

# CHAPTER I

## INTRODUCTION

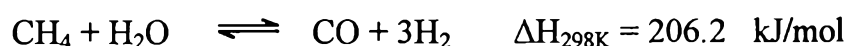
Vast reserves of natural gas generally contains methane as its principle component (see Table 1.1). They have been discovered in various parts of the world. Its present utilization strategies have relied on combustion application as a low-price environmentally safe fuel. Attempts of converting methane to higher carbon molecules of hydrocarbon products such as ethane, ethylene or some liquid oxygenates such as methanol or formaldehyde are now receiving increased interest as a new upgrading route for methane utilization.

**Table 1.1** Composition of natural gas in Thailand (NPC paper, 1995)

Composition	%Vol.
Methane	68.0
Ethane	8.6
Propane	4.5
CO <sub>2</sub>	15.6
Others	3.3

The development of methane conversion, though commercially available, still has to be based upon multi-step reaction processes starting with steam reforming. The natural gas is mixed with steam at a temperature about 425-550°C and then subjected to catalytic reforming to provide 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 CH<sub>4</sub>:



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 process are



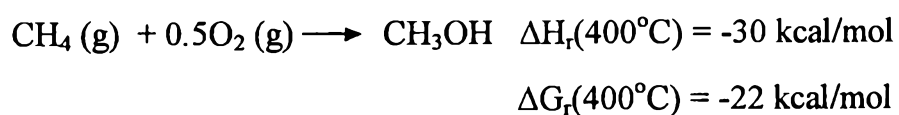
The first two reactions are exothermic and lead to a reduction in volume. Normally, the first and the third reactions are used for this purpose. Moreover, synthesis gas can be converted to liquid hydrocarbon via the so-called Fischer-Tropsch (FT) synthesis (Bhatnagar, 1993).

From that natural gas or methane-based methanol, the gasoline-type hydrocarbons as well as ethylene and propylene can be produced catalytically from the Methanol-to-Gasoline (MTG) or Methanol-to-Olefins (MTO) reactions with the aid of zeolite catalysts. The success of the MTG process is currently settled in New Zealand and the commercial FT plant was already reported being constructed in Malaysia (Baerns, 1992).

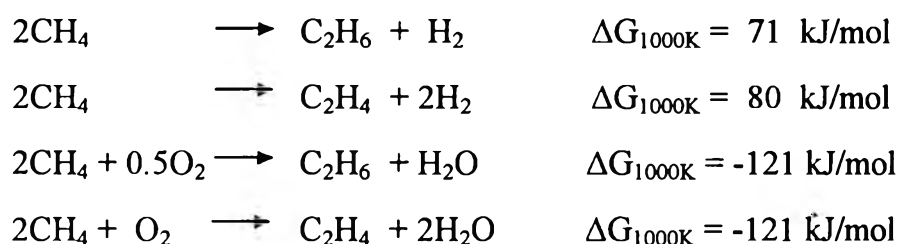
With the recognition of economic-intensive investment and high production costs of these processes, the direct methane conversion paths have therefore been the subject of recent studies by many researchers. Two major routes for this conversion are the direct partial oxidation of methane (POM) to methanol and the oxidative coupling of methane (OCM) to ethane and ethylene. Against the principles of all those multi-steps reaction processes, these two routes 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.

Furthermore, another major reason that has much influence on the increasing interest of direct methane conversion is an abundant methane in natural gas. Since most of the large deposits of natural gas are geographically located in very remote areas, precluding any economic means of its transportation to the place of consumption via pipeline networks. This causes vast quantities of natural gas to be frequently flared in those remote wells where crude oil production are associated. And it has recently been recognized during the last decade that flaring is not acceptable from an environmental point of view. Therefore, in order to make the utilization of such remote natural gas reserves feasible, efficient methods will have to be employed to convert those remote gases into any transportable products, particularly in the form of liquid. Obviously, this intention will be even more applicable for the cases of those large offshore natural gas deposits which will eventually outpace crude oil resources in the long-range future. (Chaumette et al., 1988) This idea, coupled with the substantial need to improve the current technology on the methane conversion, has undoubtedly encouraged the increased study of direct methane conversion.

Abundant literature could be cited to illustrate the evidence of the great efforts attempting to develop direct methane conversion processes, particularly on POM and OCM reactions. (Gesser et al., 1985; Walsh et al., 1992; Periana et al., 1993; Omata et al., 1994; Casey et al., 1994; Chen and Willcox, 1994). In almost all cases, the oxygen molecule (O<sub>2</sub>) is required to participate in these reactions in order to activate the methane molecule (CH<sub>4</sub>). In the direct partial oxidation of methane to methanol (CH<sub>3</sub>OH), methane is oxidized at 350-500°C under high pressure condition according to the following exothermic reaction (Thanyachotpaiboon, 1996):



The presence of oxygen in the case of oxidative coupling of methane to  $C_2+$  hydrocarbons is required for thermodynamic reasons if the reaction is to be carried out at the temperature significantly below 1600 K. This can be illustrated by the following reactions of 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, it can further oxidize these intermediates, desired products, into a mixture of carbon dioxide ( $CO_2$ ), carbon monoxide ( $CO$ ) and water ( $H_2O$ ). This undesirable reaction is sometimes referred as “deep oxidation reaction”. Consequently, to suppress the deep oxidation reaction and to gain substantial yields from these thermal reactions, selective catalysts as well as the proper reaction conditions are extremely desired to selectively convert the methane to those desired products. This knowledge has long been the basis for most of those studies on the direct methane conversion process subjected to date (Casey, McAllister and Foger, 1944).

Based upon the thermodynamic consideration, there has been an expectation that if the reaction between methane and oxygen can be carried out in lower temperature regions, the carbon oxide 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. One of the most powerful sources to

generate such species is to applied a kind of dielectric-barrier discharge or plasma.

Some fundamentals about the plasmas and the electric discharge environment will be discussed in chapter 2. At this point, it is necessary to mention clearly that it was the aim of this work to demonstrate the feasibility of introducing such electric discharge environment as a new mean of activating the direct methane conversion to produce the higher valuable hydrocarbons.