CHAPTER I
INTRODUCTION

In recent years, natural gas has become one of the most useful energy resources in the world due to the depletion of oil reserves. Therefore, the value of natural gas as an alternative fuel is currently increasing (Jeong *et al.*, 2001). Generally, natural gas contains a large amount of methane and significant amounts of ethane, propane, carbon dioxide, and nitrogen, and its composition varies according to the geological conditions in different parts of the world. Because methane is not only an inexpensive fuel but also an environmentally safe fuel, attempts of converting methane to hydrogen and higher hydrocarbons with alternatives of new technology have been increasingly studied. Moreover, the direct utilization of methane and carbon dioxide has been area of great interest due to its environmentally friendly concept for decreasing greenhouse gas emission.

In carbon dioxide reforming of methane, the natural gas can be used as a potential feed to produce synthesis gas shortly called as syngas, a mixture of hydrogen and carbon monoxide, which is used in various petrochemical processes, such as methanol synthesis and the so-called Fischer-Tropsch synthesis to produce liquid hydrocarbons. It has raised interest in its use as an alternative energy source because of the two main advantages of producing the hydrogen energy and reducing the greenhouse effect simultaneously.

Nevertheless, carbon dioxide reforming of methane, as shown in Eq. (1), using conventional catalytic methods often encounters two problems. It is a highly endothermic reaction consuming much energy, and the deactivation of catalysts used due to coke deposition on the catalyst surface usually occurs under various reaction conditions (Li *et al.*, 2004).

Carbon dioxide reforming of methane;

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \qquad \Delta H_{298K} = 247 kJ/mol \qquad (1)$$

The second route for methane conversion to syngas is the steam reforming, as shown in Eq. (2). This reaction is also highly endothermic, which is the same as the carbon dioxide reforming, resulting in high energy consumption. Steam reactors generally run with excess amounts of water in order to prevent the deposition of carbon on catalysts (Hwang *et al.*, 2003). Steam reforming of methane has poor selectivity to CO and produces syngas with a high H_2/CO ratio, while carbon dioxide reforming of methane gives a high CO selectivity (Xu *et al.*, 1999).

Steam reforming of methane;

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad \Delta H_{298K} = 206.2 \text{ kJ/mol} \qquad (2)$$

Another way to produce syngas is catalytic partial oxidation of methane as shown in Eq. (3). The catalysts investigated are mainly supported Ni and noble metal catalysts. The latter are more active but comparatively cost-ineffective, while nickel-based catalysts show high activity and selectivity with low cost but coke deposition on nickel occurs much easier than on noble metals (Juan-Juan *et at.*, 2004). This process gives high activity and selectivity but cannot be easily controlled because of the generation of hot spots in the catalytic bed due to its exothermic nature (Xu *et al.*, 1999).

Partial oxidation of methane;

$$CH_4 + \tfrac{1}{2} O_2 \longrightarrow CO + 2H_2 \qquad \Delta H_{298K} = -38 \text{kJ/mol} \qquad (3)$$

The combination of these reactions can potentially provide good and synergistic results. For example, a combination of carbon dioxide reforming and steam reforming of methane can reduce the carbon formation on the catalyst surface because the C/H ratio, as well as the C/O ratio, in the feed decrease, resulting in a controlled and limited carbon formation (Effendi *et al.*, 2002). In addition, a combination of carbon dioxide reforming and partial oxidation of methane has a benefit in terms of balancing the heat load (Supat *et al.*, 2003).

One attractive method for reforming hydrocarbon compounds is to use non-thermal plasma processes. The plasma contains highly active species, such as electron, ions, and radicals, which can catalyze conversions of feed into more valuable products. The non-thermal plasma processes basically generate energetic electrons by applying a high voltage across electrodes to create electric discharge. The electric discharge produced also provides heat to the system, apart from generating radical and excited species to initiate and enhance the plasma chemical reactions (Paulmier and Fulcheri, 2005). Furthermore, the plasma reforming processes can be operated at mild conditions with less power consumption, and they have been employed for many applications (Chavadej *et al.*, 2007; Eliasson *et al.*; 1987, Krawczyk, K., and Młotek, M., 2001; Rosacha *et al.*, 1993). A gliding arc discharge is a new discharge type of non-thermal plasma, which successfully provides the most effective non-equilibrium plasma with high productivity and good selectivity. The gliding arc discharge has at least two diverging knife-shaped electrodes, which are placed in a rapid feed gas flow. A high voltage is generated across the fast gas between the electrodes. The electric discharge initially forms at the narrowest gap and then spreads along the knife-edges of the electrodes and finally disappears. New discharges instantaneously reform at the initial point repeatedly. Therefore, there are several researches reporting the utilization of gliding arc discharge for many purposes, including natural gas and methane conversion for production of higher hydrocarbons and synthesis gas (Rueangjitt *et al.*, 2007-2008; Sreethawong *et al.*, 2007).

The purpose of this study was to apply the multistage gliding arc plasma system for a combined reforming and partial oxidation of simulated natural gas, which contained a CH_4:C_2H_6:C_3H_8:CO_2 molar ratio of 70:5:5:20, to produce hydrogen and higher hydrocarbons. The effect of the stage number of plasma reactors was mainly investigated on the system performance under two series of system with fixed feed flow rate and fixed residence time. Both pure oxygen and air were comparatively used as the oxygen source. The optimum stage number with corresponding power consumption was obtained.