Combined Plasma Reforming of CO_2-Containing Natural Gas with Steam and Partial Oxidation in a Multistage Gliding Arc Discharge System: Effect of Stage Number

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Nowadays, the energy consumption all around the world has rapidly increased, resulting in a decrease in available reserved fuels including natural gas. Natural gas is mainly composed of methane which can be converted into a more valuable product, called synthesis gas (H_2 and CO). Commercially for converting methane to synthesis gas, conventional catalytic processes require both high temperature and high pressure, resulting in high energy consumption and catalyst deactivation. Non-thermal plasma is considered to be a promising alternative technology for synthesis gas production because it can be operated in ambient conditions. In this research, the effect of stage number of multistage gliding arc discharge system on the process performance of the combined steam reforming and partial oxidation of simulated natural gas was investigated. The simulated natural gas contained 70 % methane, 10 % ethane, 10 % propane and 20 % carbondioxide, the experiments were carried out to investigate reactant conversions, product selectivities and yields, and power consumptions by varying either residence time and stage number of plasma reactors. Moreover, the optimum conditions for a maximum synthesis gas production were determined. The results show that the increasing stage number from 1 to 3 stages at constant feed flow rate enhanced the reactant conversions, and H_2 yield with the reduction of energy consumption. The lowest energy consumption of 3.49×10^{-17} Ws per molecule of reactants converted or 2.04×10^{-17} Ws per molecule of hydrogen produced was obtained from 3 stages of plasma reactors at residence time and feed flow rate of 4.11 s and 100 cm^3/min, respectively

1. Introduction

Natural gas is a flammable mixture of hydrocarbons, which is mainly composed of methane (70-90 %), ethane, propane and butane (0-20 %), carbon dioxide (0-20 %). The most important route of natural gas utilization is to convert into more valuable product called synthesis gas (H_2 and CO) by using methane as a reactant (www.naturalgas.org).

There are three conventional methods to produce synthesis gas from methane. The first method is the steam reforming of methane (Eq. 1). The reaction is strongly endothermic that consumes high energy. Generally, the reaction is operated over Ni catalyst with a high H_2O/CH_4 ratio to prevent coke formation on catalyst surface.

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \quad \Delta H_{298K} = 206 \text{ kJ/mol} \qquad (1)$$

Next method is the partial oxidation of methane, which is mildly exothermic, consumes low energy, and produces a H_2/CO ratio equal to 2 (Eq. 2). The mainly used catalyst in this method is Ni, which gives high activity and selectivity, however, coke can deposit easily due to the generation of hot spot of catalyst.

$$CH_4 + 1/2O_2 \longrightarrow CO + 2H_2; \Delta H_{298K} = -38 \text{ kJ/mol} \tag{2}$$
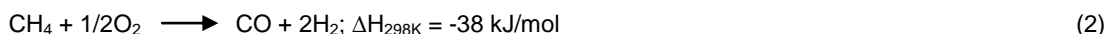
The last method is CO_2 reforming of methane. The reaction is strongly endothermic, requires high energy, uses a conventional catalyst, and produces a low H_2/CO ratio (Eq. 3).

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 ; \Delta H_{298K} = 247 \text{ kJ/mol} \tag{3}$$
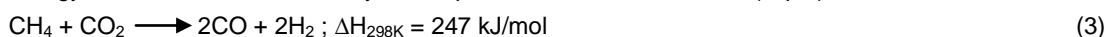
Because CO_2 is a component of greenhouse gas and found in many natural gas resources, especially in Asia, the reforming of natural gas containing CO_2 is of interest because it cut down the CO_2 emission as well as the process cost of synthesis production.

As many drawbacks are found in those three conventional processes, recently new technology known as non-thermal plasma is introduced. Gliding arc discharge is one kind of non-thermal plasma, which has been introduced to be another option in reforming natural gas. Gliding arc discharge can occur when the plasma is generated after applying voltage across a pair of knife-shaped electrodes. Its advantages are high-energy efficiency and environmental friendliness. Therefore, it was selected for producing synthesis gas in this research.

2. Experimental

2.1 Materials
The simulated natural gas use in this study consisted of methane, ethane, propane, and carbon dioxide, with a $CH_4:C_2H_6:C_3H_8:CO_2$ molar ratio of 70:5:5:20, was specially manufactured by Thai industry Gas (Public) Co., Ltd. Ultra-high purity oxygen used for performing the plasma reforming of the simulated natural gas with partial oxidation, was also obtained from Thai industry Gas (Public) Co., Ltd.

2.2 Experimental Procedures
The experimental setup of the multistage AC gliding arc discharge system with 4 stages in series which was made of a glass tube with 9 cm OD and 8.5 cm ID. The reactor consisted of two diverging knife-shaped electrodes that were made of stainless steel sheets. The width of each electrode was 12 mm. The electrode gap distance between the electrode pairs could be varied. Two teflon sheets were placed at top and bottom of the electrodes to direct the feed gas to pass through the reaction zone. For the power supply unit, the domestic AC input of 220 V and 50 Hz was connected to the DC power supply converter to convert to DC of about 80 V. The DC was supplied through a 500 W power amplifier, which was connected to a Instek function generator to generate waveform and to amplify voltage and frequency. The amplified current passed through the transformer to step up to 230 V AC. Thereafter, the variable output was transmitted to a high voltage current by a factor 130. A Lutron power analyzer was used to measure current, frequency, and voltage at the low side of the power supply unit.

The flow rates of the simulated natural gas sample and O_2 were controlled by a set of mass flow controllers and transducers supplied by AALBORG. A 7-µm stainless steel filter was placed upstream of each mass flow controller in order to trap any solid particles in the reactant gases. The check valve was also placed downstream of each mass flow controller to prevent any backflow. A water flow rate was controlled by a syringe pump supplied by Cole-Parmer. The temperature of the stainless tube carrying steam was controlled at 120 °C for complete water vaporization.

The feed mixture and the effluent gas samples were analyzed by an on-line gas chromatograph (HP, 5890) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The quantitative analysis of the percent volumes of all gaseous components was carried out by correlating their peak area responses obtained from the GC chromatograms. The HP 5890 gas chromatograph was installed with a 10-port valve in order to separate the analyzed gas into two parts with independent sample loops. The first part was connected to a Carboxen 1000 column with the TCD. The second part was sent to a PLOT Al_2O_3"S" column connected with the FID.

2.3 Reaction Performance Evaluation

The conversion of reactant gases was calculated using the following equation:

$$\% \text{ conversion} = \frac{\{\text{moles reactant in}\} - \{\text{moles reactant out}\}}{\{\text{moles reactant in}\}} \cdot 100 \tag{4}$$

The percent selectivity for products containing carbon atoms was calculated on the basis of the amount of carbon converted from the reactants into any specified products. In case of hydrogen product, the hydrogen selectivity was calculated based on hydrogen converted from the reactants.

$$\% \text{ selectivity for any hydrocarbon product} = [P](C_P)(100) / \sum[R](C_R) \tag{5}$$

where
[P]	=	moles of product in effluent
[R]	=	moles of reactant in feed to be converted
C_P	=	numbers of carbon atom in a product molecule
C_R	=	numbers of carbon atom in a reactant molecule

$$\% \text{ selectivity for hydrogen} = [P](H_P)(100) / \sum[R](H_R) \tag{6}$$

where
H_P	=	numbers of hydrogen atom in a product molecule
H_R	=	numbers of hydrogen atom in a reactant molecule

The product yield was calculated as follows:

$$\% \text{ yield of C2 hydrocarbons} = \sum(\% \text{ conversion of CH4, C2H6, C3H8, CO2}) \tag{7}$$
$$\times \sum(\% \text{ selectivity of } C_2H_2, C_2H_4) / (100)$$

$$\% \text{ yield of } H_2 = \frac{\sum(\% \text{ conversion of } CH_4, C_2H_6, C_3H_8) \cdot (\% \text{ selectivity of } H_2)}{100} \tag{8}$$

The power consumption was calculated in a unit of Ws per a C-containing reactant molecule converted or per a hydrogen molecule produced (Ws/M) using the following equation:

$$\text{Power consumption} = (P)(60) / (\tilde{N})(M) \tag{9}$$

where
P	=	Power (W)
$\tilde{N}$	=	Avogadro's number = 6.02×10^{23} molecules·g-mol^{-1}
M	=	Rate of converted carbon in feed or rate of produced hydrogen.

3. Results and discussion

3.1 Effect of stage number of plasma reactors on reactant conversions and product yields

Figure 1(a) illustrates the influence of the residence time on the reactant conversions and product yields at a constant total feed flow rate. The results show that all reactant conversions tended to increase with increasing stage number of plasma reactors, especially in C_3H_8 conversion. Surprisingly, the CO_2 conversion was found to reach to a positive value when the system was operated at 3 or 4 stages, which was different from the previous work [Rueangjitt, 2009]. Furthermore, the CO yield dramatically increased with increasing stage number corresponding to increasing residence time, whereas the C_2 yield slightly increased - Figure 1(a). In the meantime, the H_2 yield initially increased with increasing stage number from 1 to 3 stages but the H_2 yield remained almost unchanged with increasing stage number of plasma reactors from 3 to 4. The results can be explained by the fact that the increase in stage number of plasma reactors at a constant feed flow rate simply increases residence time of the system, causing more reactants to be collided with the generated electrons. .

The reactant conversions and product yields as a function of stage number of plasma reactors at a constant residence time of 4.11 s are depicted in Figure 1(b). The results reveal that both CH_4 and C_2H_6 conversions and the C_2 yield remained almost unchanged with increasing stage number of plasma reactors, while the C_3H_8 tended to primarily increased and then remained almost unchanged. Besides, CO_2 conversion and CO yield tended to increase with increasing stage number of plasma reactors from 1 to 3 stages, and then declined with increasing stage number of plasma reactors from 3 to 4 stages. It is interesting that the O_2 conversion showed the opposite trend. The results suggest that

an increasing in stage number increases the oxidation of CO to reproduce CO_2. Besides, it was found that increasing stage number of plasma reactors from 1 to 4 stages had an insignificant impact on the H_2 yield. It can be implied that the H_2 yield was independent of stage number of plasma reactors in the investigated range.
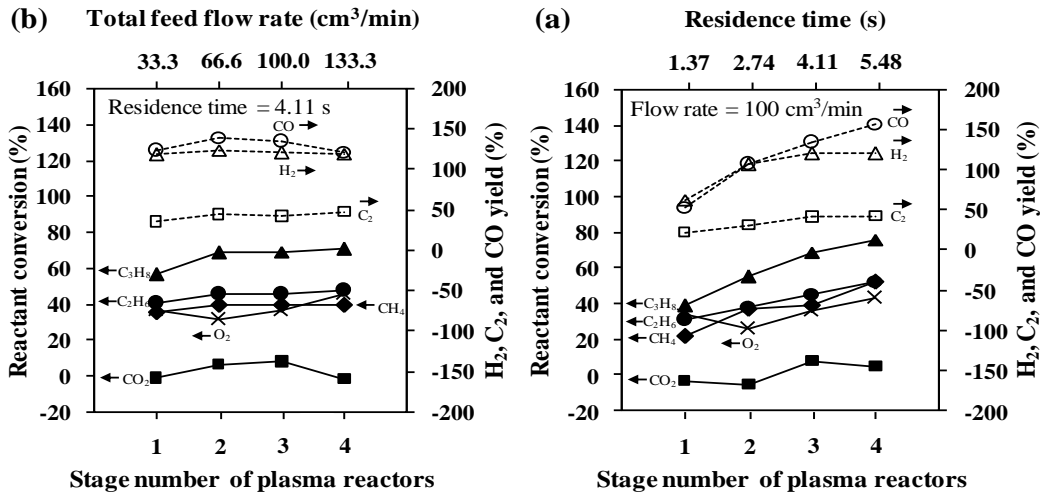

Figure 1: Effect of stage number of plasma reactors on reactant conversions and product yields for the combined steam reforming and partial oxidation of simulated natural gas (a) at a constant total feed flow rate of 100 cm^3/min and (b) at constant residence time of 4.11 s (steam content, 10 mol%; input voltage, 14.5 kV; input frequency, 300 Hz; and electrode gap distance, 6 mm)
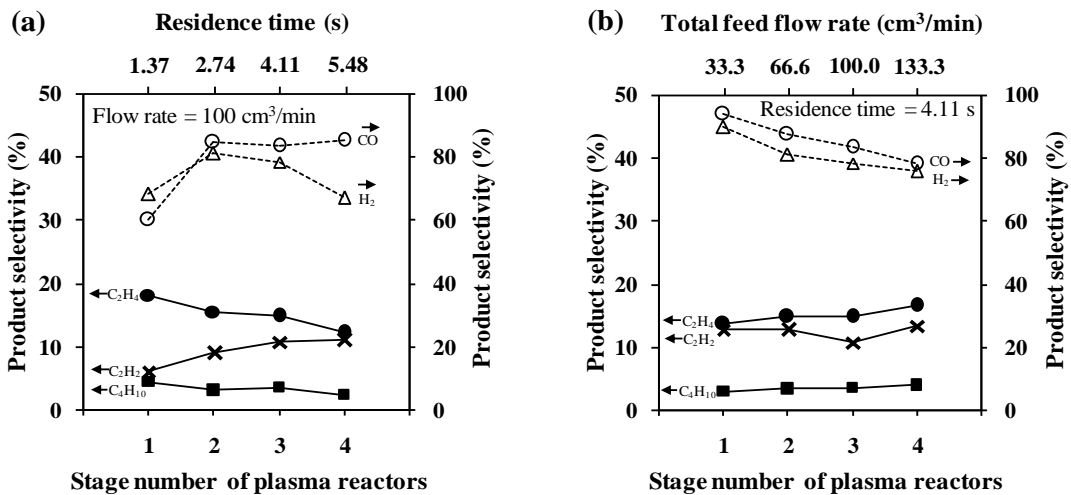

Figure 2: Effect of stage number of plasma reactors on product selectivities for the combined steam reforming and partial oxidation of simulated natural gas (a) at a constant total feed flow rate of 100 cm3/min and (b) at constant residence time of 4.11 s (steam content, 10 mol%; input voltage, 14.5 kV; input frequency, 300 Hz; and electrode gap distance, 6 mm)

3.2 Effect of stage number of plasma reactors on product selectivities and product molar ratios
The effect of stage number of plasma reactors on product selectivities at a constant feed flow rate of 100 cm^3/min is shown in Figure 2a. With increasing stage number from 1 to 4 corresponding to

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residence time from 1.37 to 5.48 s, both C_2H_2 and CO selectivities tended to increase, whereas the C_2H_4 and C_4H_{10} selectivities decreased. These results well correlated to the decreases in C_2H_4/C_2H_2, H_2/C_2H_2, H_2/CO molar ratios (Figure 3a). It is interesting to point out that the H_2 selectivity dramatically increased when increasing stage number from 1 to2), and then decreased with further increasing stage number from 2 to 4.

Figure 2b shows the effect of stage number of plasma reactors on product selectivities at a constant residence time of 4.11 s. The selectivities for both H_2 and CO significantly decreased with increasing stage number of plasma reactors from 1 to 4. On the other hand, the selectivities for C_2H_4, C_2H_2 and C_4H_{10} slightly increased with increasing stage number of plasma reactors, corresponding to the decreases in the molar ratios of H_2/C_2H_4 and H_2/C_2H_2, whereas C_2H_4/C_2H_2 slightly increased (Figure 3b). Besides, it is found that increasing stage number of plasma reactors had insignificant impact on C_2H_2 selectivity.
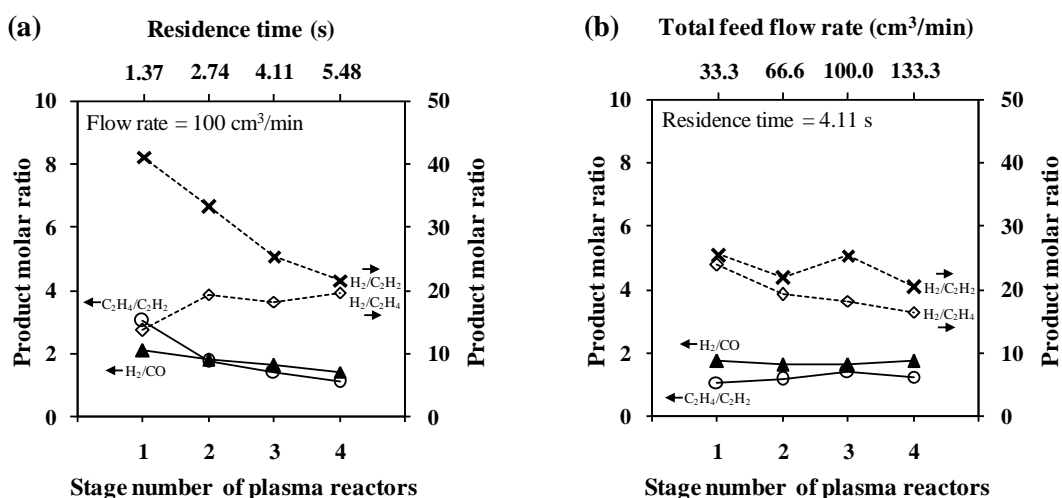

Figure 3: Effect of stage number of plasma reactors on product molar ratio for the combined steam reforming and partial oxidation of simulated natural gas (a) at a constant feed flow rate of 100 cm3/min and (b) at constant residence time of 4.11 s (steam content, 10 mol%; input voltage, 14.5 kV; input frequency, 300 Hz; and electrode gap distance, 6 mm)

4. Conclusions

The effect of stage number of plasma reactors on the combined steam reforming and partial oxidation of CO_2-containing natural gas was investigated by using non-thermal multistage gliding arc discharge under two experimental conditions at a constant feed flow rate (varying residence time with stage number) and a constant residence time (varying total feed flow rate with stage number). The major products were mainly hydrogen and carbon monoxide. From the experimental results, the stage number of plasma reactors more affected the reactant conversions, product yields, and product selectivities than residence time. Under the operating conditions at a HCs/O_2 feed molar ratio of 2/1, an applied voltage of 14.5 kV, an input frequency of 300 Hz, and an electrode gap distance of 6 mm, the lowest power consumptions were 3.49×10^{-17} Ws per molecule of reactants converted and 2.04×10^{-17} Ws per molecule of hydrogen produced was obtained from 3 stages of plasma reactors at a residence time and feed flow rate of 4.11 s and 100 cm^3/min, respectively.

References

Sreethawong T., Piyaphon T., Chavadej S., 2007, Partial oxidation of methane with air for synthesis gas production in a multistage gliding arc discharge system. International Journal of Hydrogen Energy, 32 , 1067 – 1079

Rueangjitt N., Jittiang W., Pronmai K., Chamnanmanoohtham J., Sreethawong T., Chavadej S., 2009. Combine reforming and partial oxidation of CO_2-containing natural gas using an arc multistage gliding arc discharge system: effect of stage number of plasma reactors. Plasma Chemistry and Plasma Processing, Thailand.