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Sustainable energy from biogas reforming in a microwave discharge reactor

N. Tippayawong[a,]*, E. Chaiya[a], P. Thanompongchart[a], P. Khongkrapan[b]

[a]*Department of Mechanical Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai 50200, Thailand*
[b]*School of Renewable Energy, Maejo University, Chiang Mai 50300, Thailand*

Abstract

Biogas is one of the most important renewable energy sources in modern societies. Generated from livestock manure and industrial wastewater, it can provide considerable savings in energy costs and reducing environmental impacts. Thailand is reported to have the potential to produce over one billion m^3 of biogas a year. The biogas is generally utilized for heating, mechanical shaft works, and electricity generation. If pipeline networks or purification and compression facilities are not available, use of biogas is normally limited to only within and around farm areas. Alternatively, biogas may be converted via reforming reactions into synthetic gas. Because of presence of sulphur compounds in biogas, a catalytic reformer may face serious poisoning problem. In this work, non-catalytic, plasma assisted reforming of biogas was carried out at atmospheric pressure and room temperature in an 800 W, laboratory microwave discharge reactor. Effects of CH_4/CO_2 ratio (1, 2.33, 9), feed flow rate (8.33 – 50 cm^3/s), and oxygen addition in terms of CH_4/O_2 ratio (1, 1.5, 2) on reactor performance (yield, selectivity, conversion, H_2/CO and energy consumption) was investigated. It was found that biogas was successfully reformed into synthetic gas by a microwave plasma reactor under room temperature and non-catalytic conditions. For dry reforming of biogas, high H_2 and CO yields were obtained at low energy consumption. Presence of oxygen enabled partial oxidation reforming that produced higher CH_4 conversion, compared to purely dry reforming process. By varying CH_4/CO_2 as well as CH_4/O_2 ratios, synthetic gas with a wide range of H_2/CO ratios can be generated. From the findings, it was suggested that the microwave plasma reactor may be practically used to reform biogas to produce more valuable intermediates or products such as synthetic gas.

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Keywords: biomass, microwave plasma, renewable energy, reaction engineering.

* Corresponding author. Tel.: +66-5394-4146; fax: +66-5394-4145.
E-mail address: n.tippayawong@yahoo.com

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1. Introduction

Nowadays, it is a serious challenge for any country to undercut energy consumption without undermining economic growth. Thailand is a major agricultural country with plenty of agricultural residues to be utilized for renewable energy. Biogas is an important renewable energy source in Thailand. The main constituents of biogas are methane and carbon dioxide [1, 2]. It is normally used at the farm level for heating, mechanical and electrical powers. The biogas may be upgraded to biomethane by removing carbon dioxide, hydrogen sulphide and moisture [3-5], or to synthetic gas via reforming reactions [6, 7].

There are many routes for converting biogas into synthetic gas. Steam reforming (Eq. 1) is a popular reaction to produce H_2 from natural gas in the refinery of crude petroleum. Dry reforming reactions (Eqs. 2 and 3) generate synthetic gas by reacting CO_2 with CH_4. Advantages of dry reforming are that CO_2 (a greenhouse gas) is consumed, and it is easier to control than steam reforming [8]. Partial oxidation can reform hydrocarbons to generate H_2 and CO, as shown in Eq. 4. It is an exothermic reaction, so no input power is required. However, the limited amount of oxygen is necessary and the reaction efficiency was low [9]. Autothermal reforming is a combination between steam reforming or dry reforming with partial oxidation, as shown in Eq. 5. Autothermal reforming can produce more H_2 than partial oxidation, and use lower power than steam reforming [10].

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = 206 \text{ kJ/mol} \qquad (1)$$
$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H = 247 \text{ kJ/mol} \qquad (2)$$
$$CH_4 + 2CO_2 \rightarrow 3CO + H_2 + H_2O \qquad \Delta H = 288 \text{ kJ/mol} \qquad (3)$$
$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \qquad \Delta H = -38 \text{ kJ/mol} \qquad (4)$$
$$2CH_4 + O_2 + CO_2 \rightarrow 3CO + 3H_2 + H_2O \qquad (5)$$

However, when catalytic reforming reactions of hydrocarbon fuels are used, there are some concerns over high operating temperature (around 900^{o}C), and those associated with coking and poisoning of the catalysts. Non-thermal plasma assisted reforming of hydrocarbon fuels may have potential in generating synthetic gas.

Plasma is the fourth state of matter. It is ionized gas containing energetic ions and electrons. Energy is important to strip electrons from atoms to make plasma. The energy can be originated from various sources such as thermal, electrical and light. There are two main types: thermal and non-thermal plasma [11]. Thermal plasma is in thermodynamic equilibrium. The neutral species are at high temperature between 5,000 - 10,000 K. Its electron density is about 10^{21} to 10^{26} m^{-3}. Non-thermal plasma is in thermodynamic non-equilibrium. The electron temperatures are at high temperatures while the bulk species temperature does not increase significantly.

There have been many investigations on CH_4 reforming by various sources of plasma. Indrato et al. [12] used gliding arc discharge to produce fuel gas from methane. Wang et al. [13] produced synthetic gas by dry reforming methane in dielectric barrier discharge reactor. Zhang et al. [14] used microwave plasma to reform of CH_4 with CO_2 into CO, C_2H_2, C_2H_4 and H_2. Yang [15] used corona discharge to conversion and reforming of methane. Li et al. [16] produced synthetic gas from CH_4 with CO_2 by glow discharge.

Nomenclature

C_{in}	amount of CH_4 or CO_2 (mol) input
C_{out}	amount of CH_4 or CO_2 (mol) output
C_{CH4}	amount of CH_4 (mol) input
C_{CO2}	amount of CO_2 (mol) input
$nH_{2produced}$	amount or H_2 (mol) product
$nCO_{produced}$	amount or CO (mol) product
S_{H2}	selectivity of H_2
S_{CO}	selectivity of CO
Y_{H2}	yield of H_2
Y_{CO}	yield of CO
η	conversion of CH_4 or CO_2

Microwave plasma is an interesting type of non-thermal plasma. It is an alternative technology used to produce synthetic gas from biomethane. It is easy to control, fast, compact, and economical. It may be generated using a magnetron in household microwave ovens [17, 18]. In this work, synthetic gas production from reforming of compressed biomethane using microwave plasma was studied.

2. Materials and methods

Fig. 1 shows the experimental set up, where (1) compressed biomethane tank, (2) CO_2 tank, (3) O_2 tank, (4) rotameter, (5) mixing chamber, (6) bubble flow meter, (7) microwave oven, (8) reaction zone, (9) quartz tube, (10) gas filter, (11) gas dryer, and (12) gas chromatography. The reactor was modified from a microwave oven. The microwave plasma was generated using maximum power of 800 W from a 2.45 GHz magnetron. A quartz tube was mounted vertically and centrally in the oven chamber. The quartz tube in reactor has 27/30 mm of internal/external diameter and 400 mm of length.

Before each experimental run, the residual gas in the tube was displaced out from the system by purging with He gas at a flow rate of 5 lpm for 3 min to prevent combustion in the system. For dry reforming, the simulated biomethane was fed from the bottom into the reactor at CH_4/CO_2 ratio between 1, 2.33, and 9. The biomethane flow rate was varied between 0.5 to 3 lpm. This was controlled by a rotameter and a bubble flow meter. The microwave was switched on to reform the biomethane in the quartz tube. The generated gas downstream of the reactor was subsequently collected in a sampling gas bag. Composition of the gas was analyzed by a sensitive gas chromatography fitted with a ShinCarbon ST Micropacked column and a thermal conductivity detector for determining concentrations of H_2, O_2, N_2, CH_4, CO and CO_2. In subsequent experiments of partial oxidation, oxygen was added into the simulated biomethane. CH_4/O_2 ratio was varied between 1 to 2. For data processing,

Conversion of CH_4 and CO_2:

$$\eta = (C_{in} - C_{out}) / C_{in} \tag{6}$$

Selectivity of H_2 and CO:

$$S_{H2} = n_{H2\ produced} / (2 \times C_{CH4}) \tag{7}$$

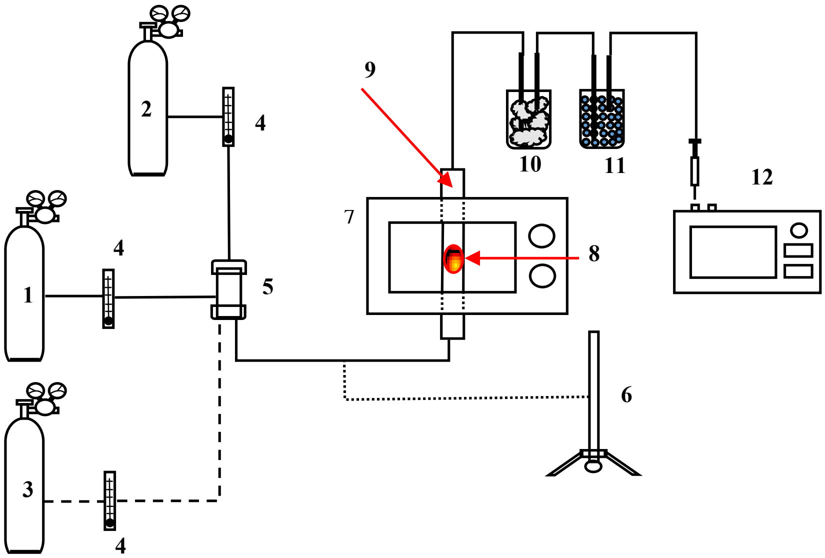


Fig. 1 Schematic of the microwave plasma reactor setup.

$$S_{CO} = n_{CO\ produced} / (C_{CH4} + C_{CO2}) \tag{8}$$

Yield of H_2 and CO:

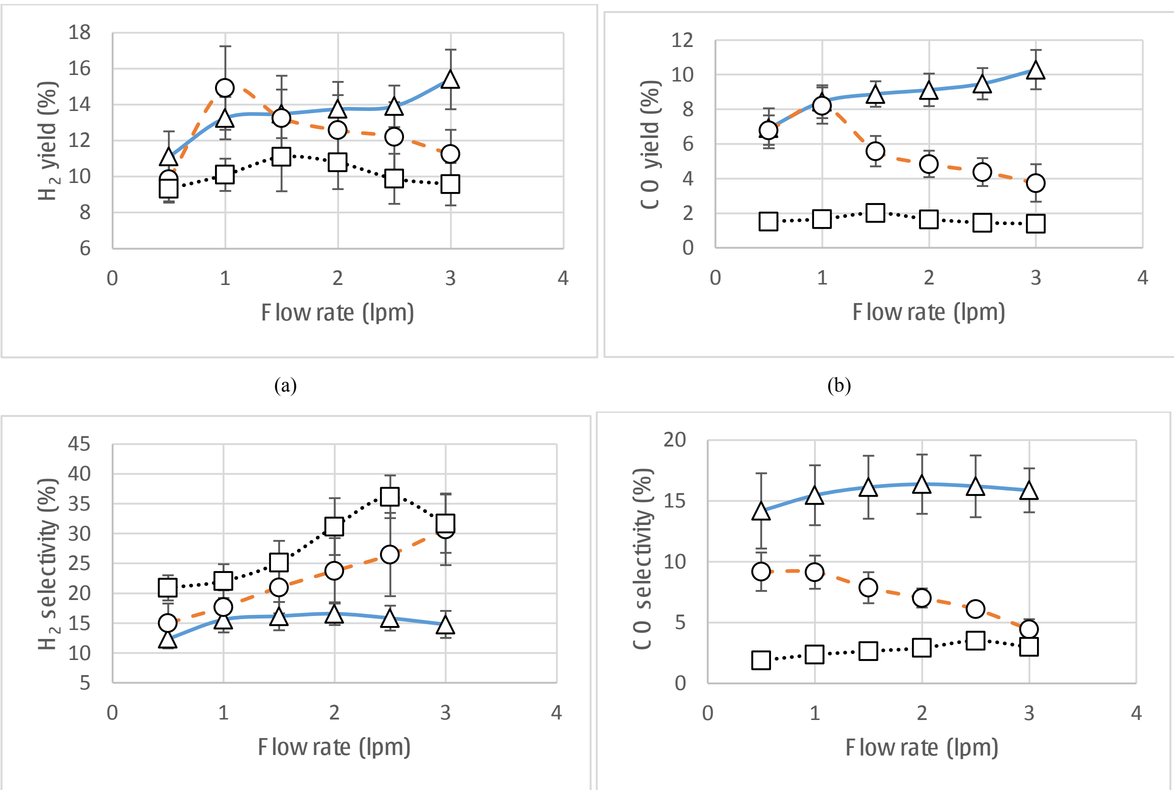
$$Y_{H2} = n_{H2\ produced} / (2 \times CH_{4\ feed}) \tag{9}$$

$$Y_{CO} = n_{CO\ produced} / (CH_{4\ feed} + CO_{2\ feed}) \tag{10}$$

3. Results and discussion

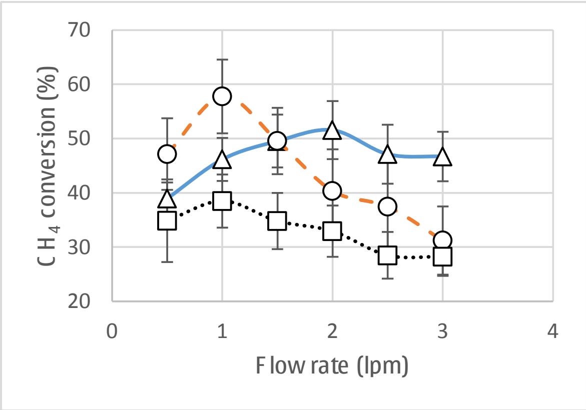
3.1 Effect of CH_4/CO_2 ratio.

For the reforming of biomethane to synthetic gas, power input was fixed at 800 W. Composition of simulated biogas mixture was varied for CH_4/CO_2 between 1, 2.33 and 9. The mixture flow rate was varied between 0.5 – 3 lpm. Fig. 2 shows yields and selectivity of H_2 and CO, conversion of CH_4 and CO_2 and H_2/CO ratio as a function of CH_4/CO_2 ratio and mixture flow rate. H_2 yield was found to decrease when CH_4/CO_2 ratio was increased from 1 to 9. The maximum yield of H_2 was 15% at CH_4/CO_2 ratio of 1 and the flow rate of 3 lpm. Yield of CO was shown in the Fig. 2(b). CO yield was decreased with increasing CH_4/CO_2 ratio. From dry reforming process, the maximum yields of H_2 and CO occurred because CO_2 was reacted with CH_4 in chemically correct proportion. At higher CH_4/CO_2 ratio, availability of CO_2 to react was less. For a fixed supply of energy, Eq. (1) was more likely to occur than Eq. 2.

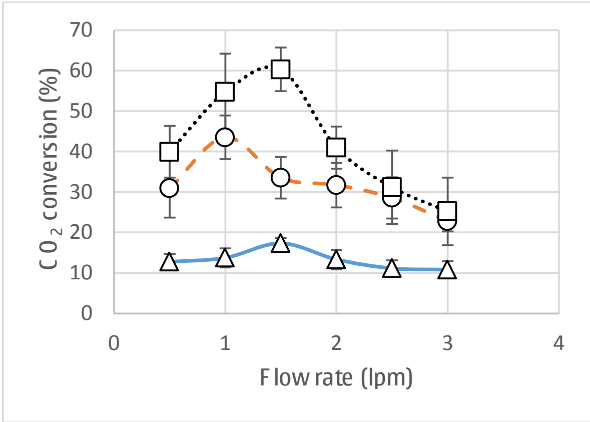


(a) (b)

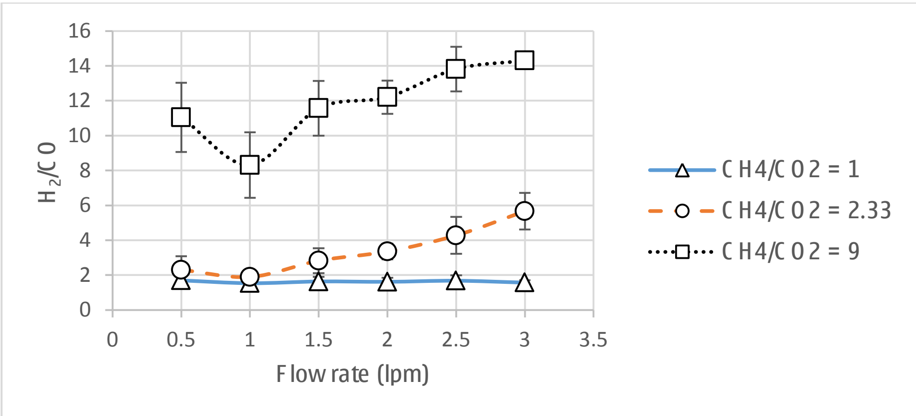
(c) (d)



(e)



(f)



(g)

Fig. 2 Effects of CH_4/CO_2 ratio and mixture gas flow rate on biogas reforming performance

Selectivity of H_2 is presented in Fig. 2(c). It was observed to increase with increasing CH_4/CO_2 ratio. It was directly opposite to selectivity of CO, shown in Figure 2(d). Conversion of CH_4 and CO_2 are shown in Figs. 2(e) and 2(f). CH_4 conversion was decreased when the amount of CH_4 was increased. But the conversion of CO_2 was increased with increasing amount of CH_4 in the mixture. H_2/CO ratio was found to vary between 2 to 14, for CH_4/CO_2 ratio from 1 to 9, shown in Fig. 2(g). The value of H_2/CO ratio was increased when CH_4/CO_2 ratio was increased.

3.2 Effect of flow rate

The effect of flow rate of CH_4/CO_2 was also studied. It was found that at CH_4/CO_2 = 1, increasing flow rate of the gas mixture led to increasing yields of H_2 and CO from 11 to 15% and 7 to 10%, respectively, as shown in Figs. 2(a) and 2(b). However, at higher CH_4/CO_2 ratios, the yields tended to decrease or stay constant with increasing flow rate. The conversion of CH_4 and CO_2 were found to a peak in the range of flow rates considered. The maximum conversion of CH_4 and CO_2 were 58 and 60%, respectively at the flow rate between 1 to 1.5 lpm, as shown in Figs. 2(e) and 2(f). For H_2/CO ratio, it was observed to stay constant with increasing flow rate at CH_4/CO_2 = 1. But, the H_2/CO ratio was increased with the flow rate at higher CH_4/CO_2 ratios, as shown in Fig. 2(g).

3.3 Effect of O_2 content

When O_2 was input into the simulated biogas, partial oxidative reaction was enabled. It assisted in reforming of CH_4 to generate H_2 and CO. For the effect of O_2 on reforming reaction of biogas, the power input, CH_4/CO_2 ratio and the flow rate of CH_4/CO_2 were fixed at 800 W, 2.33, and 1 lpm, respectively. Ratio of CH_4/O_2 was varied between 1, 1.5 and 2. At the lowest CH_4/O_2 ratio, largest amount of O_2 was available. From the results obtained, it was shown that H_2 yield and selectivity were slightly increased with decreasing availability of O_2, as shown in Figs. 3(a) and 3(b). The trends of yield and selectivity of CO were opposite to those of H_2.

The conversion of CH_4 and CO_2 are shown in Fig. 3(c). They were found to be maximum at CH_4/O_2 = 1. The maximum conversion CH_4 and CO_2 were 68 and 50%, respectively. As O_2 availability was decreased, both conversions were reduced. These findings were consistent with those reported in the published literature [19]. For H_2/CO ratio shown in Fig. 3(d), it was initially increased up to CH_4/O_2 = 1.5, after which, it stayed constant with further increase in CH_4/CO_2 ratio.

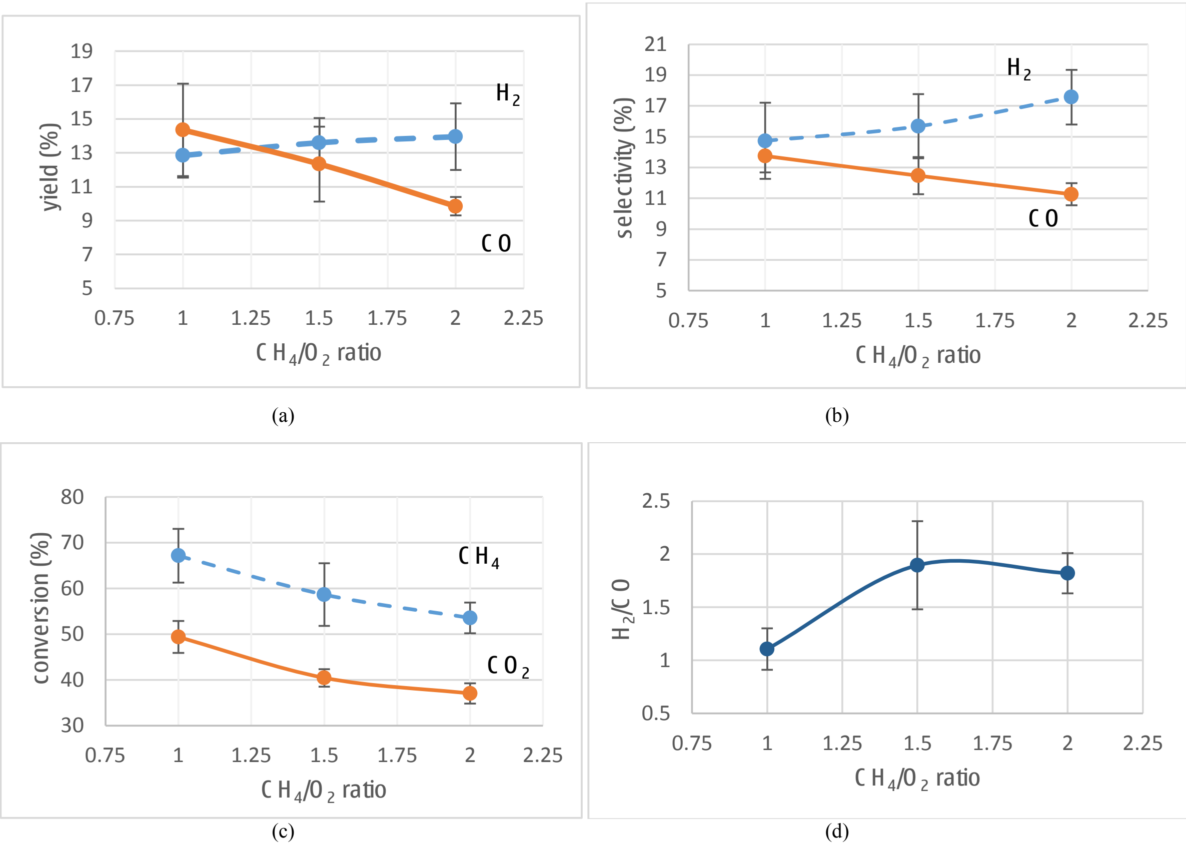


Fig. 3 Effect of CH_4/O_2 ratio on biogas reforming performance (flow rate of 1 lpm, CH_4/CO_2 ratio of 2.33)

Table 1 shows the comparison of the performance for dry reforming and partial oxidation reforming of CH_4 between a gliding arc and a microwave discharge reactor. For dry reforming, the microwave plasma reactor in this work was shown to produce higher H_2 yield, CH_4 and CO_2 conversion. This may be attributed to the fact that higher input power was used. For partial oxidation in this work, the CO yield, conversion of CH_4 and CO_2 was higher than other technologies. But the H_2 yield and H_2/CO ratio exhibited similar values. However, the selectivity of H_2 and CO were less, despite the higher conversion of CH_4 and CO_2 and higher selectivity of H_2 and CO.

Table 1: Comparison with literature on plasma assisted dry reforming and partial oxidation of methane.

	Flow (lpm)	Power (W)	CH_4/ O_2	CH_4/ CO_2	Yield (%)		Selectivity (%)		η (%)		H_2 / CO
					H_2	CO	H_2	CO	CH_4	CO_2	
Dry reforming											
[19]	1	100	-	1	6.3	1.9	45	22	13.6	4.87	n/a
[20]	1	200	-	1	n/a	n/a	n/a	70	20	n/a	n/a
This work	1	800	-	1	13.25	8.44	15.6	15.45	46.16	13.74	1.9
Partial oxidation											
[21]	1	100	1	2.33	13.5	6.9	n/a	n/a	22.6	12.8	n/a
	1	100	2.2	2.33	13.9	10	51.2	41.6	27.1	n/a	2
[22]	7	600	1	pure CH_4	55	n/a	70	90	n/a	n/a	1.5
This work	1	800	1	2.33	12.84	14.35	14.73	13.75	67.12	49.37	1.1
	1	800	1.5	2.33	13.6	12.34	15.68	12.47	58.64	40.44	1.9
	1	800	2	2.33	13.96	9.85	17.57	11.26	53.54	37.02	1.8

4. Conclusion

In this study, a microwave discharge system was developed. Plasma assisted reforming of biogas was investigated at 1 atm with no catalyst used. Experiments were carried out for varying composition of biogas (CH_4/CO_2), flow rate of the gas mixture, and the effects of O_2 addition on yield and selectivity of H_2 and CO, conversion of CH_4 and CO_2, as well as H_2/CO ratio of the generated synthetic gas.

It was shown that conversion of CH_4 and CO_2 to synthetic gas can be performed by dry reforming and autothermal reforming reactions. For dry reforming process, optimum CH_4/CO_2 ratio was 1 in order to achieve maximum yields of H_2 and CO, and maximum selectivity of CO. Partial oxidation was also found to generate high yield of synthetic gas.

Non-thermal plasma reactor proved to be an efficient system for producing synthetic gas from biomethane in the absence of catalytic process.

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References

[1] X. Tao, M. Bai, X. Li., CH_4-CO_2 reforming by plasma challenges and opportunities, Progress in Energy and Combustion Science, 37(2) (2011), 113–124.
[2] P. Thanompongchart, N. Tippayawong., Progress in plasma assisted reforming of biogas for fuel gas upgrading, American Journal of Scientific Research, 76 (2012), 70–87.
[3] P. Aggarangsi, N. Tippayawong, J. C. Moran, P. Rerkkriangkrai., Overview of livestock biogas technology development and implementation in Thailand, Energy for Sustainable Development, 17(4) (2013), 371-377.
[4] N. Tippayawong, P. Thanompongchart., Biogas quality upgrade by simultaneous removal of CO_2 and H_2S in a packed column reactor, Energy, 35(12) (2010), 4531-4535.
[5] E. Ryckebosch, M. Drouillon, H. Vervaeren., Techniques for transformation of biogas to biomethane, Biomass and Bioenergy, 35(5) (2011), 1633-1645.
[6] J. R. Rostrup-Nielsen., Syngas in perspective, Catalysis Today, 71(3-4) (2002), 243–247.
[7] V. Goujard, J.-M. Tatibou¨et, C. Batiot-Dupeyrat., Use of a non-thermal plasma for the production of synthesis gas from biogas, Applied Catalysis A: General, 353(2) (2009), 228– 235.
[8] G. Jianjun, L. Hui, Z. Hong, C. Dingfeng, Z. Xiaoming., Dry reforming of methane over nickel catalysts supported on magnesium aluminate spinels, Applied Catalysis A: General, 273 (2004), 75-82.
[9] D. O. Christensen, , P. L. Silveston, E. Croiset, R. R. Hudgin., Production of hydrogen from the noncatalytic partial oxidation of ethanol, Industrial and Engineering Chemistry Research, 43 (2004), 2636–2642.
[10] M. Jasi´nski, D. Czylkowski, B. Hrycak, M. Dors, J. Mizeraczk., Production of hydrogen via methane reforming using atmospheric pressure microwave plasma, Journal of Power Sources, 181 (2013), 41–45.

[11] Y. N. Chun, Y. C. Yang, K. Yoshikawa., Hydrogen generation from biogas reforming using a gliding arc plasma catalysis reformer, Catalysis Today, 148(2008), 283-289.
[12] A. Indrato, J. W. Choi, H. Lee, H. K. Song., Effect of additive gases on methane conversion using gliding arc discharge, Energy, 31(2006), 2986-2995.
[13] Q. Wang, B. H. Yan, Y. Jin, Y. Chang., Investigation of dry reforming methane of methane in dielectric barrier discharge reactor, Plasma Chemistry and Plasma Process, 29(3) (2009), 217-228.
[14] J. Q. Zhang, Y. J. Yang, J. S. Zhang., Study on the conversion of CH_4 and CO_2 using a pulsed microwave plasma under atmospheric pressure, Acta Chemica Sinica, 60(11) (2002), 1973-1980.
[15] Y. Yang., Methane conversion and reforming by non-thermal plasma on pins, Industrial and Engineering Chemistry Research, 41(24) (2002), 5918-26.
[16] D. Li, X. Li, M. Bai, X. Tao, S. Shang, X. Dai, Y. Yin., Discharge plasma: a high conversion ability CO_2 reforming of CH_4 by atmospheric pressure glow, International Journal of Hydrogen Energy, 34 (2009), 308–313.
[17] P. Khongkrapan, N. Tippayawong, T. Kiatsiriroat., Thermochemical conversion of waste papers to fuel gas in a microwave plasma reactor, Journal of Clean Energy Technologies, 1(2) (2013), 80 – 83.
[18] G. Petitpas, J. D. Rollier, A. Darmon, J. Gonzalez-Aguilar, R. Aetkemeijer, L. Fulcheri., A comparative study of non-thermal plasma assisted reforming technologies, International Journal of Hydrogen Energy, 32 (2007), 2848-2867.
[19] P. Thanompongchart, N. Tippayawong., Experimental investigation of biogas reforming in gliding arc plasma reactors, International Journal of Chemical Engineering, (2014), Article ID 609836, 9 pages
[20] N. H. Khiabani, M. S. Yaghmaee, A. Sarani, B. Shokri., Synthesis-gas production from CH_4-CO_2-Ar via microwave plasma torch, Advanced Studies in Theoretical Physics, 6(26) (2012), 1273 – 1287.
[21] P. Thanompongchart, P. Khongkrapan, N. Tippayawong., Partial oxidation reforming of simulated biogas in gliding arc discharge system, Periodica Polytechnica - Chemical Engineering, 58(1) (2014), 31 – 36.
[22] C. H. Tsai, T. H. Hsieh, M. Shih, Y. J. Huang, T. C. Wei., Partial oxidation of methane to synthesis gas by a microwave plasma torch, AIChE Journal, 51(10) (2005), 2858-2853.