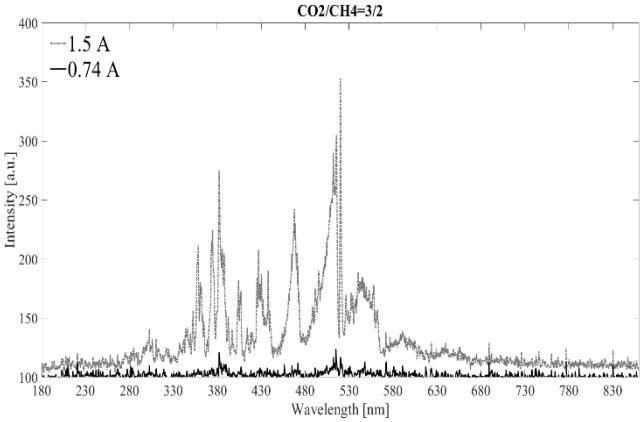

Fig. 4 OES spectra at RGA peak currents of 0.74 and 1.50 A.

A series of experiments at higher flow rates (results not reported here) were also performed and a decrease in conversion was observed. Our results suggest that decreasing the volumetric flow rate of the gas injected that passes through the plasma zone and higher peak currents enhance the overall reactivity by: increasing the residence time in the plasma zone and the electron density as some previous studies report [5,11,12].

4. Conclusions and future work

DRM reaction was performed using a rotating gliding arc plasma source, with a CO_2/CH_4 ratio of 1.5 and 70 % argon, with peak currents of 0.74 and 1.50 A, corresponding to peak power levels of 595 and 1196 W. Higher conversion of carbon and hydrogen was obtained with 1.50 A, with and average conversion of carbon of 7.1 % and 7.9 % for hydrogen. Although the conversion is not so high, the results are promising, as modifications in the homemade power supply and reaction conditions can be made to increase the conversion. Besides, the amount of acetylene formed was negligible, so high selectivity of CO and H_2 formed can be considered.

Future work includes a deeper study of the reaction conditions such as: different flow rates and stoichiometric ratios of the reactants, and electric currents provided by the current driver power supply. Moreover, the so-called "synergistic effect" between plasma and catalysis will be studied by adding a fluidized catalyst bed downstream of the active RGA zone.

5. References

[1] North American Power Plant Air Emissions, Montreal, Quebec, Canada, 2011.

[2] NASA, (2018).

[3] Climate Change Evidence & Causes, 2014.

[4] J.-M. Lavoie, Front. Chem. 2 (2014) 81.

[5] X. Tu, J.C. Whitehead, Int. J. Hydrogen Energy 39 (2014) 9658–9669.

[6] G. Chen, V. Georgieva, T. Godfroid, R. Snyders, M.-P. Delplancke-Ogletree, Appl. Catal. B Environ. 190 (2016) 115–124.

[7] K. Li, J.-L. Liu, X.-S. Li, X. Zhu, A.-M. Zhu, Chem. Eng. J. 288 (2016) 671–679.

[8] J. Pacheco, G. Soria, R. Valdivia, M. Pacheco, F. Ramos, H. Frías, M. Durán, M. Hidalgo, J. Salazar, J. Silva, M. Ibañez, Ieee Trans. Plasma Sci. 42 (2014) 2800–2801.

[9] M. McNall, S. Coulombe, J. Appl. Phys. 51 (2018).

[10] A. Indarto, J.-W. Choi, H. Lee, H.K. Song, Energy 31 (2006) 2986–2995.

[11] Q. Lin, G. Ni, Q. Guo, W. Wu, L. Li, P. Zhao, H. Xie, Y. Meng, IEEE Trans. Plasma Sci. 46 (2018) 2528–2535.

[12] K. Krawczyk, M. Młotek, B. Ulejczyk, K. Schmidt-Szałowski, Fuel 117 (2014) 608–617.