PAPER • OPEN ACCESS

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

To cite this article: Nabil Majd Alawi *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **579** 012022

View the article online for updates and enhancements.

IOP ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

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

Nabil Majd Alawi[1,2], Gia Hung Pham[1], Ahmed Barifcani[1], Minh Hoang Nguyen[1] and Shaomin Liu[1]

[1]Department of Chemical Engineering, Curtin University, Perth, Western Australia 6845, Australia
[2]Petroleum Technology Department, University of Technology, Baghdad, Iraq
Corresponding author's e-mail address: n.alawi@postgrad.curtin.edu.au

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 H /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 CH_4, CO_2 and N_2 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 H /CO. The test results show that a higher CH_4 conversion (82.74%), H 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 H_2/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 (CO_2) 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 CO_2 [1]. Syngas, a mixture of hydrogen (H_2) 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 (CO_2 reforming) and partial oxidation [11-13]:

   Steam Reforming of Methane (SRM)

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

$$\Delta H = +206 \ k \ /m$$

   Dry Reforming of Methane (DRM)

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \tag{2}$$
$$\Delta H = +247\ kJ/mol$$

Partial Oxidation of Methane (POM)

$$CH_4 + \tfrac{1}{2}O_2 \rightleftharpoons CO + 2H_2 \tag{3}$$
$$\Delta H = -36\ kJ/mol$$

SRM is the most important process for syngas production at large scale, because of it 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].

$$3CH_4 + 2H_2O + CO_2 \rightarrow 8H_2 + 4CO \tag{4}$$
$$\Delta H = +712\ kJ/mol$$

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_2O, 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):

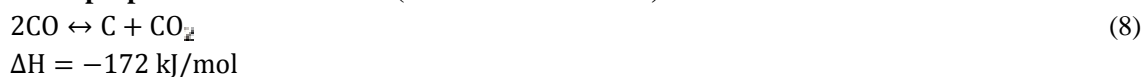$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{5}$$
$$\Delta H = -41\ kJ/mol$$

Reverse water gas shift (RWGS):

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{6}$$
$$\Delta H = +41\ kJ/mol$$

Methane decomposition (Methane Cracking Reaction):

$$CH_4 \leftrightarrow C + 2H_2 \tag{7}$$
$$\Delta H = +75\ kJ/mol$$

Disproportionation Reaction (Boudouard Reaction):

$$2CO \leftrightarrow C + CO_2 \tag{8}$$
$$\Delta H = -172\ kJ/mol$$

Carbon Gasification:

$$C + H_2O \leftrightarrow CO + H_2 \tag{9}$$
$$\Delta H = -131\ kJ/mol$$

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 CH_4, selectivity and yield of H_2. 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 H_2/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 (CH_4, CO_2, and N_2) 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].
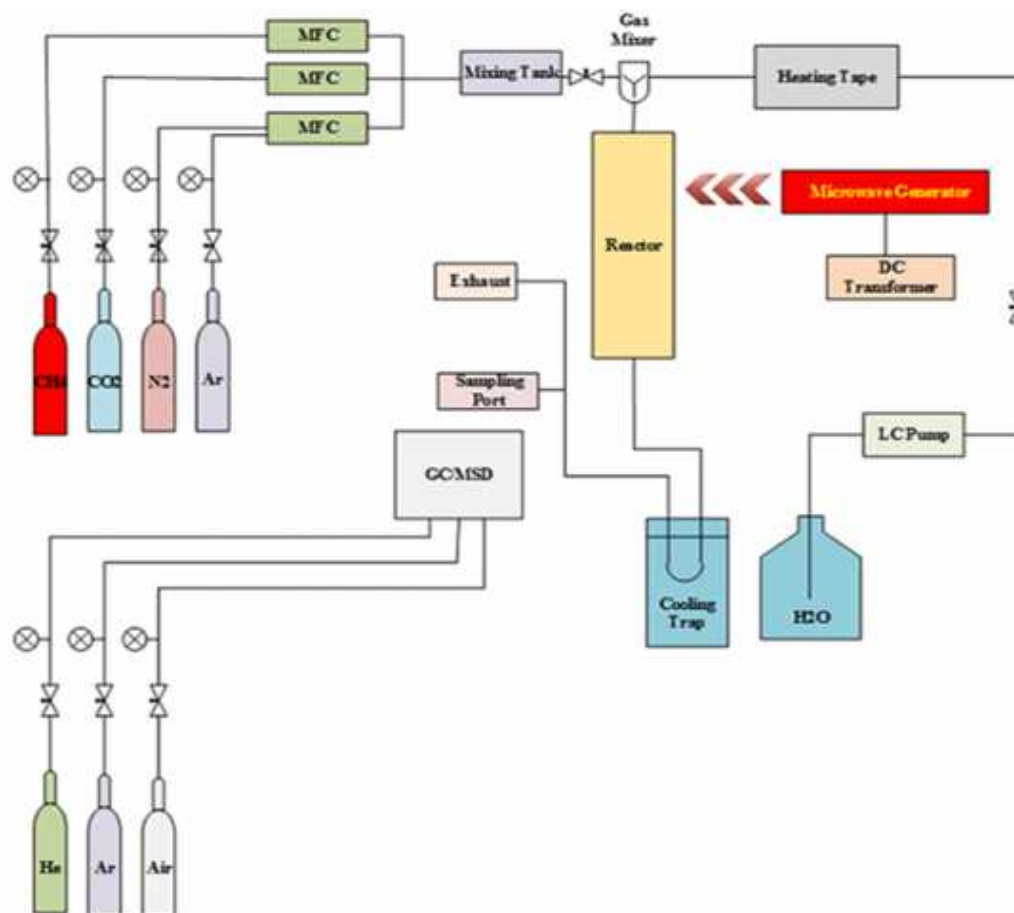
Figure 1. Schematics Diagram of the experimental Process

CH4, CO2 and N2

25.5 mm

1.68 mm

126 mm

Electromagnetic Field

Synthesis Gas
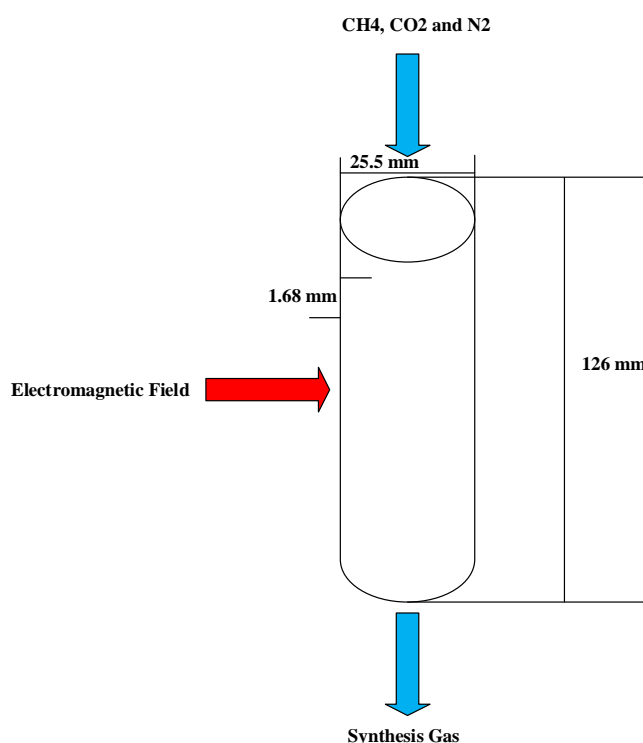
Figure 2. Quartz tube reactor

3. Results and Discussions

3.1 Microwave Plasma Dry Reforming of Methane

3.1.1 Effect of CO_2/CH_4 molar ratio

The CO_2/CH_4 molar ratio has a significant effect on the conversions of CH_4 and CO_2, the selectivity's and yields of H_2 and CO and the H_2 to CO molar ratio, as shown in Figure 3(a-d). In our experiments, keeping the CH_4 and N_2 flow rates constant of 0.2 L/min and 1.5 L/min and microwave power of 700 W. The CO_2/CH_4 molar ratio was changed from 2/1 to 5/1. Figure 3(a)-(d) depict the result of the influence of the CO_2/CH_4 ratio 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 was investigated by varying the CO_2/CH_4 ratio. As shown in Figure 3(a) and (b), the conversions of CH_4 and the selectivity to CO escalated when increasing CO_2/CH_4 ratio. Conversely, the increase of CO_2/CH_4 ratio leads to decreasing the conversion of CO_2, the selectivity's and the yields of H_2, CO and H_2/CO ratio, as shown in Figure 3(a)-(d), respectively. The decreased in CO_2 conversion could be explained because the main reaction of CH_4 and CO_2 under microwave plasma at atmospheric pressure was the plasma reforming reaction (see Equation (2)). When CO_2 amount exceeds the reaction stoichiometry of the main reaction, the conversion of CO_2 decreased while the conversion of CH_4 increased [31]. The conversion of CH_4 is higher than that of CO_2 under all testing conditions.

In addition, 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 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 H_2, CO and the H_2/CO ratio significantly decreased when the CO_2 content in the gas mixture increased, as shown in Figure 3(b)-(d), respectively [32].

The conversion of CH_4 was always higher than those of CO_2. 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].
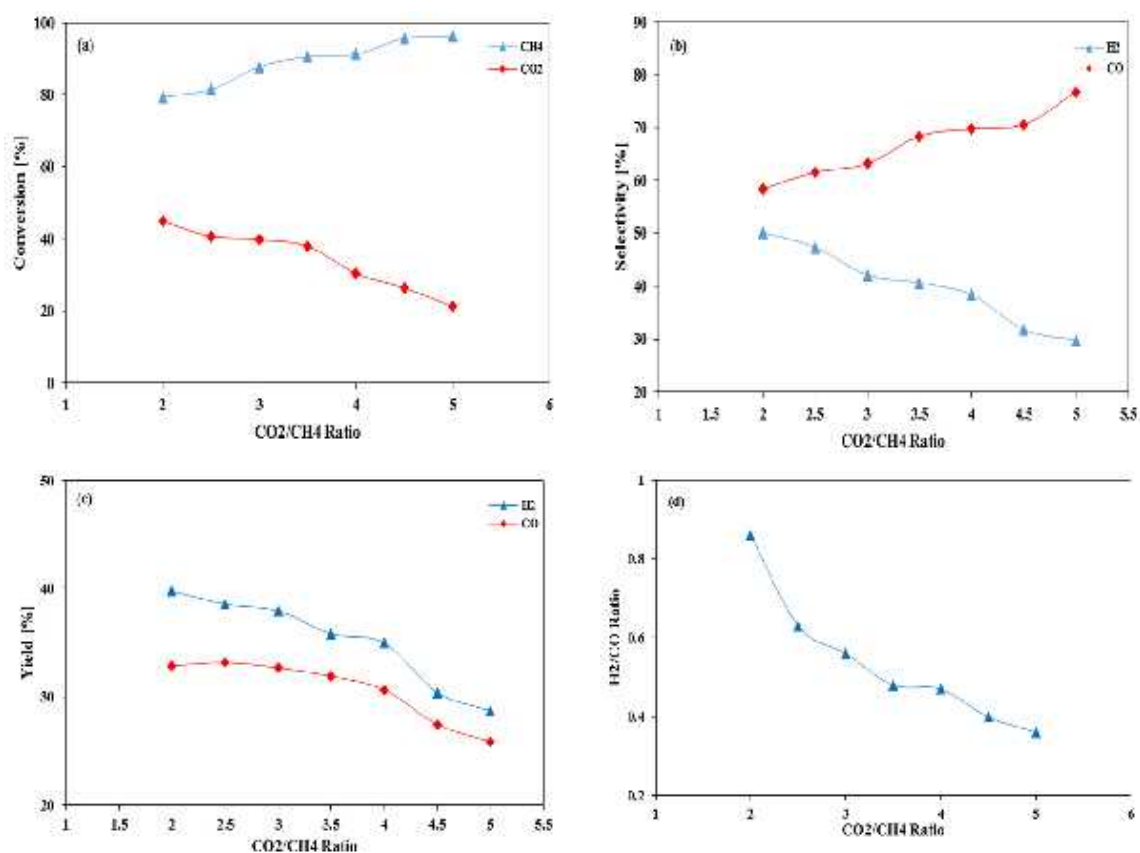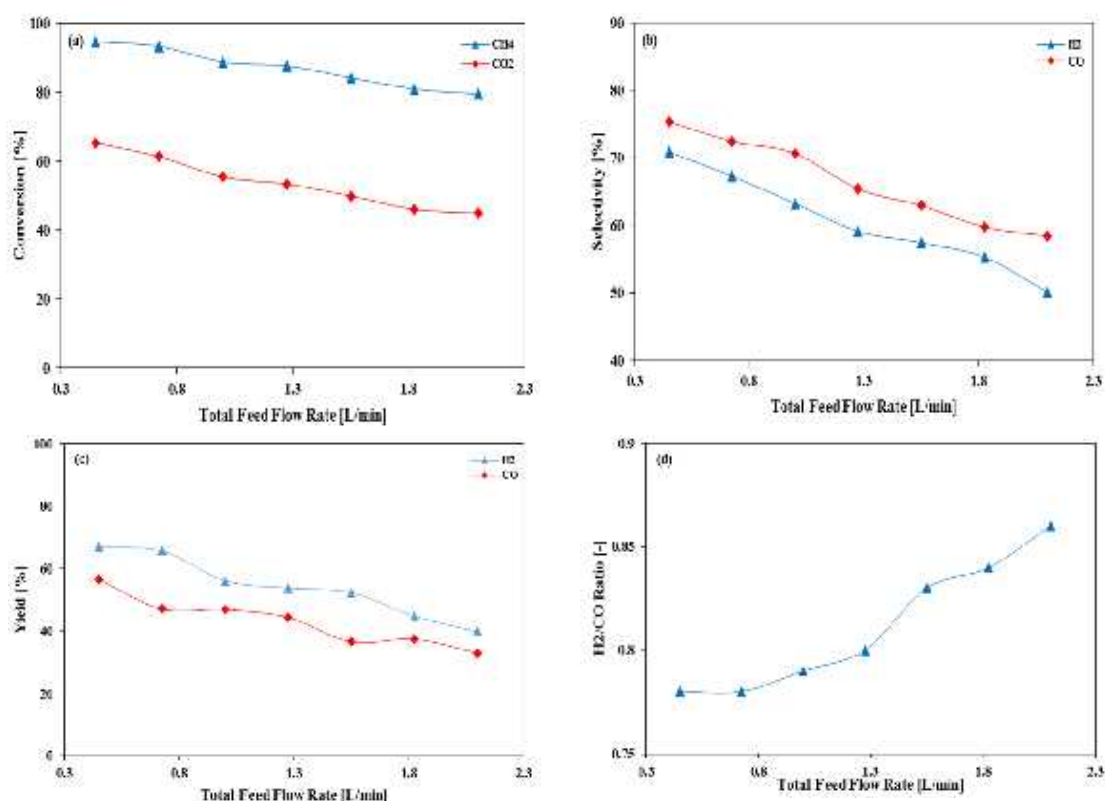

Figure 3. Effect of CO_2/CH_4 Ratio on the Performance Microwave Plasma Dry Reforming Reaction; (a) Conversion of CH_2 and CO_2; (b) Selectivity of H_2 and CO; (C) Yield of H_2 and CO; (d) H_2/CO Ratio (input microwave power at 700 W).

Additionally, the rate of dissociation of methane molecule depends on the initial supplied energy. On the other hand, the rate of thermal dissociation of CO_2 was lower due to its dependence on both temperature and the initial concentrations of CO_2 [34] which adversely affect the conversion of CO_2. N_2 gas is dissociated due to applied microwave energy, so that it is expected the side reaction, which consumes N_2 may occurs. However the results and discussions on N_2 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 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 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 CO_2/CH_4 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 CH_4 and CO_2, the selectivity's and yields of H_2, CO and the H_2/CO ratio slightly decreased with increasing total flow rates. This is because of the reduction in conversion of CH_4 and CO_2 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].
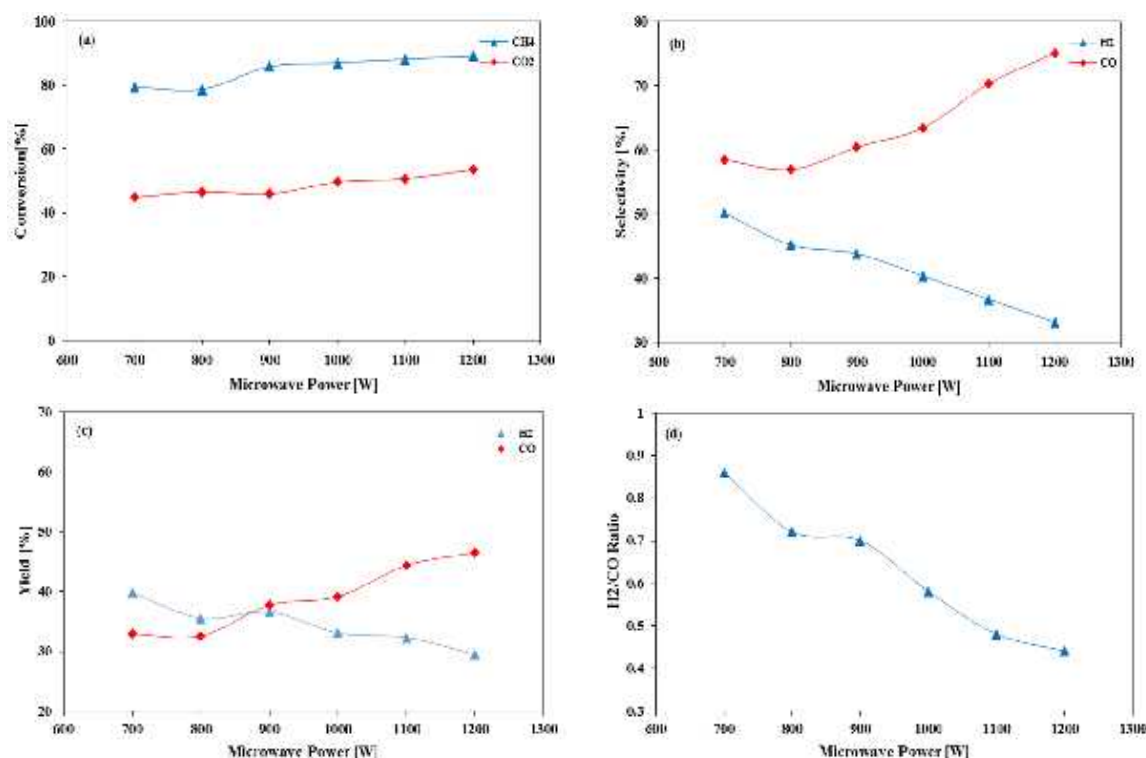
Figure 4. Effect of Total Gas Feed Flow Rate on the Performance Microwave Plasma Dry Reforming Reaction; (a) Conversion of CH_4 and CO_2; (b) Selectivity of H_2 and CO; (C) Yield of H2 and CO; (d) H_2/CO Ratio; (CO_2/CH_4 ratio at 2/1; input microwave power: 700 W).

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, 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].
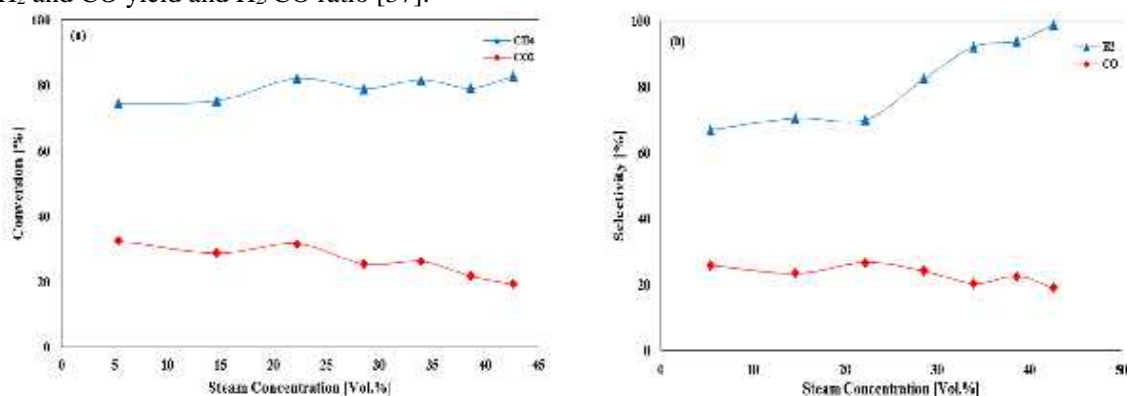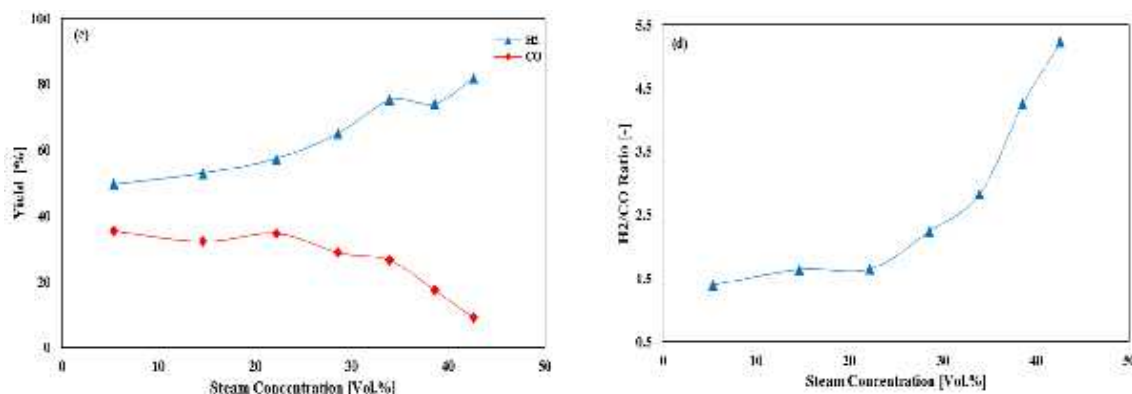
Figure 5. Effect of Input MW Power on the Performance Microwave Plasma Dry Reforming Reaction; (a) Conversion of CH_4 and CO_2; (b) Selectivity of H_2 and CO; (C) Yield of H_2 and CO; (d) H_2/CO Ratio (CO_2/CH_4 ratio at 2/1; the feed gas rate at 2.1 L min^{-1}).

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 CH_4, CO_2 of 0.008, 0.016 mole min^{-1}, CO_2/CH_4 ratio of 2/1 and input microwave power of 700 W. Figure 6(a)-(d) show the effects of steam concentration on the CH_4 and CO_2 conversions, H_2 and CO the selectivity's and yields and the H_2/CO ratio. As shown in Figure 6(a)-(d), CH_4 conversions, selectivity and yield of H_2 and H_2/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 CO_2 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 CH_4 conversion, H_2 and CO selectivity, H_2 and CO yield and H_2/CO ratio [37].
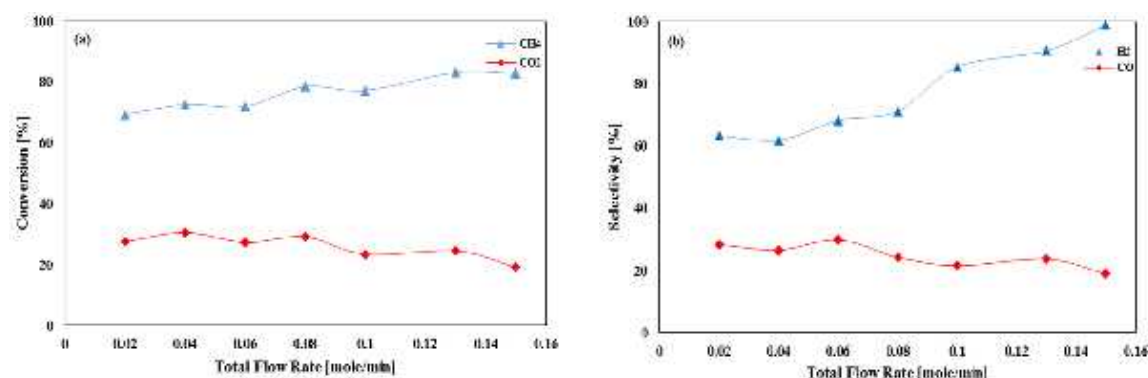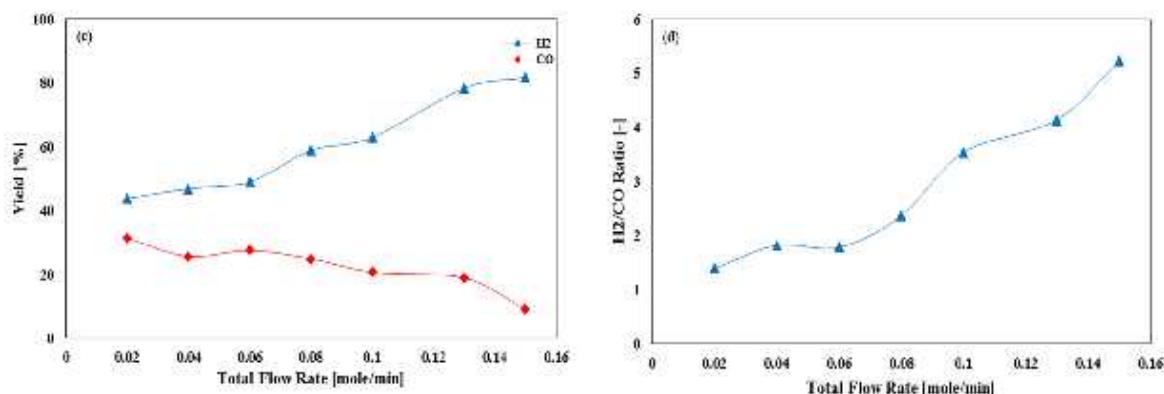
Figure 6. Effect of Steam Concentration on the Performance Microwave Plasma Dry Reforming Reaction; (a) Conversion of CH_4 and CO_2; (b) Selectivity of H_2 and CO; (C) Yield of H2 and CO; (d) H_2/CO Ratio; (feed flow rate of CH_4, CO_2 at 0.008, 0.016, 0.062 mole min^{-1}, CO_2/CH_4 ratio at 2/1 and 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_2O, 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_2O 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_2O 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_2O were dampened as a result of the RWGS reaction (see Equation (6)).
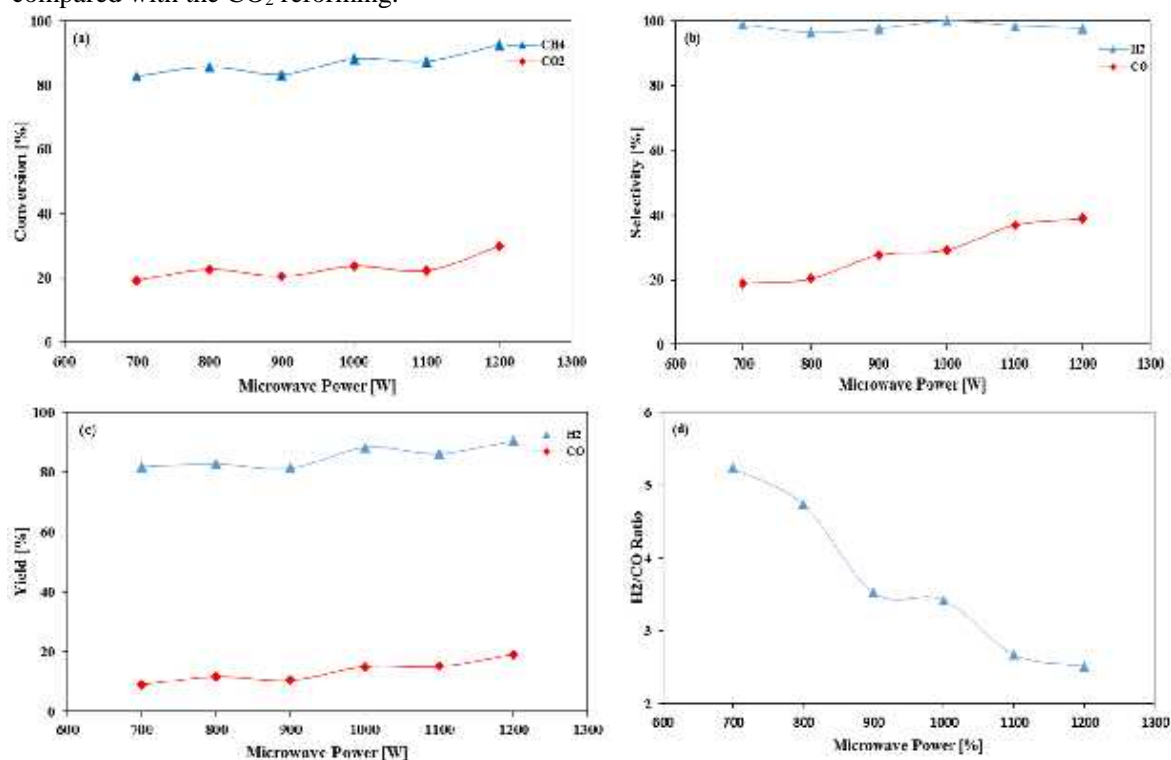
Figure 7. Effect of Total Gas Feed Flow Rate with Water on the Performance Microwave Plasma Dry Reforming Reaction; (a) Conversion of CH_4 and CO_2; (b) Selectivity of H_2 and CO; (C) Yield of H2 and CO; (d) H_2/CO Ratio; (input microwave Power at 700W).

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 H2 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 CH_4 and CO_2 over dry reforming of methane were about 79.35%, and 44.82% respectively, the selectivity's and yields of H_2 and CO, and the H_2/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 CH_4, selectivity and yield of H_2 and synthesis ratio were improved apparently, as shown in Figure 9(a)-(c), respectively. The conversions of CH_4 and CO_2 were 82.74% and 19.23% respectively. The selectivity's, yields to H_2 and CO and the H_2/CO ratio were 98.79%, 18.87%, 81.73%, 9.04% and 5.23, respectively. The conversions of CH_4 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 H_2 and H_2/CO ratio were also improved under combined of steam and dry reforming of methane. However, it was observed for conversion of CO_2 decreased with adding the steam. The selectivity of H_2 was 98.79% and that of H_2/CO ratio was 5.23, which was even higher than those obtained in dry reforming of methane.
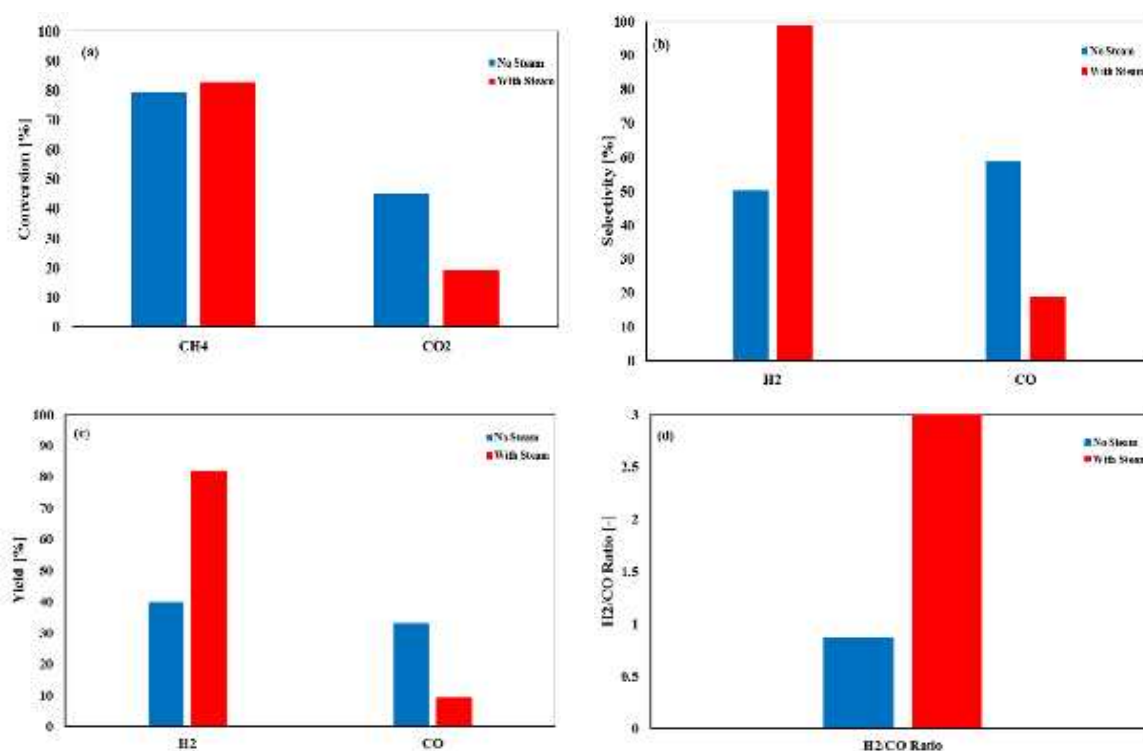
Figure 9. Effect of H_2O on equilibrium (a) CH_4 and CO_2 Conversions; (b) H_2 and CO Selectivities; (c) H_2 and CO Yields and (d) H_2/CO Ratio for combined DR-SR as a function of Microwave Power at 700 W (CO_2/CH_4: 2/1; the total gas feed rate at 2.1 L min⁻¹ and the total feed steam rate at 24.5 L 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 H_2O addition, the high conversions of CH_4 and CO_2 were 82.74% and 19.23% of the steam reforming of methane can achieved. At these conversion levels, the selectivity's of H_2 and CO, the yields of H_2 and CO and H_2/CO ratio were 98.79%, 18.87%, 81.73%, 9.04% and 5.23, respectively.
2. The CH_4 conversion, H_2 and CO selectivity, H_2 and CO yield, and H_2/CO ratio were affected by the H_2O 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 H_2/CO for F-T process can be reached by optimising the H_2O concentration in the feed and input microwaves power.

Acknowledgements

References

[1] X. Tu, J.C. Whitehead, Plasma dry reforming of methane in an atmospheric pressure AC gliding arc discharge: co-generation of syngas and carbon nanomaterials, international journal of hydrogen energy 39(18) (2014) 9658-9669.

[2] J. Ross, A. Van Keulen, M. Hegarty, K. Seshan, The catalytic conversion of natural gas to useful products, Catalysis Today 30(1-3) (1996) 193-199.

[3] D. Pakhare, J. Spivey, A review of dry (CO_2) reforming of methane over noble metal catalysts, Chemical Society Reviews 43(22) (2014) 7813-7837.

[4] M.M. Ghouri, S. Afzal, R. Hussain, J. Blank, D.B. Bukur, N.O. Elbashir, Multi-scale modeling of fixed-bed Fischer Tropsch reactor, Computers & Chemical Engineering 91 (2016) 38-48.

[5] A. Kasht, R. Hussain, M. Ghouri, J. Blank, N.O. Elbashir, Product analysis of supercritical Fischer-Tropsch synthesis: utilizing a unique on-line and off-line gas chromatographs setup in a bench-scale reactor unit, American Journal of Analytical Chemistry 6(08) (2015) 659.

[6] J.R. Rostrup-Nielsen, New aspects of syngas production and use, Catalysis today 63(2) (2000) 159-164.

[7] M. Usman, W.W. Daud, H.F. Abbas, Dry reforming of methane: influence of process parameters—a review, Renewable and Sustainable Energy Reviews 45 (2015) 710-744.

[8] B. Abdullah, N.A.A. Ghani, D.-V.N. Vo, Recent advances in dry reforming of methane over Ni-based catalysts, Journal of Cleaner Production 162 (2017) 170-185.

[9] W. Wang, S. Wang, X. Ma, J. Gong, Recent advances in catalytic hydrogenation of carbon dioxide, Chemical Society Reviews 40(7) (2011) 3703-3727.

[10] P.L. Spath, D.C. Dayton, Preliminary screening-technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas, National Renewable Energy Lab Golden Co, 2003.

[11] J. Pacheco, G. Soria, M. Pacheco, R. Valdivia, F. Ramos, H. Frías, M. Durán, M. Hidalgo, Greenhouse gas treatment and H_2 production, by warm plasma reforming, international journal of hydrogen energy 40(48) (2015) 17165-17171.

[12] S. Rowshanzamir, M. Eikani, Autothermal reforming of methane to synthesis gas: Modeling and simulation, international journal of hydrogen energy 34(3) (2009) 1292-1300.

[13] G. Centi, E.A. Quadrelli, S. Perathoner, Catalysis for CO_2 conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries, Energy & Environmental Science 6(6) (2013) 1711-1731.

[14] J. Hubert, M. Moisan, A. Ricard, A new microwave plasma at atmospheric pressure, Spectrochimica Acta Part B: Atomic Spectroscopy 34(1) (1979) 1-10.

[15] S.T. Oyama, P. Hacarlioglu, Y. Gu, D. Lee, Dry reforming of methane has no future for hydrogen production: comparison with steam reforming at high pressure in standard and membrane reactors, international journal of hydrogen energy 37(13) (2012) 10444-10450.

[16] G.A. Olah, A. Goeppert, M. Czaun, T. Mathew, R.B. May, G.S. Prakash, Single step bi-reforming and oxidative bi-reforming of methane (natural gas) with steam and carbon dioxide to metgas ($CO-2H_2$) for methanol synthesis: self-sufficient effective and exclusive oxygenation of methane to methanol with oxygen, Journal of the American Chemical Society 137(27) (2015) 8720-8729.

[17] M.M. Noureldin, N.O. Elbashir, M.M. El-Halwagi, Optimization and selection of reforming approaches for syngas generation from natural/shale gas, Industrial & Engineering Chemistry Research 53(5) (2013) 1841-1855.

[18] A.N. Pour, M. Mousavi, Combined reforming of methane by carbon dioxide and water: Particle size effect of Ni–Mg nanoparticles, International Journal of Hydrogen Energy 40(38) (2015) 12985-12992.

[19] A.R. Kim, H.Y. Lee, D.H. Lee, B.-W. Kim, C.-H. Chung, D.J. Moon, E.J. Jang, C. Pang, J.W. Bae, Combined Steam and CO2 Reforming of CH4 on LaSrNiO x Mixed Oxides Supported on Al2O3-Modified SiC Support, Energy & Fuels 29(2) (2015) 1055-1065.

[20] V.R. Choudhary, K.C. Mondal, CO2 reforming of methane combined with steam reforming or partial oxidation of methane to syngas over NdCoO3 perovskite-type mixed metal-oxide catalyst, Applied Energy 83(9) (2006) 1024-1032.

[21] D. Czylkowski, B. Hrycak, M. Jasi ski, M. Dors, J. Mizeraczyk, Microwave plasma-based method of hydrogen production via combined steam reforming of methane, Energy 113 (2016) 653-661.

[22] L. Li, H. Wang, X. Jiang, Z. Song, X. Zhao, C. Ma, Microwave-enhanced methane combined reforming by CO 2 and H 2 O into syngas production on biomass-derived char, Fuel 185 (2016) 692-700.

[23] R. Snoeckx, Y. Zeng, X. Tu, A. Bogaerts, Plasma-based dry reforming: improving the conversion and energy efficiency in a dielectric barrier discharge, RSC Advances 5(38) (2015) 29799-29808.

[24] W.-C. Chung, M.-B. Chang, Dry reforming of methane by combined spark discharge with a ferroelectric, Energy Conversion and Management 124 (2016) 305-314.

[25] P. Jamróz, W. Kordylewski, M. Wnukowski, Microwave plasma application in decomposition and steam reforming of model tar compounds, Fuel Processing Technology 169 (2018) 1-14.

[26] M.S. Aw, I.G.O. Crnivec, P. Djinovic, A. Pintar, Strategies to enhance dry reforming of methane: Synthesis of ceria-zirconia/nickelecobalt catalysts by freeze-drying and NO calcination, international journal of hydrogen energy 39(12636) (2014) e12647.

[27] M. Nüchter, B. Ondruschka, W. Bonrath, A. Gum, Microwave assisted synthesis–a critical technology overview, Green chemistry 6(3) (2004) 128-141.

[28] J. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E.G. Calvo, J.M. Bermúdez, Microwave heating processes involving carbon materials, Fuel Processing Technology 91(1) (2010) 1-8.

[29] S. Heijkers, R. Snoeckx, T.s. Kozák, T. Silva, T. Godfroid, N. Britun, R. Snyders, A. Bogaerts, CO2 conversion in a microwave plasma reactor in the presence of N2: elucidating the role of vibrational levels, The Journal of Physical Chemistry C 119(23) (2015) 12815-12828.

[30] N.M. Alawi, A. Barifcani, H.R. Abid, Optimisation of CH4 and CO2 conversion and selectivity of H2 and CO for the dry reforming of methane by a microwave plasma technique using a B ox–B ehnken design, Asia-Pacific Journal of Chemical Engineering (2018) e2254.

[31] A. Serrano-Lotina, L. Daza, Influence of the operating parameters over dry reforming of methane to syngas, International Journal of Hydrogen Energy 39(8) (2014) 4089-4094.

[32] C.-H. Liao, R.-F. Horng, Experimental study of syngas production from methane dry reforming with heat recovery strategy, International Journal of Hydrogen Energy 42(40) (2017) 25213-25224.

[33] J.W. Moore, C.L. Stanitski, Chemistry: The molecular science, Cengage Learning2014.

[34] S. Rayne, Thermal carbon dioxide splitting: A summary of the peer-reviewed scientific literature, (2008).

[35] A. Indarto, J.-W. Choi, H. Lee, H.K. Song, Effect of additive gases on methane conversion using gliding arc discharge, Energy 31(14) (2006) 2986-2995.

[36] A. Aziznia, H.R. Bozorgzadeh, N. Seyed-Matin, M. Baghalha, A. Mohamadalizadeh, Comparison of dry reforming of methane in low temperature hybrid plasma-catalytic corona with thermal catalytic reactor over Ni/ -Al 2 O 3, Journal of Natural Gas Chemistry 21(4) (2012) 466-475.

[37] T. Jiang, Y. Li, C.-j. Liu, G.-h. Xu, B. Eliasson, B. Xue, Plasma methane conversion using dielectric-barrier discharges with zeolite A, Catalysis Today 72(3) (2002) 229-235.

[38] J. Sutherland, M.C. Su, J. Michael, Rate constants for H+ CH4, CH3+ H2, and CH4 dissociation at high temperature, International Journal of Chemical Kinetics 33(11) (2001) 669-684.

[39] A. Bonard, V. Daële, J.-L. Delfau, C. Vovelle, Kinetics of OH Radical Reactions with Methane in the Temperature Range 295– 660 K and with Dimethyl Ether and Methyl-tert-butyl Ether in the Temperature Range 295– 618 K, The Journal of Physical Chemistry A 106(17) (2002) 4384-4389.