THERMODYNAMIC ANALYSIS OF METHANE DRY REFORMING

KONG ZI YING

UNIVERSITI MALAYSIA PAHANG

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REFORMING

KONG ZI YING

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a_{ik}	Number of atom of the element present ineach molecule of species*i*.
A_k	total number of atomic masses of k^{th} element in the feed
n_i	number of molecules of species *i*
P^0	standard-state pressure of 100kPa,
P	pressure (kPa)
R_g	Gas constant
T	Temperature (K)
y_i	Mole fraction of species *i* in a gas phase
λ_k	Lagrange multiplier of the k^{th} element,
ΔG^{o}_{fi}	Standard Gibbs energy change of formation for species *i*(J/mol)

ANALISA TERMODINAMIK TINDAK BALAS METANA DENGAN KARBON DIOKSIDA

ABSTRAK

Metana adalah gas asli yang wujud alam kuantiti yang terbanyak di muka bumi ini. Metana boleh bertindak balas dengan karbon dioksida untuk menghasilkan gas sintesis (campuran gas hydrogen dan karbon monoksida). Dalam situasi petrokimia di dunia yang semakin berkurangan, gas sintesis boleh ditukar kepada petrol gred bahan api melalui tindak balas kimia *Fischer-Tropsch*. Objektif tesis ini adalah untuk mengkaji aspek termodinamik tindak balas metana-karbon dioksida (CH_4-CO_2) dari suhu 500 ke 1000K di bawah tekanan atmosfera serta perbezaan nisbah metana kepada karbon dioksida. Kaedah yang digunakan dalam kajian ini adalah peminimunan tenaga bebas Gibbs. Keputusan pengiraan menunjukkan bahawa suhu mempengaruhi komposisi produk keluaran. Pada suhu rendah (500K), termodinamik menunjukkan bahawa tindak balas CH_4-CO_2 adalah hampir tidak wujud. Perbezaan nisbah CO_2:CH_4 mengurangkan suhu pengaktifan bermulanya pemendapan karbon. Pemendapan karbon berlaku di mana perbezaan nisbah CO_2:CH_4 mengurangkan suhu tindak balas. Pada suhu 1000K dan nisbah CO_2:CH_4 bersamaan tiga, nilai pembentukan karbon ialah 1.7.

THERMODYNAMIC ANALYSIS OF METHANE DRY REFORMING

ABSTRACT

It is well known that methane (a natural gas that is abundantly available) can be reacted with carbon dioxide to produce synthesis gas (a mixture of hydrogen gas and carbon monoxide). Syngas may be converted to gasoline-grade fuels via Fischer-Tropsch synthesis since the petrochemicals in the world was becoming lesser and lesser. In lieu of the significance of the said reaction, the objective for the current work is to study the thermodynamic aspect of methane dry reforming at reforming temperature from 500 to 1000K at atmospheric pressure and different methane to carbon dioxide ratios. The method used in this research is Gibbs free energy minimization. Computation results showed that the temperature affected the product distribution. At low temperature (500K), thermodynamic consideration alone indicated that the methane dry reforming reaction is almost non-existent. Different CO_2/CH_4 ratios decrease the temperature at which the onset of carbon deposition occurs. Carbon forms at lower temperature and high reactant ratio. At temperature 1000K and CO_2:CH_4 ratio of 3, the carbon formation value is 1.7.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Hydrogen (H_2) is primarily produced from reforming process. Currently, more than 60% of the world's feedstock of hydrogen production is coming from natural gas (Chen, 2009), a mixed of methane gas, light hydrocarbons and non-hydrocarbon gases. Typically, it is found near the crude oil reservoir. Natural gas contains more than 85% of methane (CH_4), with higher hydrocarbons (ethane to hexane or short carbon chain paraffin) present in a quantity of up to a maximum of 16%, while diluents (nitrogen and carbon dioxide (CO_2)) can account to a maximum of 15% (Tung, 2005). In the natural gas, CH_4 is the most abundant gas compared to the other constituents in alkanes group *i.e.* ethane, propane and *etc*. Significantly, CH_4 can react with CO_2 to produce synthesis gas (also known as syngas), therefore presenting a viable solution to utilization of both gases since CH_4 and CO_2 are greenhouse culprits. In addition, CH_4 and CO_2 are both inexpensive gases, exhibit low reactivity and hence explain its thermodynamic stability (Tung, 2005). The reaction between CH_4 and CO_2 or carbon dioxide reforming of methane is expected to address some environment issues whilst contribute to downstream petrochemical activities via gas-to-liquid (GTL) technology.

1.2 Problem Statement

There are three problem statements in this research. Firstly, deposition of carbon is not desirable during methane dry reforming as it will deactivate the catalyst. From this work, carbon lay down region is duly identified.

Secondly, the effects of temperature and reactant ratio on product distribution to obtain the desired syngas whilst minimize any side reactions will be identified. During methane dry reforming, in addition to the main reaction; there are other side-reactions that compete with the primary reaction resulting in the decrease of major products. The extent of all these reactions is normally a function of reaction conditions, *i.e*. pressure, temperature and reactant ratio. Fortunately, thermodynamic is an effective tool that professes a first-hand perspective into reforming reaction from theoretical framework. In particular, there are also scarcities of thermodynamic studies in the open literature for methane dry reforming. Hence, it will be of great interest to apply thermodynamic study in the current system that involves CH_4 and CO_2.

Thirdly, methane steam reforming is traditionally employed in petrochemical industry to produce H_2/syngas (mixture of H_2 and CO) for further downstream processes. Nevertheless, for regions with water-scarcity issue, dry reforming (using CO_2 to replace water) of methane presents an attractive solution to extract the same products from methane. Furthermore, CO_2 is a greenhouse gas and its damaging effect to the environment need to be checked via appropriate CO_2 capture and utilization.

1.3 Research Objective

The objective of this research is to study the thermodynamic aspect of methane dry reforming system using Gibbs free energy minimization method at reforming temperature from 500 to 1000K at atmospheric pressure and different ratios of methane to carbon dioxide.

1.4 Significance of Research

Syngas is a useful gas in chemical industries. In particular, syngas production from methane dry reforming presents an effective reaction pathway in reducing global warming as both CH_4 and CO_2 are greenhouse gases. This research will provide a theoretical insight into variation of product distribution as a function of reaction temperature and reactant ratios during methane dry reforming. From the results obtained, ideal conditions that suppress the side reactions resulting in optimal yield of H_2/syngas can be identified before actual laboratory work being undertaken. Significantly, this also helps in elucidating plausible reaction mechanisms.

1.5 Scopes of Research

The scopes of this research are listed below:

i. To identify all plausible reactions during methane dry reforming
ii. To study the reaction equilibrium constant ($K_{equilibrium}$) as function of reaction temperature
iii. To study the effect of temperature and reactant ratios on product distribution
iv. To identify the effect of temperature and reactant ratios on carbon deposition

1.6 Structure of Thesis

This study comprises of five chapters which are introduction, review of literature, methodology, result and discussion as well as conclusions and recommendations. In introduction, the chapter is sub-divided into introduction, problem statement, research objective, significance of research, scope of research and structure of thesis. Review of literature is about finding the prior studies related to the study of the thermodynamic of methane dry reforming. The literature review is divided into several parts, viz. introduction, CH_4, CO_2, reforming process and thermodynamics. Methodology is sub-divided into data analysis and computation procedures by Gibbs free energy minimization method. The next chapter is result and discussion which divided into four parts which are introduction, reaction equilibrium constants, heat of reaction, product distributions and carbon formation region. Conclusions and recommendations are discussed in the last chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Recently, there is a renewed solicitude among the mass population with the greenhouse gases and its potentially catastrophic effects to the global weather. Specifically, methane (CH_4) and carbon dioxide (CO_2) are both greenhouse gases. Hence, a reduction of both species in our atmosphere is extremely vital (Wang and Lu, 1996).

It has been claimed that CH_4 is 21 times more dangerous greenhouse agent than CO_2. Significantly, the concentrations of CH_4 gas have been increasing rapidly in atmosphere compared to CO_2. CH_4 can stay in the atmosphere for about seven years while CO_2 is longer than CH_4 which is approximately 10 years. These gases in the atmosphere will trap the heat, subsequently reflected the heat wave back to the earth. As a consequence, the earth warmed due to this dose of energy. The greenhouses gases are contributed by the combustion of petroleum, natural gas, coal mining, animal agriculture, waste water sludge, manure and others.

According to Guido and Foster, one ton of hydrogen can produce 9 to 12 tons of CO_2 depends on the quality of natural gas. In local front, emission of CO_2 is on the increase every year since 1970 (Figure 2.1). This is primarily caused by unrestrained logging and insufficient photosynthesis. Fortunately, CO_2 and CH_4 can be harnessed into synthesis gas production.

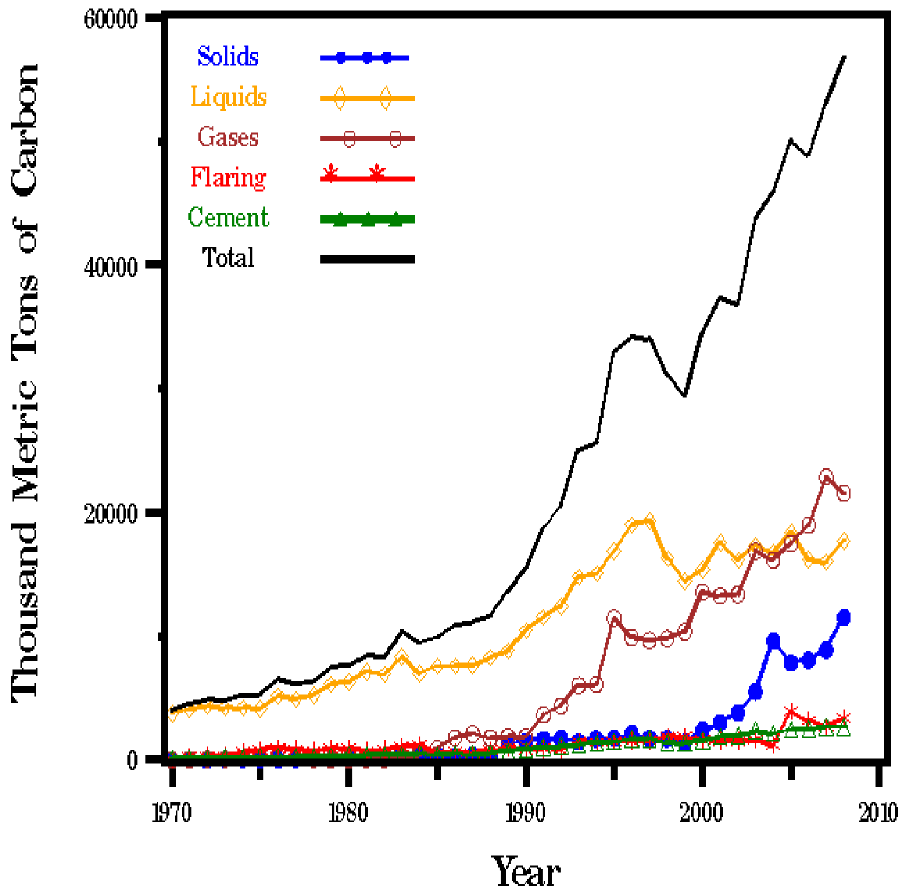

Figure 2.1 CO_2 Emission from Malaysia (source: CDIAC, 2012)

Syngas is a combination of carbon monoxide (CO) and hydrogen (H_2) gas with different ratios. Syngas is an important intermediate for converting hydrocarbon resources into useful chemicals such as methanol, dimethyl ether and others. It may be produced from the reformation of hydrocarbon, gasification of coal and others. In addition, it can also be produced by dry reforming in the excess of coke over gases. This is because the coke over gases contain CH_4, CO, H_2 and nitrogen gas (N_2) (Fidalgo and Menendez, 2011). The process of producing syngas is depicted in the syngas cycle as shown in Figure 2.2 (Rostrup-Nielsen, 2002). Syngas is the building block for liquid fuel production via Fischer-Tropsch (F-T) process. It is also a major source of hydrogen in the refinery processing (Nikoo and Amin, 2010). According to Tung (2005), syngas is an important component in the chemical and petrochemical industries such as methanol, production of ammonia, and others.

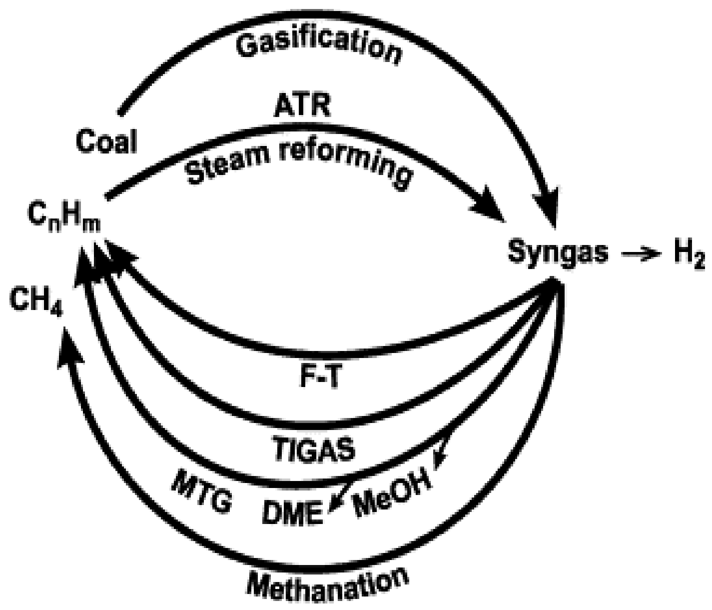

Figure 2.2 Syngas Cycle

Syngas is used as an intermediate in producing synthetic fuel for use as fuel via F-T process. Significantly, it has been employed by Mobil Company in converting methanol to gasoline process. Apart from that, ethanol can also be formed from syngas as a desired biofuel.

According to The Columbia Electronic Encyclopedia (2007), F-T process is a method of synthesis of hydrocarbons and other aliphatic compounds. Syngas, a mixture of hydrocarbon and carbon monoxide are reacted in the presence of an iron or cobalt catalyst and heat is evolved. The products such as CH_4, synthetic gasoline and waxes, and alcohols are formed while water or CO_2 as a byproduct. The process is named after F. Fischer and H. Tropsch for their pioneering work in 1923.

Figure 2.3 shows the F-T technology. Natural gas, coal and biomass can undergo syngas production to produce a mixture of carbon monoxide and hydrogen to go through F-T liquid synthesis. Liquid fuels are the downstream product of syngas. Different ratios of hydrocarbon and CO will produce different types of transportation fuels such as diesel.

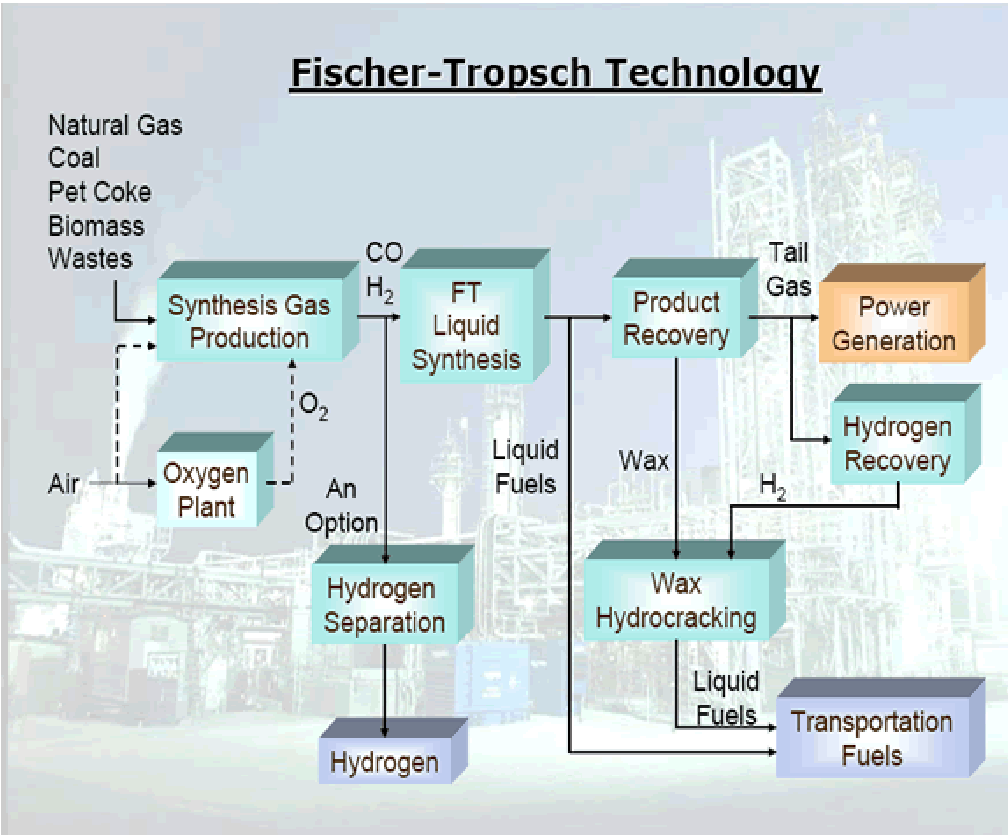

Figure 2.3 Fischer-Tropsch Technology

In the Fischer Tropsch industrial process, carbon monoxide is reacted with hydrogen to form hydrocarbons at 150 bar and 700 K in the presence of catalyst. The chemical reactions of natural gas to liquids applications are (Ragheb, 2010):

$$CH_4 + \frac{1}{2}O_2 \rightarrow 2H_2 + \mathrm{CO} \tag{2.1}$$

With Ni and Co as catalyst:

$$2\mathrm{nH_2} + \mathrm{nCO} \xrightarrow{\mathrm{Ni,CO}} \mathrm{nH_2O} + \mathrm{C_nH_{2n}} \tag{2.2}$$

With Fe catalyst:

$$\mathrm{nH_2} + 2\mathrm{nCO} \xrightarrow{\mathrm{Fe}} \mathrm{nCO_2} + \mathrm{C_nH_{2n}} \tag{2.3}$$

2.2 Methane

Figure 2.4 shows the structure of CH_4 in tetrahedral shape. Methane is a chemical compound with a chemical formula of CH_4. The CAS number of methane is 74-82-8. It is also known as carbon tetrahydride, hydrogen carbide, marsh gas and methyl hydride. CH_4 is the principal component (~90 percent) of natural gas.

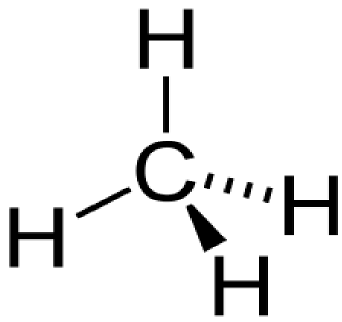

Figure 2.4 Structure of Methane

2.2.1 Physical Properties

CH_4 is an odorless, tasteless, colorless flammable gas which is lighter than air. The molar mass of CH_4 is 16.04g/mol. The boiling point of CH_4 is 109-113K while melting boiling is 90.7K. It is a non-polar molecule and is insoluble in water. It is a renewable source of natural gas since it comes from decaying garbage (Indiamart, 2012). Specific gravity of CH_4 is 0.565 while the solubility in water is 22.7 mg/L.

2.2.2 Chemical Properties

Table 2.1 lists some chemical properties of CH_4 at 298K:

Table 2.1 Chemical Properties of CH_4

Chemical properties	Value
Standard enthalpy of formation, $\Delta H^0_{298\ K}$	-74.87kJ/mol
Standard enthalpy of combustion, $\Delta H^0_{298\ K}$	-890.3kJ/mol
Standard molar entropy, $S^0_{298\ K}$	186.25J/kmol
Specific heat capacity, C	35.69J/kmol

2.3 Carbon Dioxide

Carbon dioxide is usually considered as an undesired material in the waste stream. According to Ragheb (2010), CO_2 is generated as a waste byproduct in fossil fuels combustion, chemicals production and others. Sometimes, natural gas contains some sizeable amount of CO_2. Normally, CO_2 produced through human activities such as burning of fossil fuels. CO_2 undergoes photosynthesis to produce oxygen but, increasing deforestation terminates the cycle. The amount of CO_2 in the atmosphere is around 0.034 volume percent (v/v%) (Tung, 2005). Behr (1988) has estimates that total amount of carbon exists as CO_2 gas in atmosphere is about 720 x 109 tones.

CO_2 is a non-toxic material at temperature -78.9^{0}C and releases 645kJ/kg energy when heated from -78.9^{0}C to 0.0^{0}C (Aresta and Forti, 1986). CO_2 is mostly use in chemical industry such as refrigerant agent, carbonate drinks and others.

2.4 Reforming Process

There are three primary pathways to carry out the reforming process of CH_4 to syngas. These are:

i. Steam reforming
ii. Dry reforming
iii. Partial oxidation using oxygen (POX)

2.4.1 Steam Reforming

Steam reforming produces syngas with a H_2/CO ratio of three (Gaur, 2011). Steam reforming process needs higher operating pressure than dry reforming (typified by 30-40 bars). This causes expensive operating costs. It has been shown that dry reforming process has the lowest operating expenses since CH_4 and CO_2 are both inexpensive materials (Gaur, 2011). Methane reacts with steam to produce carbon monoxide and hydrogen. According to Guido and Foster, 95% of hydrogen for refinery process is produced by hydrocarbon steam reforming. With emergence of advanced catalyst, steam reforming process can produce higher selectivity of hydrogen (Authayanun *et al.*, 2011). Steam reforming of methane involves two reactions as stated Eq. (2.4) and (2.5) (Hacarlioglu and Oyama, 2006; Sun, 2011):

$$CH_4\,(g) + H_2O\,(g) \leftrightarrow CO\,(g) + 3H_2\,(g) \qquad \Delta H^0_{298} = 206\text{kJ/mol} \qquad (2.4)$$

$$CO\,(g) + H_2O\,(g) \leftrightarrow CO_2\,(g) + H_2\,(g) \qquad \Delta H^0_{298} = -41\text{kJ/mol} \qquad (2.5)$$

2.4.2 Dry Reforming

Dry reforming is a method in which CH_4 reacts with CO_2 to produce syngas. It is also known as carbon dioxide reforming of methane. Dry reforming produces a hydrogen-carbon ratio of two, thus the syngas is well suited for liquid-fuel synthesis (Niclolas, 2011; Neal *et al.*, 2011). Since it has low H_2/CO ratio, it undergoes complete conversion. Dry reforming is useful in remote gas fields where there is an abundance of CO_2. Dry reforming favours high temperatures and low pressures.

Thermodynamically, dry reforming occurs at temperatures higher than 640 ℃ but in reality, temperature higher than 800 ℃ is needed to achieve acceptable conversion due to the stoichiometric ratio of CH_4/CO_2. If the reaction undergoes at temperature lower than 800 ℃, carbon deposition may be formed. Carbon deposition is produced from decomposition of CH_4 at high temperature (Fidalgo and Menendez, 2011).

$$CH_4\ (g) + CO_2\ (g) \leftrightarrow 2CO\ (g) + H_2\ (g) \qquad \Delta H^0_{298} = 247 kJ/mol \qquad (2.6)$$

2.4.3 Partial Oxidation using Oxygen (POX)

POX produces syngas with a H_2/CO ratio of two (Gaur. S, 2011). The reaction is exothermic and easily undergoes without any catalyst (Hoang *et al.*, 2005). Piboon *et al.* (1999) found that partial oxidation of CH_4 can be carried out over platinum or ruthenium, on CeO_2-ZrO_2 supported catalyst in the absence of gaseous oxygen.

$$CH_4\ (g) + \frac{1}{2}O_2\ (g) \leftrightarrow CO\ (g) + 2H_2\ (g) \qquad \Delta H^0_{298} = -38\ kJ/mol \qquad (2.7)$$

2.5 Thermodynamics

There are many ways to investigate the dry reforming process. One of the ways is thermodynamic analysis. It provides a fundamental study into methane dry reforming process. Thermodynamic can be applied in science and engineering such as phase transition, chemical reaction and transport phenomena.

Thermodynamic analysis plays an important role in chemical engineering. It is used to develop suitable strategies to get the most desired products. Thermodynamic aspect is a branch to define macroscopic variables such as temperature, pressure, enthalpy, entropy and heat that describe how they are related. Previously, catalyst studies of CH_4 react with different type of catalyst such as nickel, Pt/ZrO_2 and others to accelerate the process, decrease the activation energy to get the desirable product.

Dry reforming of CH_4 is endothermic and requires a large amount of heat. According to Sun *et al*. (2011), dry reforming of CH_4 is reversible and highly endothermic, resulting in the formation of syngas, a mixture of CO and H_2. Dry reforming of CH_4 is appealing due to its high purity and lower H_2/CO ratio of syngas than steam reforming and POX. Edwin *et al.* (2012) also stated that the major advantages of dry reforming of CH_4 are the H_2/CO ratio closed to 1 which makes it suitable for the F-T synthesis. The reaction of dry reforming of CH_4 takes place as ideal which is high temperature and low pressure. Table 2.2 shows the lower and upper limit temperature for dry reforming reaction of methane.

The reaction of dry methane reforming is stated Eq. (2.8):

$$CH_4 (g) + CO_2 (g) \leftrightarrow 2CO (g) + H_2 (g) \quad (2.8)$$

However, the process may be accompanied by unwanted side reaction as shown Eq. (2.9-2.13) (Li and Xiao, 2006):

$$CO_2 (g) + H_2 (g) \leftrightarrow CO (g) + H_2O (g) \quad (2.9)$$