Bi-reforming with a ratio of $CH_4/CO_2/H_2O$ = 3/1/2 by plasma catalysis for power to fuels

Jing-Lin Liu and Ai-Min Zhu

Laboratory of Plasma Physical Chemistry, Center for Hydrogen Energy and Environmental Catalysis, Dalian University of Technology, Dalian 116024, China

Abstract: Bi-reforming of CH_4 in plasma catalytic reforming (PCR) was studied, aiming on directly produce high-quality syngas with an ideal $H_2/CO = 2$. PCR was composed of a gliding arc plasma and a tubular catalytic reactor with $Ni/CeO_2/Al_2O_3$ packing. Results shown that CO_2 conversion is more favourable than H_2O conversion in warm plasma, on the contrary, H_2O conversion is more favourable over catalysts. Therefore, bi-reforming of CH_4 can be really achieved with a stoichiometric ratio of $CH_4/CO_2/H_2O$ = 3/1/2. And then high-quality syngas with H_2/CO=2 is obtained at an energy efficiency of 65% and near conversions of 65$\pm$1% for CH_4, CO_2 and H_2O.

Keywords: Plasma reforming, Plasma catalysis, CH_4 conversion, CO_2 conversion.

1. Introduction

Bi-reforming of CH_4,

$$3CH_4 + CO_2 + 2H_2O \rightarrow 4CO + 8H_2 \qquad \text{(R1)}$$

is a promising process can directly produce high quality syngas with an ideal $H_2/CO = 2$. This process has been studied by conventional catalytic method. However, it is found that H_2O conversion is much favourable than CO_2 conversion, resulting this process can't be realized at the stoichiometric ratio of R1. In addition, the strong endothermic feature of R1 is also one of the challenge for conventional method.

In plasmas, electron can be accelerated selectively and obtains almost all the plasma energy to form a non-thermal equilibrium to induce reaction at a mild condition. Up to now, various plasma types have been studied for chemical processes. Amongst those plasmas, warm plasma formed by gliding arc (GA) has been believed to be one of the most promising plasma types, because it operates at atmospheric pressure, and exhibits a high energy efficiency. Especially, the vibrational excitation of CO_2 in GA plasma results the efficient dissociation of CO_2. Moreover, plasma is commonly generated by electric power and can be quickly switched on/off. Hence, it is feasible to power plasma with the fluctuant solar electricity and store it to fuels. In Laboratory of Plasma Physical Chemistry (LPPC), Dalian University of Technology, we have developed an efficient reactor and technique of plasma catalytic reforming (PCR) by combining GA plasma with catalysts [1, 2, 3]. In this work, we studied bi-reforming of CH_4 in PCR. The really bi-reforming of CH_4 reacting at its stoichiometric ratio is achieved, because PCR supplies activation for both of CO_2 and H_2O. Moreover, high-quality syngas with H_2/CO=2 is obtained at an energy efficiency of 65%.

2. Experimental

Fig. 1 shows a schematic diagram of the PCR reactor developed at LPPC. The numbers 1, 2, 3, 4, 5, 6, 7, 8, represent the high-voltage electrode, ceramic insulator, plasma zone, catalyst bed zone, heater, two movable thermocouples for recording the temperature of the catalyst bed and the reactor wall (6 for TCB and 7 for TRW), and a static thermocouple (8 for TH) located at the half-height of the heater. To avoid carbon deposition in plasma reactor, the reactants are fed from two inlets. One flow (F1), which is a mixture of $CH_4/CO_2/H_2O$ = 3/x/6-x, $0 \le x \le 6$, is used to form vortex flow in GA reactor with a flow rate of 2.2 SLM. The other flow (F2), which is pure CH_4 with flow rate of 0.7 SLM, is fed after GA reactor but before catalyst bed to adjust the total molar ratio of $CH_4/CO_2/H_2O$ = 6/x/6-x (x = 2 is the reaction molar ratio for bi-reforming). A DC high-voltage power source is connected to the high-voltage electrode, to generate a GA discharge at atmospheric pressure. The discharge voltage, current and power are recorded by an oscilloscope (DPO 4104B, Tektronix) via a voltage probe (P6015A, Tektronix) and a sampling resistor (51Ω), respectively. A spectrograph (Shamrock SR-750, Andor) with an ICCD detector (iStar DH734, Andor) was adopted to record optical emission spectra (OES) of GA plasma. The $Ni/CeO_2/Al_2O_3$ catalysts with weight of 10 g, containing Ni of 11 wt.% and Ce of 8 wt.%, are packed in the post-plasma zone. A home-made heater is employed for additional heating of the catalyst bed. The gaseous products are analyzed by two online gas chromatographs (Agilent 1790 and Agilent 6890 N) by using N_2 as internal standard of CO, CH_4, CO_2 and hydrocarbons (C_2H_6, C_2H_4 and C_2H_2), and helium as internal standard of H_2.

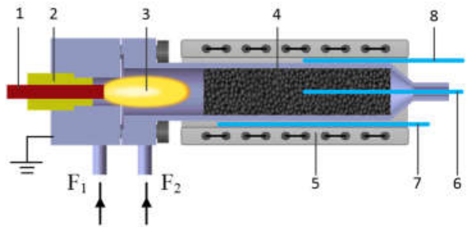

Fig. 1 Schematic diagram of the PCR reactor

3. Results and discussion

The waveforms at $F1$ molar composition of $CH_4/CO_2/H_2O$ = 3/1/2 and discharge power of 180 W is illustrated in Fig. 2. It is shown that the GA discharge possesses the classic ignition-evolution-extinguishment with a period of ~1.6 ms. The arc channel is ignited at voltage of ~3.5 kV. Once the arc ignited, the discharge voltage drops to ~2.6 kV at a current of ~69 mA, and then voltage and current increases and decreases gradually to extinguishment (re-ignition), respectively, with arc gliding. As the opposite trends of voltage and current, the discharge power fluctuates in 180 ± 6 W.

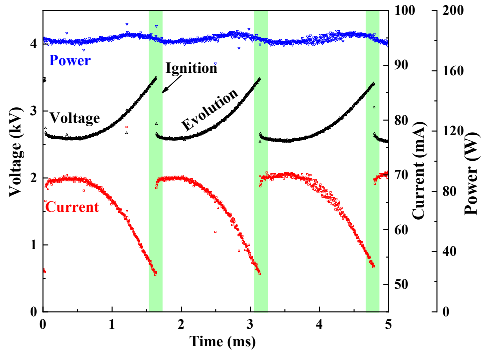

Fig. 2 Waveforms of discharge voltage, current and power

Plasma parameters of GA plasma in a mixture of $CH_4/CO_2/H_2O$ were determined with OES in a wavelength range of 300 - 800 nm. Molecular spectra of OH, CH, CO and C2 were observed. In addition, atomic lines of H_α and H_β from Balmer lines and oxygen triple lines at 777 nm from O atom were detected. Amongst those spectra, C2 Spectra was used to evaluate vibrational and rotational temperatures. By comparing the simulated and measured spectra of C2 as shown in Fig. 3, the vibrational and rotational temperatures can be estimated as 3900 K and 2500 K, respectively. The rotational temperature can be a measure for gas temperature in the arc channel, because they are in the thermal equilibrium. In addition, vibrational temperature is higher than rotational temperature. Obviously, this was attributed to the non-thermal equilibrium feature of GA plasma. Moreover, from Stark broadening of H_β deriving from its line profile (see Fig. 3b), the electron density was calculated as 1.2×10^{14} cm^{-3}. Note that we also measured the plasma parameter at various molar ratios of $CH_4/CO_2/H_2O$ at *SEI* of 110 kJ/mol, results shown that the vibrational temperature, rotational temperature and electron density were insensitive with gas composition.

Fig. 4 presents the effect of $CO_2/(CO_2+H_2O)$ molar ratio on reactant conversions and outlet temperature of GA reactor at discharge power of 180 W and F1 gas mixture of $CH_4/CO_2/H_2O$ = 3/x/6-x. With increasing $CO_2/(CO_2+H_2O)$ molar ratio from 0 to 1, conversions of CH_4 and CO_2 remained around 25% and 36%, respectively. However, H_2O conversion monotonously decreased with $CO_2/(CO_2+H_2O)$ molar ratio. This implied that the warm plasma supplied a favorable condition for CO_2 conversion, but not for H_2O. This should be attributed to the efficiently vibrational excitation of CO_2 in warm plasma.

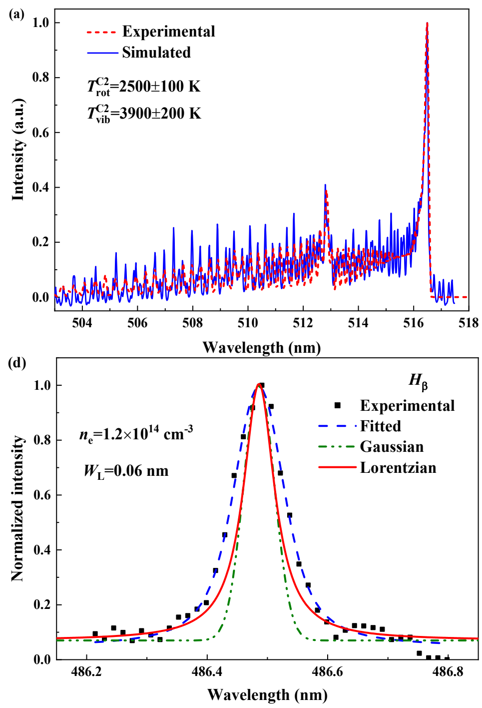

Fig. 3 Simulated and measured spectra of (a) C2 and (b) H_β at discharge power of 180 W and a gas mixture of $CH_4/CO_2/H_2O$

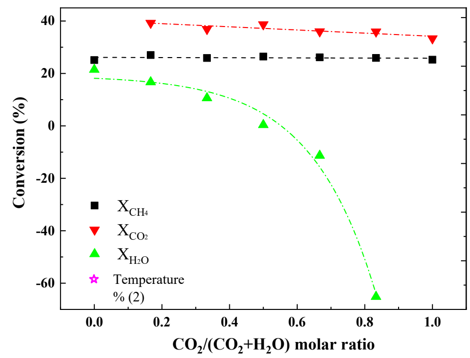

Fig. 4 Effect of $CO_2/(CO_2+H_2O)$ molar ratio on conversions and outlet temperature of GA reactor

Fig. 5 illustrated comparison of bi-reforming of CH_4 for plasma only (WP), conventional catalytic (CC) and plasma catalytic (WPC) cases at an overall molar ration of $CH_4/CO_2/H_2O$ = 3/1/2 and discharge power of 180 W and catalyst bed of 850 ^{0}C. Results clearly shown that CO_2 conversion is higher than H_2O conversion in WP case, but it is lower than H_2O conversion in CC. Therefore, in PCR case, similar conversions of CH_4, CO_2 and H_2O were achieved at around 65±1%. In addition, selectivities of H_2 and CO in CC and PCR cases were close to 100% due to effect of catalysis. The energy efficiency of bi-reforming of CH_4 in PCR was the highest amongst those three cases. Moreover, the ideal syngas with H_2/CO=2 was obtained directly.

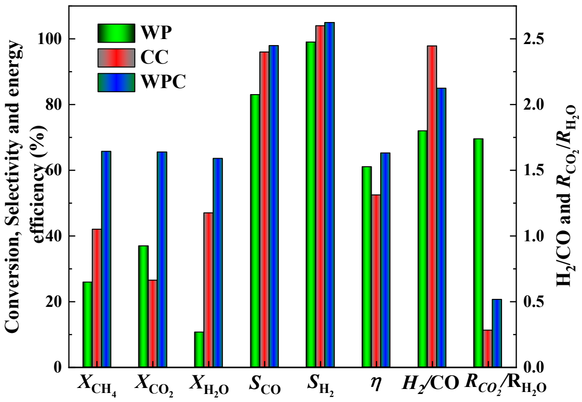

Fig. 5 Comparison of bi-reforming of CH4 for WP, CC and WPC cases

4. Conclusion

Bi-reforming of CH_4 in plasma catalytic reforming (PCR), composed of a GA plasma and $Ni/CeO_2/Al_2O_3$ catalyst, was studied. Electron density, vibrational and rotational temperature in GA plasma was diagnosed as 1.2×10^{14} cm^{-3}, 3900 K and 2500 K, which are typical parameter of warm plasma. Comparison of bi-reforming in WP, CC and WPC cases shown that, CO_2 conversion is higher than H_2O conversion in WP case, but it is lower in CC case. Thus similar conversions of CH_4, CO_2 and H2O are obtained in WPC case at reaction stoichiometric of bi-reforming of CH_4. Consequently, high-quality syngas with an ideal $H_2/CO = 2$ was achieved at an energy efficiency of 65% and near conversions of $65 \pm 1\%$ for CH_4, H_2O and CO_2.

5. Acknowledgements

This project is supported by the National Natural Science Foundation of China (11705019).

6. References

[1] K. Li, J. L. Liu, X. S. Li, X. Zhu, A. M. Zhu, Chem. Eng. J. **288**, 671(2016).
[2] J. L. Liu, K. Li, X. S. Li, X. Zhu, A. M. Zhu, Catal. Today, **256**, 96 (2015).
[3] K. Li, J. L. Liu, X. S. Li, H. Y. Lian, X. Zhu, A. Bogaerts, A. M. Zhu, Chem. Eng. J. **353**, 297 (2018).