

CHAPTER I INTRODUCTION

Vast reserves of natural gas, which have been discovered in various parts of the world, commonly contain methane as its principal component (in the range of 60-90 %). It is considerably one of not only low price fuel supplies but also an environmental safe fuel.

Attempts of converting methane to higher hydrocarbon products such as ethane, ethylene or some liquid oxygenates such as methanol or formaldehyde have been receiving huge increasing interests as the new upgrading route of the methane utilization.

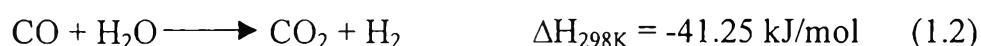
Most of those proven technologies and efforts on the development of such methane conversion, though commercially available, still have to be based upon the multi-step reaction process starting with the transformation of methane and water into synthesis gas, i.e., principally the mixture of CO and H₂, via the steam reforming process before being converted further into either methanol or via the so-called Fischer-Tropsch (FT) synthesis to liquid hydrocarbons.

The development of methane conversion, though commercially available, still has to be based upon multi-step reaction processes starting with steam reforming. The nature gas is mixed with steam at a temperature about 425-550°C and then subjected to catalytic reforming to produce synthesis gas. The following reactions that take place in the reactor seem to be highly endothermic and require a large amount of fuel (Bhatnagar, 1993).

Steam Reforming of CH₄:



Water Gas Shift:



The synthesis gas is then used to manufacture methanol by using a copper based catalyst at lower pressure (5-25 MPa) and temperature around 200-300°C. The major reactions, which take place in this processes are



The first two reactions are exothermic and lead to a reduction in volume. Normally, the first and the third reaction are used for this purpose. Moreover, synthesis gas can be converted to liquid hydrocarbon via the so-called Fischer-Tropsch (FT) synthesis (Bhatnagar, 1993).

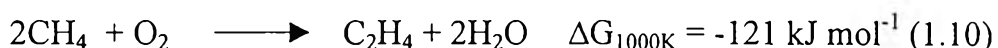
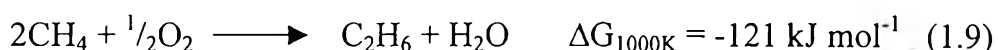
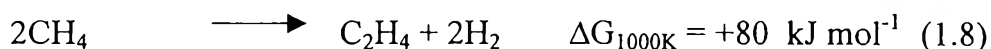
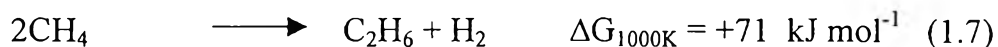
With the recognition of high investments and high production costs of these processes, the direct methane conversion paths including its direct partial oxidation (POM) to methanol and its oxidative coupling (OCM) to C₂-hydrocarbons have therefore been subjected into recent studies by many researchers. Against the principles of all those multi-step reaction processes, these two reaction are considered to be much more energy-efficient in the sense that they can bypass the highly energy-intensive step of the synthesis gas formation which is considered to be extremely endothermic reaction requiring both enormous quantities of fuel and severe reaction conditions (Poonphatanapricha, 1998).

In almost all cases, oxygen molecule (O₂) is required to be participated in these reactions in order to activate the methane molecule (CH₄). In the direct partial oxidation of methane to methanol (CH₃OH), methane is oxidized, in the situation of O₂ deficiency, at 350-500°C under high pressure condition according to the following exothermic reaction.



While the presence of oxygen, in the case of oxidative coupling of methane to C₂₊-hydrocarbon, is required for thermodynamic reasons if the reaction is to be carried out at temperature significantly below 1,600 K. This

can be illustrated by the following reactions of the methane coupling to produce either ethane or ethylene (Thanyachotpaiboon, 1996).



Unfortunately, since all these reactions would have to be operated at elevated temperatures while all those desired products (i.e., CH_3OH , C_2H_6 , C_2H_4 , etc.) tend to be far more reactive than the starting methane molecule itself, then as long as the oxygen is introduced into the reaction system, it can further oxidize these intermediate desired products into the mixture of carbon dioxide (CO_2), carbon monoxide (CO) and water (H_2O). This undesirable reaction is sometimes referred to as “deep oxidation reaction” (McAllister *et al.*, 1944).

Based upon the thermodynamic consideration, there has been an expectation that if the reaction between methane and oxygen can be carried out at low temperature regions, the carbon oxides formation can be substantially reduced (Gesser *et al.*, 1985). However, to activate the methane molecule at low temperature, active species are necessary to be provided in order to activate the methane molecule. Air is not only an alternative source of oxygen, which comprises of nitrogen and oxygen in proportion of 79 and 21 percent, respectively but also being prevalent in the atmosphere. One of the most powerful sources to activate methane molecules is pronounced by the plasmas generated in the so-called electric discharges environment.

At this point, it is necessitated to mention clearly that it was the aim of this work to illustrate the feasibility of introducing AC electric discharges environment as a new mean of activating the methane molecules with air to initiate and thereby carry out the methane and oxygen conversions to produce synthesis gas as well as higher valuable hydrocarbon products.