CHAPTER I
INTRODUCTION

1.1 State of Problems

In recent years, the demand for energy around the world has been markedly increased. As a result, many countries have realized the shortage of fuels in the near future and have tried to increase the use of alternative energy sources in order to cut down the demand of fossil fuels. There are three categories of fossil fuels: oil, coal, and natural gas. Oil is of the first priority use among those types of fossil fuels; however, the drawback is the strong impact to climate change because of its huge emission of CO_2. While coal is mainly used to produce electricity and also has a huge effect to environmental from gas emission, especially CO_2 and SO_2. Among the available fossil fuels, natural gas is currently considered to be an economical and clean fuel, and it is becoming the most interesting alternative fuel for both community and industry (Jeong, 2001).

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%, and the remaining other compositions, such as O_2, N_2, and H_2S (www.naturalgas.org). Generally, the composition of natural gas depends on geology and reservoir conditions and it is known that most natural gas, with a high concentration of carbon dioxide, has been found in Asia (Rueangjitt, 2007). Several techniques are now available for conversion of natural gas into a more valuable product called synthesis gas (H_2 and CO). They are including three conventional methods, steam methane reforming, partial oxidation of methane, and CH_4-CO_2 reforming.

The first method is the steam reforming of methane (Equation 1) over Ni/Al_2O_3 catalysts. Since steam methane reforming is highly endothermic reaction, a huge amount of supplied energy is required. The reaction normally takes place at a very high temperature of about 425-550 °C (Sreethawong, 2007).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^0_{298} = +206 \text{ kJ/mol} \qquad (1)$$

The partial oxidation of methane is also an attractive alternative for converting methane to H_2/synthesis gas. This reaction is an exothermic reaction (Equation 2); therefore, it can reduce the energy demand for the methane reforming reaction (Anderson, 2005).

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + H_2 \qquad \Delta H^0_{298} = -36 \text{ kJ/mol} \qquad (2)$$

CH_4-CO_2 reforming becomes more attractive because it not only lessons methane consumption but also use of carbon dioxide (Tao, 2010). Stoichiometrically, (Equation 3) shows that it could save half of the methane required to obtain the same amount of CO compared with either steam reforming or partial oxidation since CO_2 is also a carbon source in the reforming reaction. Therefore, CH_4-CO_2 reforming is directly beneficial for high CO_2-containing natural gases. However, CH_4-CO_2 reforming is also strongly endothermic reaction; it normally requires special methods to achieve a considerable reaction rate to meet industrial requirements.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^0_{298} = 247 \text{ kJ/mol} \qquad (3)$$

Apart from the aforementioned conventional processes, non-thermal plasma is a new efficient technique, which can be used for successfully converting natural gas into synthesis gas as well as other valuable products. Under ambient temperature and pressure, it provides highly active species (electrons, ions, and free radicals), which can initiate natural gas reforming reactions at a low temperature (Rueangjitt, 2008). The gliding arc discharge originates from an auto-oscillating phenomenon that develops between at least two diverging electrodes submerged in a laminar or turbulent gas flow. The discharge starts as thermal plasma, and it quickly becomes non-thermal plasma during the space and time evolution. This powerful and energy-efficient transition discharge combines the benefits of equilibrium and non-equilibrium discharge characteristics in a single discharge pattern. So far, there are several research studies reporting the utilization of plasma discharge for hydrocarbon reforming (Wang, 2009; Sobacchi, 2002; He, 2004; Nozaki, 2004; Kalra, 2005;

Paulmier, 2005; Wang, 2005; Ahmar, 2006; Petitpas, 2007; Yang,2009, Liu, 2996); however, to our knowledge, there have been no report on the combination of steam reforming and partial oxidation of CO_2-containing natural gas by using the gliding arc discharge system.

1.2 Objectives

The main objective of this study was to assess the roles of the gliding arc discharge plasma, in conjunction with the combined steam and partial oxidation, on the CO_2-containing natural gas reforming to produce synthesis gas. The overall objectives of this work were as follows:

1. To investigate the effect of steam on CO_2-containing natural gas reforming for the production of synthesis gas using an AC gliding arc discharge system.
2. To study the synthesis gas production from combined steam reforming and partial oxidation in an AC gliding arc discharge system.
3. To demonstrate a multistage gliding arc discharge system for the synthesis gas production from combined plasma reforming of CO_2-containing natural gas with steam and partial oxidation.

1.3 Scope of Work

In this work, simulated natural gas contained a CH_4:C_2H_6:C_3H_8:CO_2 molar ratio of 70:5:5:20 was employed as a representative of raw natural gas in Thailand, based on the data resource from PTT public company Ltd. In the first part (Chapter IV), the series of experiments were systematically carried out under different feed steam molar contents: 10, 15, 20, and 30 mol%. The interactions among the gas components of natural gas under the plasma environment as well as the significant role of steam on the plasma reaction were clarified. Additionally, the electrical parameters of input voltage and input frequency were investigated to find out the optimum conditions for the reforming of CO_2-containing natural gas with steam using an AC gliding arc discharge system. To provide a better comprehensive understanding of the plasma reforming reactions, it is worth briefly describing all the possibilities of chemical pathways occurring under the studied conditions. For the second part (Chapter V), the optimum conditions from the first part of the steam reforming were selected to study the effect of oxygen addition in reactant feed. The comparative results among different Hydrocarbons-to-oxygen (HCs-to-O_2) feed molar ratio were discussed. In addition, the operational parameters, i.e. input voltage, input frequency, and electrode gap distance were examined to find out the optimum conditions. Further third part in Chapter VI, a multistage gliding arc plasma system comprising four gliding arc discharge plasma reactors connected in series was used for the investigation of a combined plasma reforming of CO_2-containing natural gas with steam and partial oxidation to produce synthesis gas and higher hydrocarbons. Moreover, the effect of stage number of plasma reactors was investigated to maximize the process performance under two series of experiments with a fixed feed flow rate and a fixed residence time.