Partial oxidation reforming of simulated biogas in gliding arc discharge system

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Abstract
Plasma assisted, partial oxidation reforming of biogas is considered to be a promising technology to produce synthesis gas. In this work, a 0.1 kW gliding arc plasma reformer was employed to investigate the effects of biogas composition and oxygen availability on CH\textsubscript{4} and CO\textsubscript{2} conversions, as well as the product distribution. Air was used in the partial oxidation of biogas. The results showed that at low CH\textsubscript{4}/O\textsubscript{2} ratio or high oxygen availability, increasing CH\textsubscript{4} content appeared to show higher H\textsubscript{2} yield and CH\textsubscript{4} conversion. Increasing CH\textsubscript{4}/O\textsubscript{2} ratio adversely affected H\textsubscript{2} and CO yields, and CH\textsubscript{4} conversion. Optimum condition was found at CH\textsubscript{4}/CO\textsubscript{2} of 90:10 and CH\textsubscript{4}/O\textsubscript{2} of 1.2 for the maximum CH\textsubscript{4} conversion and H\textsubscript{2} yield of 45.7 and 25.3%, respectively.

Keywords
biomass · methane reforming · non-thermal plasma · renewable energy · synthesis gas

1 Introduction
Energy is recently becoming one of the most pressing issues in many societies and countries. It affects wellbeing of the people, economic development, national security, and civilization. The energy demand remains high and growing, while conventional supply from crude oils is increasingly fragile. Concerns over climate change and recent incidents at Fukushima have presently made coal and nuclear powers rather unfashionable. To tackle a major threat of energy crisis, strong energy conservation and efficiency improvement program must be adopted. At the same time, alternative energy sources must be explored and utilized. Renewable energy is, if properly integrated, able to cover all energy needs. Change from fossil fuels to renewables is happening and relevant to many nations around the World.

Among various types of renewable energy resources, biogas appeared to be one of the most promising options. Thailand has the potential to produce over one billion m\textsuperscript{3} of biogas a year from its agricultural industry alone [1]. Normally, biogas contains 45-70% CH\textsubscript{4}, 30-45% CO\textsubscript{2}, and a trace amount of other gases. Composition of biogas depends on raw biomass materials and conditions of anaerobic digestion [2,3]. The biogas produced is generally utilized at farm levels for heating, mechanical shaft works, and electricity generation. To further harness this renewable energy source, biogas may be upgraded to more attractive and marketable gaseous fuels such as compressed biogas, biomethane, or synthesis gas [1,4,5].

Synthesis gas (H\textsubscript{2} and CO) production is of great interest because it can be used as starting feed to generate synthetic chemicals and liquid fuels [6,7]. There are several technologies available for synthesis gas production through CH\textsubscript{4} rich gas, namely, steam or wet reforming, CO\textsubscript{2} or dry reforming, and partial oxidation reforming, shown in eqs. (1) to (3) below:

\[ CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H = 206 \text{ kJ/mol} \quad (1) \]

\[ CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H = 247 \text{ kJ/mol} \quad (2) \]

\[ CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \quad \Delta H = -38 \text{ kJ/mol} \quad (3) \]
Because the former two routes are highly endothermic, hence require heat input and consume large amount of energy, considerable attention has been drawn to focus on the exothermic partial oxidation. For non-catalytic partial oxidation of hydrocarbons, it usually occurs at high temperature (1300-1500°C) to complete conversion. In biogas reforming, methane decomposition and boundary reactions (4 and 5) are possible,

\[
\text{CH}_4 \leftrightarrow 2\text{H}_2 + \text{C} \quad \Delta H = 75 \text{ kJ/mol} \quad (4)
\]

\[
2\text{CO} \rightarrow \text{CO}_2 + \text{C} \quad \Delta H = -171 \text{ kJ/mol} \quad (5)
\]

For biogas, combination of carbon dioxide and partial oxidation of methane can reduce coke deposition on electrodes’ surface. Furthermore, application of plasma technology may enable high conversion at reduced energy consumption of the chemical process [8].

Plasma is ionized gas that can be generated from combustion, electric discharges (arc, spark, plasma jet, microwave discharge, corona, glow and radio frequency), and shocks (electrically, magnetically and chemically driven) [9]. It is effective in generating active species such as electrons, ions, and radicals. It can be classified into non-thermal and thermal plasma. Non-thermal plasma has low electron density (< 10¹⁹ m⁻³) and dissimilarity between electron and heavy particle temperatures. Inelastic collisions between electrodes and heavy particles create the plasma reaction species whereas elastic collisions heat the heavy particle [8,10,11]. Advantage of using non-thermal plasma is associated with lower temperatures, lower energy consumption and electrode erosion [12]. Gliding arc discharge is one of non-thermal plasma, associated with low reaction temperature, high selectivity, and compact equipment [12-14]. It has at least two diverging knife shaped electrodes. When a high voltage is applied, a relatively low current arc discharge is formed repeatedly at the narrowest gap across the electrodes, and spreads along the edges, and eventually disappears downstream.

Gliding arc plasma has been utilized in reforming of CH₄ rich gas to produce synthesis gas [10,13]. But, there have been relatively few studies investigating plasma assisted partial oxidation of CH₄/CO₂ system. Reported works using gliding arc discharge reactor were even more limited. Notable article on gliding arc plasma reforming of biogas include Sreethawong et al. [15], Yang et al. [16], Rafiq and Hustad [17,18], and Rafiq et al. [19]. It was noted that none of these works focused on non-catalytic effect at high CH₄/O₂ ratios. In this work, biogas reforming via partial oxidation under gliding arc plasma was carried out. The main objective is to explore partial oxidation of biogas to produce synthesis gas. Effects of biogas composition and rich fuel-to-air mixing on process performance were investigated.

### 2 Materials and Methods

Fig. 1 shows schematic diagram of the experimental setup for plasma reforming of biogas. It consists of a gliding arc reactor, a power supply, gas feeding line, measurement and analysis instrumentation. Simulated biogas was generated from mixing CH₄ and CO₂. Air was used as source of oxygen in partial oxidation. These gases were of research grade obtained from Thai Industry Gas Plc. The feed gas line was responsible for supplying CH₄, CO₂ and air. The main input gases were controlled by Dewar VFA gas flow meters and regulators as well as Hewlett-Packard soap film flow meter. It was injected through a cylindrical tube with diameter of 1 mm with total flow rate of 1 L/min. The reactor was made of transparent acrylic and glass plates. Knife shaped electrodes were made from stainless steel (3 mm thick). The electrode gap was 4 mm. The input power was supplied from an AC high voltage (HV) Lecip Neon transformer was fixed at 7.5 kV and 100 W. The analysis system was divided into electrical characterization, temperature measurement, and gas analysis. The electrical measurement consists of Fluke 80K-40 HV probe, Gwinstek GOS-620 oscilloscope and Pro Elec PL09564 power meter to measure the supplied electric power. The temperature measurement was carried out using Digicon ND-400N type K thermocouples. The temperature was monitored in real time from the thermocouples installed in the electrode gap, avoiding contact with electrodes and discharge region. The gas analysis was done by a Shimadzu 8A gas chromatography equipped with a thermal conductivity detector and Shin carbon column), able to analyze H₂, O₂, N₂, CO, CH₄ and CO₂.

Feed gas composition can be adjusted. Once constant composition of mixed gas passed into the gliding arc plasma reactor was established, the power supply was then switched on. The system was allowed to stabilize, then gas samples up- and downstream of the reactor were collected in Restek multilayer foil gas bags, and sent immediately for analysis. At least three experimental runs were carried out for each case, and average results were shown. Effect of the following parameters on reforming reaction were studied; biogas composition (CH₄/CO₂: 50/50, 70/30, 90/10) and oxygen content in partial oxidation process (CH₄/O₂: 0.5 - 20). To evaluate the performance of the process, equations (6) to (12) were used:

\[
\text{CH}_4 \text{ conversion: } C_{\text{CH}_4} = \frac{M_{\text{CH}_4,\text{in}} - M_{\text{CH}_4,\text{out}}}{M_{\text{CH}_4,\text{in}}} \times 100 \quad (6)
\]

\[
\text{CO}_2 \text{ conversion: } C_{\text{CO}_2} = \frac{M_{\text{CO}_2,\text{in}} - M_{\text{CO}_2,\text{out}}}{M_{\text{CO}_2,\text{in}}} \times 100 \quad (7)
\]

\[
\text{H}_2 \text{ selectivity: } S_{\text{H}_2} = \frac{2 \times M_{\text{H}_2,\text{produced}}}{M_{\text{CH}_4,\text{converted}}} \times 100 \quad (8)
\]

\[
\text{CO selectivity: } S_{\text{CO}} = \frac{M_{\text{CO,produced}}}{M_{\text{CH}_4,\text{converted}}} \times 100 \quad (9)
\]
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H₂ yield: \[ Y_{[H_2]}(\%) = \frac{M_{[H_2,\text{produced}}]}{2 \times M_{[CH_4,in]}} \times 100 \quad (10) \]

CO yield: \[ Y_{[CO]}(\%) = \frac{M_{[CO,\text{produced}}]}{2 \times (M_{[CH_4,in]} + M_{[CO_2,in]})} \times 100 \quad (11) \]

Applied energy density:
\[ \text{AED (kJ/L)} = \frac{\text{AP}}{\text{FR}} \quad (12) \]

where \( M_{[CH_4,in]} \) is amount of \( CH_4 \) input, \( M_{[CH_4,out]} \) is amount of \( CH_4 \) out, \( M_{[CO_2,in]} \) is amount of \( CO_2 \) input, \( M_{[CO_2,out]} \) is amount of \( CO_2 \) out, \( M_{[H_2,\text{produced}}] \) is amount of \( H_2 \) produced, \( M_{[CH_4,\text{converted}}] \) is \( CH_4 \) input - \( CH_4 \) output, \( M_{[CO,\text{produced}}] \) is amount of \( CO \) produced, AP is power or input electricity in kW, FR is feed gas flow rate in L/s, respectively.

3 Results and Discussion

Effects of \( CH_4/CO_2 \) and \( CH_4/O_2 \) molar ratios in plasma assisted partial oxidation on \( H_2 \) and \( CO \) yields and selectivities, as well as \( CH_4 \) and \( CO_2 \) conversions were considered. They are shown in Figs. 2 to 4. Biogas composition was varied (\( CH_4/CO_2: 50/50, 70/30, 90/10 \)), such that enrichment of methane was taken into account. In this work, large range of \( CH_4/O_2 \) molar ratios (0.5 - 20) was considered. For a fixed and very low value of \( CH_4/O_2 \) ratio, enriching \( CH_4 \) content or decreasing \( CO_2 \) content in biogas was found to produce higher yield and selectivity of \( H_2 \), while no clear pattern was emerged for yields and selectivity of \( CO \), as well as conversion of \( CH_4 \) and \( CO_2 \). Maximum \( H_2 \) yield of over 25% was obtained at \( CH_4/CO_2 = 90/10 \), whereas at \( CH_4/CO_2 = 50/50 \), around 10% was observed. There were no significant changes in \( H_2 \) yields and \( CH_4 \) conversions with increasing \( CH_4 \) content for the \( CH_4/O_2 \) ratios beyond two. It may be noted that greater presence of \( CO_2 \) in biogas seemed to encourage higher \( CO \) yields and selectivity as well as higher \( CH_4 \) conversion. Possible reaction of biogas reforming at high concentration of \( CO_2 \) is [20,21]:

\[
CH_4 + 2CO_2 \rightarrow 3CO + 2H_2 + H_2O \quad \Delta H = 288 \text{ kJ/mol} \quad (13)
\]

Increased \( CO \) yields were observed with decreasing content of \( O_2 \). However, in this work, the observed changes were relatively small.

Increasing the \( CH_4/O_2 \) ratio was found to affect the performance of the plasma reformer significantly. This was contributed to the fact that an increase in \( CH_4/O_2 \) ratio resulted in having less \( O_2 \) available to react with the fuel molecules, leading to lower conversion of \( CH_4 \), and yields of \( H_2 \) and \( CO \). For the biogas with \( CH_4/CO_2 = 90/10 \), changing the \( CH_4/O_2 \) ratios from about 1 to 10 led to declines in \( CH_4 \) conversion and \( H_2 \) yield.
from 45 to 15%, and 25 to 10%, respectively. The highest H\textsubscript{2} yield and CH\textsubscript{4} conversion were obtained at the lowest CH\textsubscript{4}/O\textsubscript{2} ratio considered. Optimum condition was found at CH\textsubscript{4}/O\textsubscript{2} of 90:10 and CH\textsubscript{4}/O\textsubscript{2} of 1.2 for the maximum CH\textsubscript{4} conversion and H\textsubscript{2} yield of 45.7 and 25.3%, respectively.

With respect to the effect on the selectivities of H\textsubscript{2} and CO, it was found that CO selectivity decreased while H\textsubscript{2} selectivity increased with increasing CH\textsubscript{4}/O\textsubscript{2} molar ratio. This was in line with Sreethawong et al. [15]'s observation. The plasma system appeared to promote two spontaneous reactions; partial oxidation of CH\textsubscript{4} and the coupling reaction. The former reaction was favorable at very low CH\textsubscript{4}/O\textsubscript{2} ratios, while the coupling reaction and the hydrogenation become more pronounced with increasing CH\textsubscript{4}/O\textsubscript{2} ratios [15]. At high CH\textsubscript{4}/O\textsubscript{2} ratios (> 10), change in oxygen availability did not significantly affect partial oxidation of CH\textsubscript{4}. At the extremely rich fuel-to-air mixture where oxygen is in short supply, the reaction was expected to behave like dry CO\textsubscript{2} reforming of CH\textsubscript{4} [10]. It should be noted that small traces of moisture as well as H\textsubscript{2}S are normally found in biogas, especially from animal farms. Their influences on reforming reaction should not be overlooked. These impurities may affect the performance of the process considered. However, this is outside the scope of the present investigation.

Table 1 shows the comparison of the performance for partial oxidation of CH\textsubscript{4} at the optimum conditions between the gliding arc, dielectric barrier, and corona discharge reactors. The gliding arc plasma systems appeared to show similar ranges of CH\textsubscript{4} conversion, H\textsubscript{2} and CO selectivities. Against other types of discharge, the gliding arc consumed much lower applied energy per unit flow rate than the dielectric barrier discharge system [22], but exhibited higher CH\textsubscript{4} conversion. Corona discharge [23] gave highest H\textsubscript{2}/CO ratios of 2.5 and 3.4, compared to 1.8 – 2.0 found in this work.

As far as energy consumption is concerned, the energy utilized in this work was calculated to be 6.0 kJ/L or MJ/m\textsuperscript{3} of feed gas. For a biomethane with CH\textsubscript{4}/CO\textsubscript{2} of 90:10, its calorific value is estimated about 38.3 MJ/kg or 28 MJ/m\textsuperscript{3}, assuming biomethane density of 0.73 kg/m\textsuperscript{3}. Hence, the energy utilized was approximately 20% of the energy contained in the feed gas. The current CH\textsubscript{4} conversion was high, around 45%, in comparison with other plasma sources reported in the literature. Nonetheless, to achieve higher conversion of methane in this plasma reactor setup, the following modifications may be needed: (i) using higher applied energy to generate more energetic active species to encourage higher conversion, (ii) combining the plasma reactor with a catalytic reformer, (iii) passing the reactants into many stages of the reactor in cascade, and (iv) increasing the feed gas injector size. The latter two modifications would increase total residence time of the feed gas within the reactor, which will result in higher conversion. So far, reactor development with regards to the gliding arc plasma reactor remains at laboratory level. Scaling up of the plasma reactor is not yet achieved in realization of industrial plants. Works on the previously mentioned modifications, investigation on other critical factors associated with fluid dynamics and transport properties, as well as process modeling and analysis should be further carried out, prior to development into pilot and industrial units.

4 Conclusions

Gliding arc plasma is a promising technology for biogas reforming into useful products. In this work, a gliding arc discharge system was utilized in partial oxidation of biogas with air to generate synthesis gas. Effects of varying composition and CH\textsubscript{4}/O\textsubscript{2} molar ratio on performance of the plasma reformer were investigated. For very low CH\textsubscript{4}/O\textsubscript{2} molar ratio, CH\textsubscript{4} conversion and H\textsubscript{2} yield were high. At higher CH\textsubscript{4}/O\textsubscript{2} molar ratios, CH\textsubscript{4} conversion and synthesis gas yields decreased. The optimum condition of the gliding arc plasma system was found at CH\textsubscript{4}/CO\textsubscript{2} of 90:10 and CH\textsubscript{4}/O\textsubscript{2} of 1.2 for the maximum CH\textsubscript{4} conversion. The gliding arc plasma system proved to successfully generate high synthesis gas yields at low energy consumption.
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Fig. 3. Effects of CH₄/CO₂ and CH₄/O₂ on H₂ and CO selectivities.

Fig. 4. Effects of CH₄/CO₂ and CH₄/O₂ on CH₄ and CO₂ conversions.

Tab. 1. Comparison with literature on plasma assisted, partial oxidative reforming of methane.

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References


