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Microwave Plasma Dry Reforming of Methane at High CO_2/CH_4 Feed Ratio

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***Abstract*—**Dry reforming of methane that converts two greenhouses gases (CH_4 and CO_2) to synthesis gas (a mixture of H_2 and CO) was studied in a commercial bench scale microwave (MW) plasma reactor system at atmospheric pressure. The CO_2, CH_4 and N_2 conversions; H_2, CO selectivities and yields, and syngas ratio (H_2/CO) were investigated in a wide range of total feed flow rate (0.45 – 2.1 L/min), MW power (700 – 1200 watt) and CO_2/CH_4 molar ratio (2 – 5). At the feed flow rates of CH_4, CO_2 and N_2 of 0.2, 0.4 and 1.5 L/min respectively, and the MWs input power of 700 W, the highest conversions of CH_4 and CO_2, selectivity and yield of H_2, CO and H_2/CO ratio of 79.35%, 44.82%, 50.12, 58.42, 39.77%, 32.89%, and 0.86, respectively, were achieved. The results of this work show that the product ratio increases slightly with the increasing total feed flow rate, but it decreases significantly with the increasing MW power and feeds CO_2/CH_4 ratio.

***Keywords*—**Atmospheric pressure, methane dry reforming, microwave plasma, synthesis gas production.

I. INTRODUCTION

CURRENTLY, the demand for the development of alternative, clean energy and the reduction of greenhouse gas emissions (CO_2 and CH_4) are becoming urgent to reduce the risk of global warming and climate change. It is therefore necessary to find modern and cost-effective technologies to convert these undesirable gases to valuable products such as synthesis gas [1]. Synthesis gas (syngas) is an important intermediate for the production of synthetic fuels and value-added chemicals through Fischer-Tropsch Synthesis (FTS) [2]. There are different methane reforming processes used to produce syngas as summarised below [3]-[5]:

Steam Reforming of Methane (SRM):

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1}$$

Dry Reforming of Methane (DRM):

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{2}$$

Partial Oxidation of Methane (POM):

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \tag{3}$$

SRM produces a syngas with the high ratio of H_2/CO. However, POM has attracted more interest than SRM, due to its mild exothermicity and a perfect H_2/CO ratio of 2, and a desirable ratio for Fischer-Tropsch (F–T) synthesis. DRM is environmentally favourable and promising way to produce syngas from CO_2 and CH_4 [6], [7]. Dry reforming of methane yields a lower syngas ratio (H_2/CO=1), which is suitable for the synthesis of oxygenated chemicals, hydrocarbons and liquid fuels from (F-T) process [7].

Plasma is considered to be the fourth state of matter, consisting of the highly reactive species such as electrons, ions, radicals and neutral particles [8]. Two main methods are used to convert chemical to plasma state and they are non-thermal (cold) such as dielectric barrier discharge (DBD), corona discharge (CD), atmospheric pressure glow discharge (APGD), gliding arc discharge (GAD), MW discharge (MWD) and thermal (hot) plasma discharge such as direct current heating [9]. The non-thermal plasma discharge processes offer some important advantages as they are cheap and easy to build at any scale for research and production [10].

In order to improve the product H_2/CO ratio in plasma DRM process, the reducing of feed ratio CO_2/CH_4 was studied [11]-[13]. Unfortunately, carbon formation during the reaction at the feed ratio ≤ 2 leads to an instability of the plasma. As a consequence, the study of the plasma DRM is very complicated and has some unavoidable errors.

In this paper, the effects of input parameters (the total feed gas flow rate, the microwave power, the ratio of CO_2/CH_4) on the performance of processes such as conversions of CH_4, CO_2 and N_2, the product selectivities and yields of H_2 and CO, and H_2/CO ratio, respectively were investigated under microwave plasma at atmospheric pressure. The results could be important information for closing the knowledge gap of plasma stability, plasma condition and side reactions in complex microwave plasma DRM reaction zone.

II. EXPERIMENTAL

The schematic diagram of the experimental set-up is shown in Fig. 1; MW plasma system fundamentally consists of gas cylinders, mass flow controllers, gas mixer, feed gas system, plasma reactor, MW generator, and gas chromatographic (GC-MSD and GC-TCD) analysis system. A commercial MW reactor system (Alter, SM 1150T, Canada) was used in this

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study. The three gases CH_4 (99.99%), CO_2 (99.99%) and N_2 (99.99%) were controlled by a mass flow controller and sent into the gas mixer prior entering the plasma zone. All experiments were performed at atmospheric pressure. The quartz reactor has a size of 1.68 mm wall thickness, 25.5 mm outer diameter and length of 126 mm. The feed and product gas samples were collected and analyzed by the GC/MSD. Each measurement was repeated three times for the data accuracy improvement purpose. The experimental conditions are presented in Table I. The calculations of H_2/CO ratio are presented by:

$$CH_4\ \%\ Conversion = \frac{\text{moles of CH4 converted}}{\text{moles of CH4 introduced}} \times 100 \quad (4)$$

$$CO_2\ \%\ Conversion = \frac{\text{moles of CO2 converted}}{\text{moles of CO2 introduced}} \times 100 \quad (5)$$

$$H_2\ \%\ Selectivity = \frac{\text{moles of H2 produced}}{2 \times \text{moles of CH4 converted}} \times 100 \quad (6)$$

$$CO\ \%\ Selectivity = \frac{\text{moles of CO produced}}{\text{[moles of CH4 +moles of CO2] converted}} \times 100 \quad (7)$$

$$H_2\ \%\ Yield = \frac{\text{moles of H2 produced}}{2 \times \text{ moles of CH4 introduced}} \times 100 \quad (8)$$

$$CO\ \%\ Yield = \frac{\text{moles of CO produced}}{\text{[moles of CH4 + moles of CO2]introduced}} \times 100 \quad (9)$$

$$\frac{H_2}{CO}\ Ratio = \frac{\text{moles of H2 produced}}{\text{mole of CO produced}} \quad (10)$$

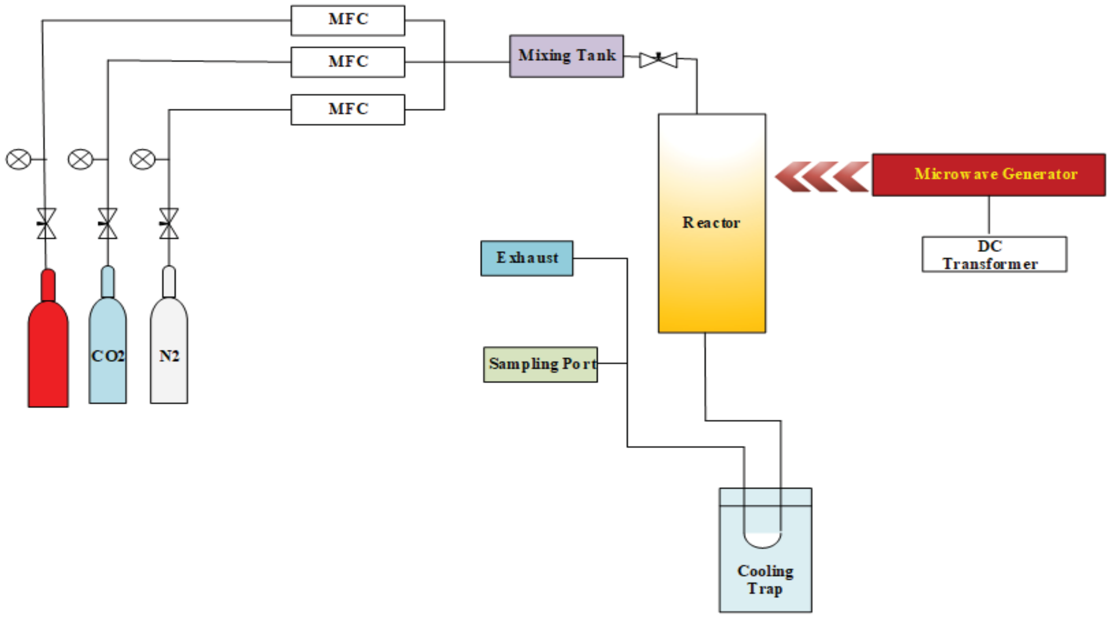

Fig. 1 Schematics Diagram of the experimental process

TABLE I
EXPERIMENTAL CONDITIONS FOR DRM

Experimental Approach	Flow Rate [Lmin^{-1}]			Total feed flow Rate [L min^{-1}]	CO_2/CH_4 Ratio	MW Power [W]
	CO_2	CH_4	N_2			
Effect of Total Flow Rate	0.1	0.05	0.3	**0.45**	2/1	700
	0.15	0.075	0.5	**0.725**		
	0.2	0.1	0.7	**1**		
	0.25	0.125	0.9	**1.275**		
	0.3	0.15	1.1	**1.55**		
	0.35	0.175	1.3	**1.825**		
	0.4	0.2	1.5	**2.1**		
Effect of MW Power	0.4	0.2	1.5	2.1	2/1	**700**
						800
						900
						1000
						1100
						1200
Effect of CO_2/CH_4 Ratio	0.4	0.2	1.5	2.1	**2/1**	700
	0.5			2.2	**2.5/1**	
	0.6			2.3	**3/1**	
	0.7			2.4	**3.5/1**	
	0.8			2.5	**4/1**	
	0.9			2.6	**4.5/1**	
	1			2.7	**5/1**	

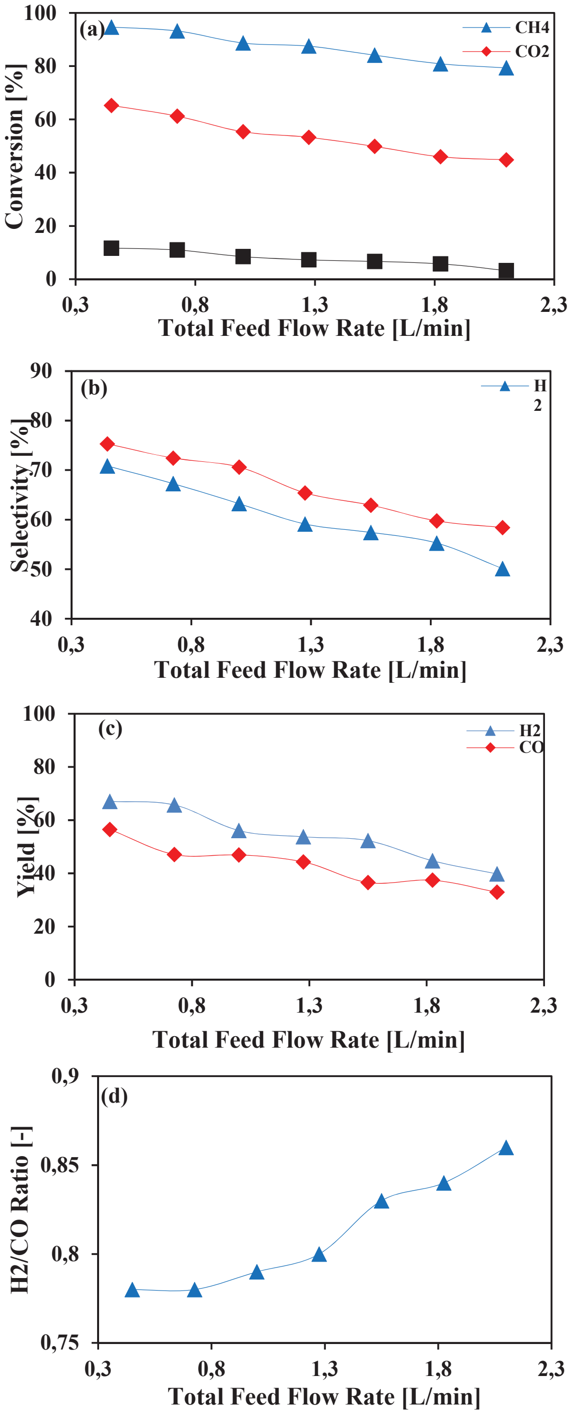

Fig. 2 Effect of Total Gas Feed Flow Rate on the Performance MW Plasma Dry Reforming Reaction; (a) CH_4, CO_2 and N_2 Conversions; (b) Selectivity of H_2 and CO; (c) Yield of H_2 and CO; and (d) H_2/CO Ratio (CO_2/CH_4: 2/1; input MW Power: 700 W)

III. RESULTS AND DISCUSSIONS

A. Effect of Total Feed Flow Rate

The influence of the feed gas mixture flow rates on the conversion of CH_4, CO_2 and N_2, selectivities and yields of H_2 and CO, and H_2/CO ratio under MW plasma discharge were determined at constant molar ratio CH_4/CO_2 of 2/1 and the input MW power of 700 W at atmospheric pressure, as shown in Figs. 2 (a)-(d). It can be seen from It can be seen from Figs. 2 (a)-(c) that the conversions of CH_4, CO_2 and N_2, selectivities and yields of H_2 and CO slightly decreased with increasing total flow rates while, the H_2/CO ratio reveal opposite trends and increased slightly with increasing the feed flow rates, as shown in Fig. 2 (d). The CO_2 and CH_4 are very stable species, so that they need to absorb enough energy to form plasma. As a result, the shorter MW absorption time the less CO_2 and CH_4 reacted [14].

B. Effect of MW Power

The input power is one of the most important factors influencing the reaction were used for this experiment. The input microwave power was used as a function of the conversions of CH_4, CO_2 and N_2; the selectivity and yield of H_2, CO, and the H_2/CO ratio under experimental conditions such as the CO_2/CH_4 molar ratio of 2/1, and the CH_4, CO_2, and N_2 flow rates of 0.2, 0.4 and 1.5 L/min respectively, as shown in Figures 3 (a)-(d). Experiments were performed in wide range of input power from 700 to 1200 W to get better understanding of the effect of input power on the conversions of CH_4, CO_2 and N_2, the selectivities and yields of H_2, CO and the molar ratio of H_2/CO.

The CH_4, CO_2 and N_2 conversions, the CO selectivity and yield increased, while the selectivity and yield of H_2 and the ratio of H_2/CO decreased with increasing the input power, as shown in Figs. 3 (a)-(d). The increase of input MW power could provide more energy to dissociate the CH_4 and CO_2 molecules and then lead to cause cracking of molecules deeply of CH_4 and CO_2. At high MW power a side reaction, which consumes H_2 ($H_2 + CO_2 \rightarrow H_2O + CO$), occurs and provides enough energy to activate CO_2 to form CO. As a consequence, the product ratio H_2/CO decreases with the increasing MW power [15].

C. Effect of CO_2/CH_4 Ratio

For better understanding of the feed composition on the reaction, test series with varying the molar ratio of carbon dioxide to methane from 2/1 to 5/1 in the feed gas at MW power of 700 W were performed. The conversions to CH_4, N_2 and selectivity to CO escalated when increasing CO_2/CH_4 ratio, as shown in Figs. 4 (a) and (b). Conversely, the increase of CO_2/CH_4 ratio leads to decreasing the conversion of CO_2, which leads to the selectivity of H_2, the yields of H_2, CO and H_2/CO ratio. The induction of high amount of CO_2 in the reactor resulted in larger amount of carbon atoms, which are cracked by electron collision. These radicals are then reacts with oxygen atoms to form carbon mono oxide ($C + O \rightarrow CO$) while the hydrogen is low because of the formation of water as a consequence of the reaction of hydrogen atoms with oxygen atoms ($H_2 + O \rightarrow H_2O$). So, the selectivity and yield of H_2, CO and the H_2/CO ratio significantly decreased when the CO_2 content in the gas mixture increased, as shown in Figs. 4 (a)-(d) [16].

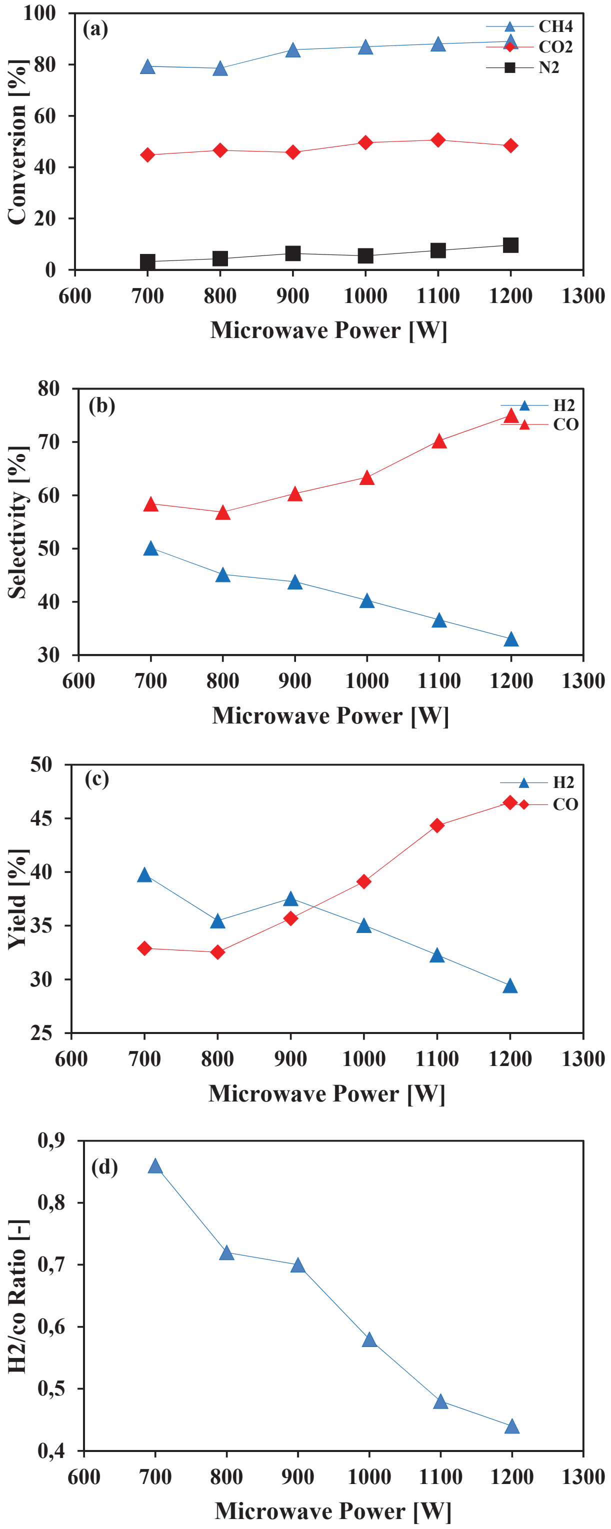

Fig. 3 Effect of Input MW Power on the Performance MW Plasma Dry Reforming Reaction; (a) CH_4, CO_2 and N_2 Conversions; (b) Selectivity of H_2 and CO; (c) Yield of H_2 and CO; and and H_2/CO Ratio (CO_2/CH_4: 2/1; the feed gas rate at 2.1 L min^{-1})

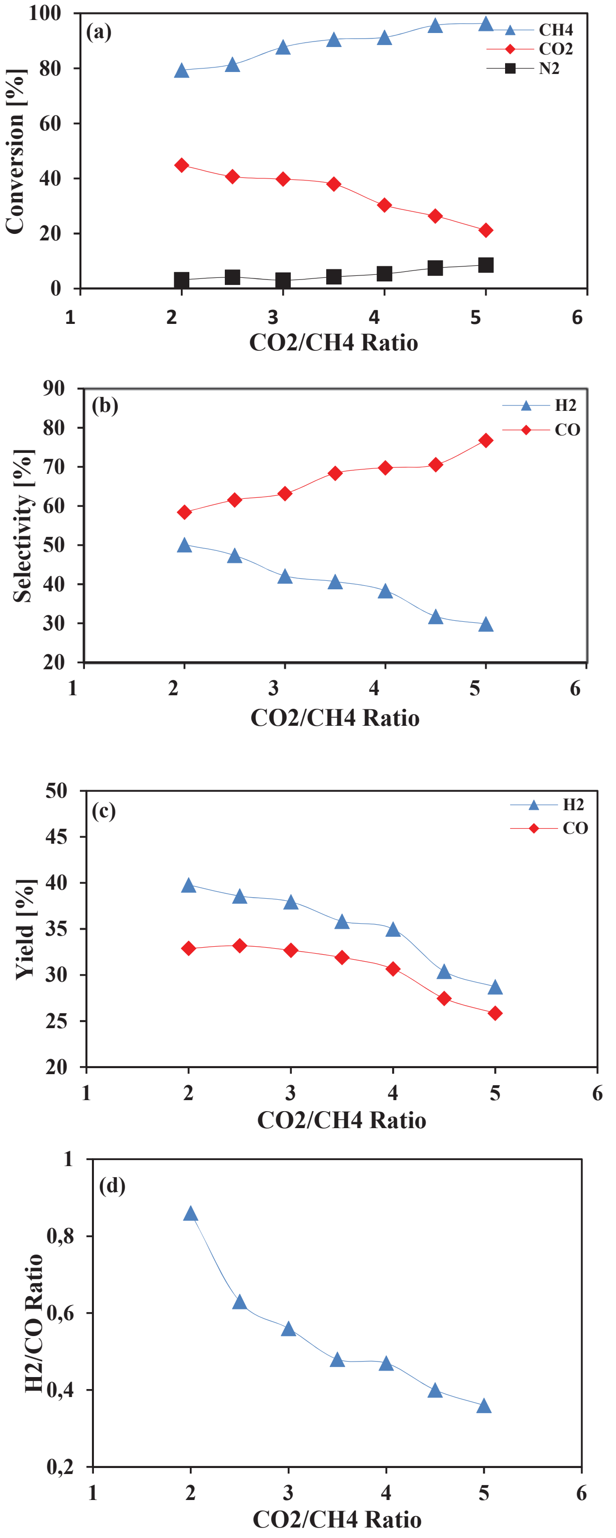

Fig. 4 Effect of CO_2/CH_4 Ratio on the Performance MW Plasma Dry Reforming Reaction; (a) CH_4, CO_2 and N_2 Conversions; (b) Selectivities of H_2 and CO; (b) Yield of H2 and CO; and H_2/CO Ratio (input MW power: 700 W)

IV. CONCLUSIONS

In this work, nitrogen-plasma dry methane reforming was investigated for MW reactor at atmospheric pressure. The effects of different reaction conditions such as total feed flow rate, MW power and CO_2/CH_4 molar ratio on the conversions of CH_4, CO_2 and N_2, selectivities and yields of H_2, CO, and H_2/CO ratio were demonstrated. The total reactant flow rate slightly affects the conversions of CH_4, CO_2 and N_2, the selectivities and yields of H_2 and CO. Meanwhile, the H_2/CO ratio was sharply increased with increasing the total feed flow rate from 0.45 to 2.1 L/min at 700 W and CO_2/CH_4 of 2/1. The study also found that the MW power significantly affects the CH_4, CO_2 and N_2 conversions, the selectivity and yield of CO. On the other hand, the MW has a negative effect on the H_2, CO selectivity and yield, and the H_2/CO ratio. The CO_2/CH_4 molar ratio increased from 2/1 to 5/1 at 700 W, the conversion of CH_4, N_2 and the selectivity of CO increased rapidly, while the conversion of CO_2, the selectivity of H_2, the yield of H_2 and CO, and the ratio of H_2/CO exhibited an opposite behaviour.

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