

CHAPTER I

INTRODUCTION

Natural gas is the most widely used and least expensive of a fuel gas. It is found throughout the world in reservoirs both in-shore and off-shore, alone and in association with crude oil. The growth of the natural gas industry has been rapid and worldwide. Natural gas now supplies over 20% of the world's total energy requirements, and its use has been increasing.

Natural gas contains several gases in different proportions. It consists mostly of methane, CH_4 , saturated hydrocarbon compound and proportions of higher hydrocarbons. Other gases are also present including carbon dioxide, nitrogen, hydrogen sulfide and helium. A typical composition of natural gas is given in Table 1.1

At present, the utilization strategies of methane, as a primary component in natural gas have basically relied on combustion application as a low-price, high heat content, and environmentally safe fuel. However, the new upgrading route of the methane utilization, which attempts to convert methane into higher hydrocarbon products like ethane, ethylene or some liquid oxygenates such as methanol or formaldehyde are now being received increasing interests.

Nowadays, methane conversion, though commercially available, still have to be based upon the multi-step reaction process starting with the transformation of methane to synthesis gas, i.e., principally the mixture of CO and H_2 , via the steam reforming process before being converted further into either methanol via the so-called Fischer-Tropsch (FT) or to liquid hydrocarbons.

Table 1.1 Approximate Composition of “wet” and “dry” natural gas (Speight,1993)

Constituents	Composition (vol %)	
	“wet”	“dry”
Hydrocarbon		
Methane	84.6	96.0
Ethane	6.4	2.0
Propane	5.3	0.6
Isobutane	1.2	0.18
n-Butane	1.4	0.12
Isopentane	0.4	0.14
n-Pentane	0.2	0.06
Hexanes	0.4	0.10
Heptanes	0.1	0.08
Nonhydrocarbons		
Carbon dioxide	0-5	0-5
Helium	0-0.5	0-0.5
Hydrogen sulfide	0-5	0-5
Nitrogen	0-10	0-10
Argon	0-0.05	0-0.05
Radon, krypton, xenon	Traces	Traces

With the recognition of economic-intensive investments and high production cost of these processes, the direct methane conversion path, including its direct partial oxidation (POM) to methanol and its coupling to C_2^+ hydrocarbons have therefore been subjected to recent studied by many

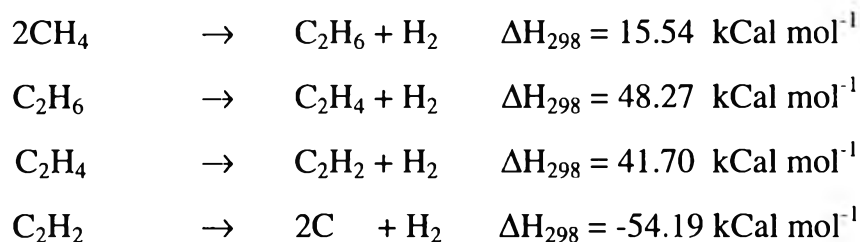
researchers.(Thanyachotpaiboon,1996.) Against the principle of all those multi-step reaction processes, these two reactions are considered to be much more energy-efficient in the sense that they can bypass the highly energy-intensive step of the synthesis gas formation, which is considered to be extremely endothermic reaction requiring enormous quantity of fuel.

Furthermore, there is another major reason that has much influence on the increasing interest of the direct methane conversion. Since most of the large deposits of natural gas (i.e., with 60-90 % of methane) are geographically located in very remote areas resulting in precluding any economic means of its transportation to the place of consumption via the pipeline networks. This causes vast quantities of natural gas being frequently flared in those remote wells where the crude oil productions are also associated with. And it has recently been recognized during the last decade that flaring is not acceptable from an environmental point of view. (Thanyachotpaiboon,1996)

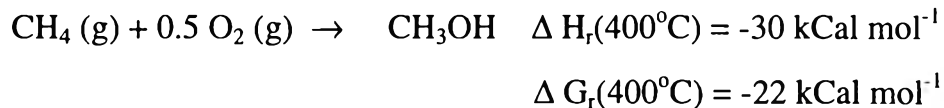
Therefore, in order to make the utilization of such remote natural gas reserves become feasible economically, some efficient methods will have to be employed to convert those remote gases into any transportable products, particularly in the form of liquid. Obviously, this intention will be even more applicable for the cases of those large offshore natural gas deposits which will eventually put pace the number of crude oil resources in the long-range future (Chaumetteet et al., 1988). This idea coupled with the substantial need to improve the current technology on methane conversion has undoubtedly encouraged studies of direct methane conversion into a spreading extent.

The direct conversion of methane can be carried out by various routes including oxidative coupling, partial oxidation, and pyrolysis. Wheellev and Wood (1928) and Fischer and Pichler (1932) were the first groups to show that by controlling the residence time of reaction, products other than carbon and hydrogen could be obtained.

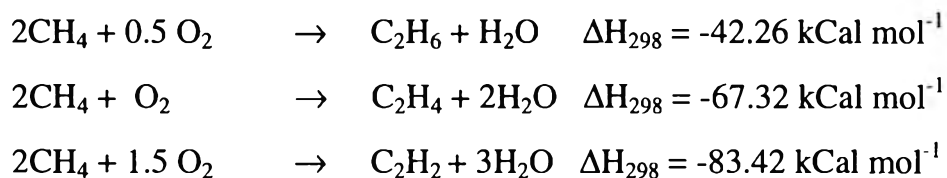
The reaction mechanism from thermal coupling of methane has been studied by various researchers (Holman et al., 1995). The overall reactions in thermal coupling of methane can be described as a stepwise dehydrogenation at high temperature.



In almost cases of partial oxidation and oxidative coupling, the oxygen molecule (O_2) is required to participate in these reactions in order to activate the methane molecule. In the direct partial oxidation of methane to methanol (CH_3OH), methane is oxidized at 350-500°C under high pressure condition according to the following exothermic reaction



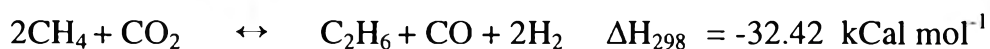
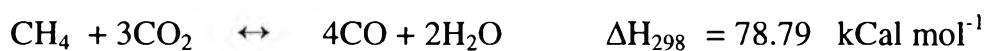
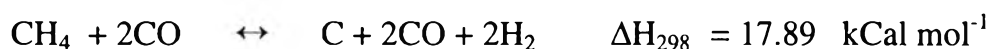
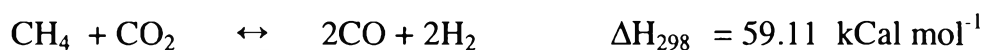
The presence of oxygen in the case of oxidative coupling of methane to C_2 hydrocarbons is required for thermodynamic reasons if the reaction is to be carried out at temperature significantly below 1600 K



Apart from methane, a primary component of natural gas, carbon dioxide is also found in a large amount in natural gas. It is usually separated and wasted to atmosphere. However, the emission of carbon dioxide plays a major role to global warming due to its greenhouse effect. The reduction and utilization of greenhouse gases such as carbon dioxide and methane, therefore, become more and more interesting. Not only to solve the global warming

problem, the products obtained from the reaction of methane and carbon dioxide will also become valuable feedstock in petrochemical industry.

The reduction of carbon dioxide by hydrocarbons, i.e. the employment of CO₂ as an oxidant, is the most promising procedure for the establishment of large scale processes involving the utilization of carbon dioxide. The direct interaction of methane with CO₂ on catalysts has been investigated by many workers (Krylov and Mamedov, 1995). It can be illustrated by the following reactions:



In generally, to activate the methane molecule at low temperature, one of the most powerful source of such species is supplied by the plasma generated in the so-called electric discharges environment.

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