Syngas formation by dry and steam reforming of methane using microwave plasma technology

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Abstract. The combined dry and steam reforming of methane at atmospheric pressure was experimentally studied by using microwave plasma technology. The effect of the process parameters such as total feed gas flow rate, steam concentration and input microwave power on the synthesis gas H₂/CO ratio was investigated using a commercial microwave reactor system. In order to minimise the carbon formation and plasma instability, the concentration of methane and carbon dioxide in nitrogen plasma were kept at a low level in this study. The long-term test results show that at the flow rate of 0.2 L min⁻¹, 0.4 L min⁻¹ and 1.5 L min⁻¹ for CH₄, CO₂ and N₂ respectively, the carbon formation was not detectable at the input power of 700 W. This reaction condition offers an opportunity to study the effect of adding water to the feed on the syngas ratio H₂/CO. The test results show that a higher CH₄ conversion (82.74%), H₂ selectivity (98.79%) and yield (81.73%) were achieved compared with those of the dry reforming at the same operating conditions. With the steam addition, the desired H₂/CO ratio for the Fischer-Tropsch synthesis process can be reached.

1. Introduction
Nowadays, the increasing energy demand of the growing population has led to the rapid consumption of fossil fuels, inevitably releasing carbon dioxide (CO₂) which is a prime contributor to global warming and climate change. For this reason, significant efforts have been devoted to developing innovative and cost-effective technologies to produce synthesis gas (syngas) from CO₂ [1]. Syngas, a mixture of hydrogen (H₂) and carbon monoxide (CO), is a versatile intermediate to the synthesis of a variety of valuable chemical feedstock and liquid fuels such as ammonia, methanol, ethanol, acetic acid, methyl format, dimethyl ether, synthetic gasoline and diesel via Fischer-Tropsch process [2-9]. Syngas can be produced from a variety of primary feedstock such as coal, natural gas (NG) and biomass. Among them, NG is the cheapest and cleanest source [10]. Many reforming technologies can be used to produce syngas including steam reforming, dry reforming (CO₂ reforming) and partial oxidation [11-13]:

Steam Reforming of Methane (SRM)

\[ \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2 \quad (1) \]
\[ \Delta H = +206 \text{ k } /\text{m} \]

Dry Reforming of Methane (DRM)
\[
C_{4} + C_{2} \rightleftharpoons 2C + 2H_{2} \\
\Delta H = +247 \text{ kJ/mol} \tag{2}
\]

**Partial Oxidation of Methane (POM)**

\[
C_{4} + \frac{1}{2}O_{2} \rightleftharpoons C + 2H_{2} \tag{3}
\]

\[
\Delta H = -36 \text{ kJ/mol}
\]

SRM is the most important process for syngas production at large scale, because of its stability. The drawbacks of this highly endothermic reaction are the high energy consumption and syngas ratio \(H_{2}/CO\), which is not suitable for the Fischer-Tropsch synthesis process (F-T process). POM is an exothermic reaction (Reaction 3), which produces the synthesis gas at the desired syngas ratio of 2 for the F-T process. Unfortunately, during the reaction carbon is developed and covers the catalyst surface. This leads to the shortening the catalyst life time. In recent years, DRM (Reaction 2) has become an important technique that produces synthesis gas from two main greenhouse gasses: natural gas (CH\(_4\)) and carbon dioxide (CO) [7, 14]. The reason for this is that it has environmental, economical, technical and industrial advantages [15]. The drawback of DRM is the low syngas ratio \(H_{2}/CO\), which can not be used to feed to the F-T process without \(H_{2}\) addition. From the above reasons, the combined SRM and DRM, abbreviated as CSDRM (Equation 4), also known as bi-reforming of methane, has recently appeared as a promising technique since it is capable of generating a suitable syngas for F-T process by using the greenhouse gasses and water [16, 17].

\[
3\text{CH}_4 + 2\text{H}_2\text{O} + \text{CO}_2 \rightarrow 8\text{H}_2 + 4\text{CO} \\
\Delta H = +712 \text{ kJ/mol} \tag{4}
\]

The CSDRM can produce the synthesis gas with flexible \(H_{2}/CO\) ratios of 2.0 [18-20]. The \(H_{2}/CO\) ratio of the synthesis gas produced via the CSDRM can be controlled by changing the composition of the feed gas (H\(_2\)O, CO\(_2\), and CH\(_4\)) [21, 22].

CSDRM is a complex process, because many side reactions can occur simultaneously as follows:

**Water gas shift (WGS):**

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \\
\Delta H = -41 \text{ kJ/mol} \tag{5}
\]

**Reverse water gas shift (RWGS):**

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \\
\Delta H = +41 \text{ kJ/mol} \tag{6}
\]

**Methane decomposition (Methane Cracking Reaction):**

\[
\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \\
\Delta H = +75 \text{ kJ/mol} \tag{7}
\]

**Disproportionation Reaction (Boudouard Reaction):**

\[
2\text{CO} \rightarrow \text{C} + \text{CO}_2 \\
\Delta H = -172 \text{ kJ/mol} \tag{8}
\]

**Carbon Gasification:**

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \\
\Delta H = -131 \text{ kJ/mol} \tag{9}
\]

Nowadays, plasma technology has been used widely in conversion of CO\(_2\) and CH\(_4\) to produce synthesis gas [23]. A plasma process is divided into two main methods; the first is non-thermal (or cold) plasma discharge including dielectric barrier discharge (DBD), corona discharge (CD),
atmospheric pressure glow discharge (APGD), gliding arc discharge (GAD), microwave discharge (MWD) and spark discharge [24].

The second is thermal plasma including direct current (DC), alternating current (AC) arc torch and radio frequency (RF) [25, 26]. The microwave plasma technology has a number of advantages that will make it useful in the industry at present. The main advantage of microwave technology is that the energy transfer is rapid and uniform heating by irradiation with microwave [27]. Additionally, the use of microwaves offers technical advantages such as smooth operation, electrodeless reactors and high plasma density [28, 29].

In recent days, some research results on methane reforming by carbon dioxide and water by using microwave plasma are reported in the literature [21, 22]. From these studies, it is found that the adding steam into the dry reforming of methane is effective and leads to increasing the conversion of CH₄, selectivity and yield of H₂. Unfortunately, some knowledge gaps about the combination effect of the steam concentration and microwave power on the process performance and product quality have been remained unknown. Therefore, the main aims of the present work will study the combination influence of the process parameters (total feed gas flow rate, steam concentration and input microwave power) on the H₂/CO ratio under microwave irradiation at atmospheric pressure.

2. Experimental Set up
The schematic diagram of the experimental set-up is shown in Figure 1; microwave plasma system fundamentally consists of a gas cylinders, mass flow controllers, gas mixer, feed gas system, steam vapour unit, plasma reactor, microwave generator, and gas chromatographic (GC-MSD and GC-TCD) analysis system. The three feeding gases (CH₄, CO₂, and N₂) were controlled by a mass flow controller (MFC Alicat Scientific, MCS-Series) and sent into the gas mixer. Deionised water was sent into a vaporiser, which works at the set temperature of 300°C, by using a HPLC pump (Shimadzu LC pump). These gases are joined with the steam in a final feed mixer before entering the plasma reactor. To avoid water recondensation before the reactor, the heated pipe line was used. The quartz reactor has a size of 1.68 mm wall thickness, 25.5 mm outer diameter and length of 126 mm, as shown in Fig. 2. However, the more experimental details were presented elsewhere [30].
Figure 1. Schematics Diagram of the experimental Process
3. Results and Discussions

3.1 Microwave Plasma Dry Reforming of Methane

3.1.1 Effect of CO₂/CH₄ molar ratio

The CO₂/CH₄ molar ratio has a significant effect on the conversions of CH₄ and CO₂, the selectivity’s and yields of H₂ and CO and the H₂ to CO molar ratio, as shown in Figure 3(a-d). In our experiments, keeping the CH₄ and N₂ flow rates constant of 0.2 L/min and 1.5 L/min and microwave power of 700 W. The CO₂/CH₄ molar ratio was changed from 2/1 to 5/1. Figure 3(a)-(d) depict the result of the influence of the CO₂/CH₄ ratio on the conversions of CH₄ and CO₂, the selectivity’s and yields of H₂ and CO, and CO and the H₂/CO ratio was investigated by varying the CO₂/CH₄ ratio. As shown in Figure 3(a) and (b), the conversions of CH₄ and the selectivity to CO escalated when increasing CO₂/CH₄ ratio. Conversely, the increase of CO₂/CH₄ ratio leads to decreasing the conversion of CO₂, the selectivity’s and the yields of H₂, CO and H₂/CO ratio, as shown in Figure 3(a)-(d), respectively. The decreased in CO₂ conversion could be explained because the main reaction of CH₄ and CO₂ under microwave plasma at atmospheric pressure was the plasma reforming reaction (see Equation (2)). When CO₂ amount exceeds the reaction stoichiometry of the main reaction, the conversion of CO₂ decreased while the conversion of CH₄ increased [31]. The conversion of CH₄ is higher than that of CO₂ under all testing conditions.

In addition, the induction of high amount of CO₂ in the reactor resulted in larger amount of carbon atoms, which are cracked by electron collision. These radicals are reacted with oxygen atoms to form carbon mono oxide (see Equation 6) while the hydrogen is low because of the formation of water as a consequence of the reaction of hydrogen atoms with oxygen atoms (see Equation 6). So, the selectivity’s and yields of H₂, CO and the H₂/CO ratio significantly decreased when the CO₂ content in the gas mixture increased, as shown in Figure 3(b)-(d), respectively [32].

The conversion of CH₄ was always higher than those of CO₂. That can be attributed to the nature of the gas molecules, where these gases have a different molecular structure with different chemical bonds.
Methane has covalent bonds, and a large amount of energy may be released when they are broken [33].

![Graph](image1)

**Figure 3.** Effect of CO₂/CH₄ Ratio on the Performance Microwave Plasma Dry Reforming Reaction: (a) Conversion of CH₄ and CO₂; (b) Selectivity of H₂ and CO; (C) Yield of H₂ and CO; (d) H₂/CO Ratio (input microwave power at 700 W).

Additionally, the rate of dissociation of methane molecule depends on the initial supplied energy. On the other hand, the rate of thermal dissociation of CO₂ was lower due to its dependence on both temperature and the initial concentrations of CO₂ [34] which adversely affect the conversion of CO₂. N₂ gas is dissociated due to applied microwave energy, so that it is expected the side reaction, which consumes N₂ may occurs. However the results and discussions on N₂ consumption are excluded from this work as they are not the aim of this study. At these parameters, the plasma reaction was stable for more than four hours with the homogeneous plasma flame in the reactor.

### 3.1.2 Effect of total feed flow rate

The effect of the total feed flow rate on the conversions of CH₄ and CO₂, the selectivity’s and yields of H₂ and CO and the H₂/CO ratio are shown in Figure 4(a)-(d), respectively. Experiments were conducted with a wide range of the flow rates of carbon dioxide (0.1-0.4 L min⁻¹) methane (0.05-0.2 L min⁻¹) and nitrogen (0.3-1.5 L min⁻¹). The molar ratio of CO₂/CH₄ of 2/1 and the input power of 700 W were kept constant for all experiments. As seen from the Figure 4(a)-(c), the conversions of CH₄ and CO₂, the selectivity’s and yields of H₂, CO and the H₂/CO ratio slightly decreased with increasing total flow rates. This is because of the reduction in conversion of CH₄ and CO₂ could be related to the residence time of the gases in the microwave discharge zone, and it is reduced with the increasing of gas feed flow rate and led to the shorter treatment time [3].
3.1.3 Effect of input microwave power

It is well known, the input power is an important factor, which affects the dry plasma reforming of methane as it supply the requested energy for plasma formation. In other words, the input power will influence the density of the active species for the reaction. The conversions of CH$_4$ and CO$_2$, the selectivity’s and yields of H$_2$ and CO, and CO and the H$_2$/CO ratio as a function of input microwave power under 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$^{-1}$ respectively, as shown in Figure 5(a)-(d), respectively. 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$_4$ and CO$_2$, the selectivity’s and yields of H$_2$ and CO, and the molar ratio of H$_2$/CO. Figure 5(a)-(c) exhibit the CH$_4$, and CO$_2$ 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 (Figure 5(b)-(d)). The increase of input microwave power could provide more energy to dissociate the CH$_4$ and CO$_2$ molecules and then leads to cracking of molecules deeply of CH$_4$ and CO$_2$ [35]. On the other hand, at high microwave power a side reaction, which consumes H$_2$ (see Equation 6), 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 microwave power [36].
3.2 Microwave Plasma Steam Combined with Dry Reforming of Methane

3.2.1 Steam Concentration

To understand the reaction pathway of CSDRM, the steam concentration was varied at a fixed feed flow rate of CH₄, CO₂ of 0.008, 0.016 mole min⁻¹, CO₂/CH₄ ratio of 2/1 and input microwave power of 700 W. Figure 6(a)-(d) show the effects of steam concentration on the CH₄ and CO₂ conversions, H₂ and CO the selectivity’s and yields and the H₂/CO ratio. As shown in Figure 6(a)-(d), CH₄ conversions, selectivity and yield of H₂ and H₂/CO mole ratio increased from 79.35%, 50.12%, 39.77% and 0.86 to 82.74%, 98.79%, 81.73% and 5.23 respectively, whereas CO₂ conversion and CO selectivity and yield slightly decreased from 44.82%, 58.42% and 32.89% to 19.23%, 18.87% and 9.04% respectively with increasing the steam concentration. This is because the steam has more reductive and oxidative radicals (H, OH, and O) in the CSDRM process, and these radicals lead to increasing CH₄ conversion, H₂ and CO selectivity, H₂ and CO yield and H₂/CO ratio [37].
Figure 6. Effect of Steam Concentration on the Performance Microwave Plasma Dry Reforming Reaction; (a) Conversion of CH$_4$ and CO$_2$; (b) Selectivity of H$_2$ and CO; (C) Yield of H$_2$ and CO; (d) H$_2$/CO Ratio; (feed flow rate of CH$_4$, CO$_2$ at 0.008, 0.016, 0.062 mole min$^{-1}$, CO$_2$/CH$_4$ ratio at 2/1 and input microwave power at 700 W).

3.2.2 Effect total feed flow rate

The steam additions have a noteworthy effect on the conversions of CH$_4$ and CO$_2$, the selectivity’s and yields of H$_2$ and CO and the H$_2$/CO ratio are shown in Figure 7(a)-(d), respectively. The total feed gas flow rate of H$_2$O, CO$_2$, CH$_4$ and N$_2$ ranged from 0.02 to 0.15 mole min$^{-1}$, as keeping constant the input power of 700 W. As is expected, CH$_4$ conversion, the product selectivity and the yields of H$_2$ and the H$_2$/CO ratio are enhanced with increasing the total feed flow rate, pointing to the fact that combined reforming by H$_2$O and CO$_2$ is stronger than dry reforming (see Figure 7(a)-(d)). This is because the steam molecules could dissociated into OH and H radicals, reacting with CH$_4$ and resulting in the lower probability of CH$_4$ recombination due to the production of CH$_3$ and other by products [38, 39]. The CH$_4$ reacted with H$_2$O instead of CO$_2$ with increasing amount of steam in the feed stream due to the more stable nature of CO$_2$. On the contrary, the increase of steam content caused a considerable decrease of the conversion of CO$_2$, CO selectivity, as shown in Figure 7(a)-(c). Although higher steam amounts resulted in the more CH$_4$ conversion, H$_2$ selectivity, H$_2$ yield and the H$_2$/CO ratio, increasing steam content did not favour CO$_2$, selectivity and yield of CO due to the fixed CO$_2$/CH$_4$ molar ratio in the feed. The conversions of CO$_2$ and H$_2$O were dampened as a result of the RWGS reaction (see Equation (6)).
Figure 7. Effect of Total Gas Feed Flow Rate with Water on the Performance Microwave Plasma Dry Reforming Reaction; (a) Conversion of CH$_4$ and CO$_2$; (b) Selectivity of H$_2$ and CO; (C) Yield of H$_2$ and CO; (d) H$_2$/CO Ratio; (input microwave Power at 700W).

3.2.3 Effect of input microwave power

The effect of microwave power on the conversions of CH$_4$ and CO$_2$, the selectivity’s and yields of H$_2$ and CO, and CO and the H$_2$/CO ratio, as shown in Figure 8(a)-(d), respectively. The input microwave power changed from 700 to 1200 W. The CO$_2$/CH$_4$ molar ratio was 2/1, and the CH$_4$, CO$_2$ and steam flow rate were 0.008, 0.016, and 0.065 mole min$^{-1}$, respectively. Figure 8(a)-(c) depict the conversions of CH$_4$ and CO$_2$, the selectivity of CO and yields of H$_2$ and CO increased, while the ratio of H$_2$/CO decreased with increasing the input power (Figure 8(d)). The reason for this has been explained previously. The selectivity of H$_2$ did not change with increase the microwave power (Figure 8(b) and (c)). In this study, we observed the amount of water, and the amount of solid carbon powder out the quartz tube low compared with the CO$_2$ reforming.

Figure 8. Effect of Input MW Power with Water on the Performance MW Plasma Dry Reforming Reaction; (a) Conversion of CH$_4$ and CO$_2$; (b) Selectivities of H$_2$ and CO; (C) Yield of H$_2$ and CO; (d) H$_2$/CO Ratio (total feed gas rate at 0.15 mole min$^{-1}$).
The combined effects of microwave plasma methane dry reforming and methane steam with dry reforming were compared and displayed in Figure 9(a)-(d). The conversions of CH₄ and CO₂ over dry reforming of methane were about 79.35%, and 44.82% respectively, the selectivity’s and yields of H₂ and CO₂, and the H₂/CO ratio were 50.12%, 58.42%, 39.77%, 32.89% and 0.86, respectively. When the steam adding with dry reforming of methane, the conversion of CH₄, selectivity and yield of H₂ and synthesis ratio were improved apparently, as shown in Figure 9(a)-(c), respectively. The conversions of CH₄ and CO₂ were 82.74% and 19.23% respectively. The selectivity’s, yields to H₂ and CO and the H₂/CO ratio were 98.79%, 18.87%, 81.73%, 9.04% and 5.23, respectively. The conversions of CH₄ was 82.74% under combined steam and dry reforming of methane, which was higher than using the dry reforming of methane. Similar tendency the selectivity and yield of H₂ and H₂/CO ratio were also improved under combined of steam and dry reforming of methane. However, it was observed for conversion of CO₂ decreased with adding the steam. The selectivity of H₂ was 98.79% and that of H₂/CO ratio was 5.23, which was even higher than those obtained in dry reforming of methane.

**Figure 9.** Effect of H₂O on equilibrium (a) CH₄ and CO₂ Conversions; (b) H₂ and CO Selectivities; (c) H₂ and CO Yields and (d) H₂/CO Ratio for combined DR-SR as a function of Microwave Power at 700 W (CO₂/CH₄: 2/1; the total gas feed rate at 2.1 L min⁻¹ and the total feed steam rate at 24.5 L min⁻¹).

### 4. Conclusions

In this paper, the effect of steam adding on the syngas formation has been studied in a microwave plasma reactor at atmospheric pressure for syngas production. Based on the measured results the following conclusions can be made:

1. With H₂O addition, the high conversions of CH₄ and CO₂ were 82.74% and 19.23% of the steam reforming of methane can achieved. At these conversion levels, the selectivity’s of H₂ and CO, the yields of H₂ and CO and H₂/CO ratio were 98.79%, 18.87%, 81.73%, 9.04% and 5.23, respectively.
2. The CH₄ conversion, H₂ and CO selectivity, H₂ and CO yield, and H₂/CO ratio were affected by the H₂O concentration in the feed significantly.
3. The combined SRM and DRM process is very sensitive with the operating conditions such as the input
microwave power and total feed flow rate.

4. The desired syngas ratio H₂/CO for F-T process can be reached by optimising the H₂O concentration in the feed and input microwaves power.

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