THERMODYNAMIC ANALYSIS OF CARBON DIOXIDE CONVERSION TO METHANOL

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By

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CANDIDATE’S DECLARATION

I hereby declare that the work, which is being presented in this dissertation entitled **“THERMODYNAMIC ANALYSIS OF CARBON DIOXIDE CONVERSION TO METHANOL”** in partial fulfilment of the requirements for the award of the degree of **Integrated Dual Degree (Bachelor of Technology and Master of technology)** in **Chemical Engineering** with specialization in **Hydrocarbon Engineering,** and submitted in the Department of Chemical Engineering of Indian Institute of Technology Roorkee, Roorkee India, is an authentic record of my own work carried out during the period from May 2015 to May 2016, under the supervision of **Dr. Prakash Biswas**, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree of this or any other Institute/University.

Date: 17.05.2016

Place: Roorkee (**MANISH KUMAR)**

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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ABSTRACT

Carbon dioxide (CO_2), a greenhouse gas, is considered to be largely responsible for global warming. Over the last two decades, mitigation of CO_2 emission has become an important area of research. One of the promising methods for mitigation of carbon dioxide emission is conversion of CO_2 into useful products and fuels such as methane, methanol, synthesis gas, di-methyl ether (DME), hydrocarbons, formates, acids, formamides etc. Thermodynamic analysis is the first step in assessing the efficacy of any chemical reaction process for practical application. In the present study, thermodynamic analysis of synthesis of methanol from CO_2 hydrogenation, dry reforming of methane and synthesis of methanol using dry reforming product was performed using the technique of Gibbs free energy minimization in MATLAB computation environment. Soave-Redlich-Kwong equation of state was used to model the real nature of reaction gases. Effects of pressure, temperature, and feed composition on conversion, selectivity and yield were investigated for each process. The conversion and product yields of the processes were compared to ascertain the suitable processes for practical application.

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Nomenclature

$\hat{a}_i$	Activity of species i in a mixture
$C^{o}_{p,i}$	Standard heat capacity of species i
$C^{o}_{p,e}$	Standard heat capacity of element e
E_j	Total number of atoms of element j
$\hat{f}_i$	Fugacity of species i in the reaction mixture
f	Fugacity of pure species i in standard state
G	Total Gibbs free energy of the system
G_i	Gibbs free energy of species i in standard state
$\Delta G_{298,i}$	Gibbs free energy change of reaction at standard conditions
ΔH_{298}	Enthalpy of formation of the species at 298 K
k	Number of elements in system
N	Number of species in system
n_i	Number of moles species i
P	Pressure of the system
$P_{c,i}$	Critical pressure of species i
P_o	Standard state pressure
R	Universal gas constant
T	Temperature of the system
$T_{c,i}$	Critical temperature of species i
y_i	Mole fraction of species i in gaseous phase
β_{ji}	Number of atoms of element j in species i
μ_i	Chemical potential of species i
$\hat{\varnothing}_i$	Fugacity coefficient of species i in reaction mixture

CHAPTER 1
INTRODUCTION

1.1. Introduction

The climate change and environmental pollution are two most serious problems of industrial age. Carbon dioxide, a major greenhouse gas, is conceded to be the paramount contributor to the greenhouse effect which leads to climate changes and global warming. Other environmental concerns that are attributed to high atmospheric concentration of Carbon dioxide are acid rains and ocean acidification (Honisch and Ridgwell, 2012). Carbon dioxide does not have immediate pernicious effect on human beings unlike other pollutants such as sulphur dioxide, hydrogen sulphide, etc.

With the boom of industrial age, atmospheric carbon dioxide concentration has risen continuously. The rampant use of fossil fuels has primary cause for rising carbon dioxide concentration. The atmospheric carbon dioxide concentration has risen from 317 ppm in 1959 to 393.81 in 2012 (NOAA). The following figure demonstrates the rise of atmospheric Carbon dioxide concentration over decades.

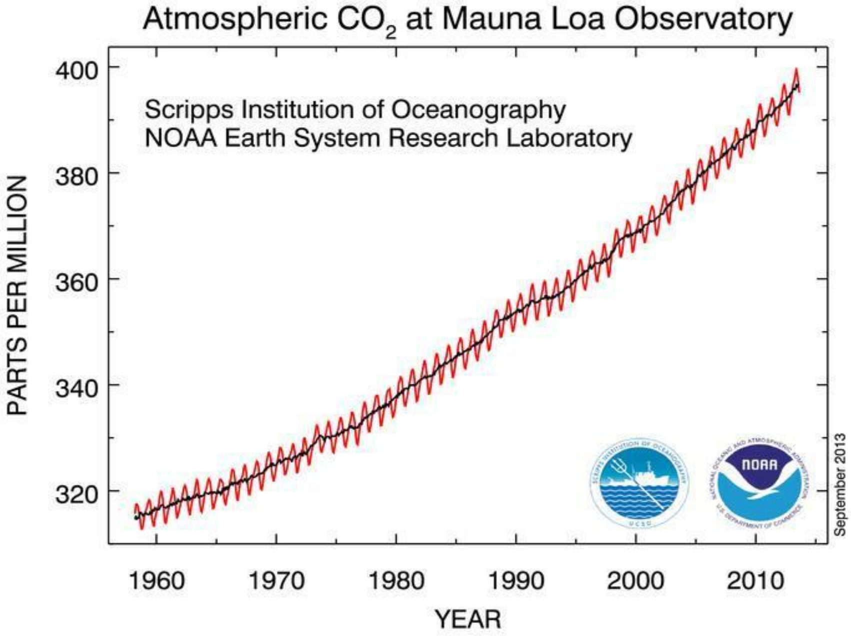

Figure 1.1- Carbon dioxide in atmosphere

(Source: National Oceanic and Atmospheric Administration Database, US Dept. of Commerce)

Gases such as nitrogen oxides, chlorofluorocarbon, carbon monoxide are stronger contributor to greenhouse effect contrasted to carbon dioxide (IPPC,*Climate Change*, 1995). The comparative strength of greenhouse effect for various gases is quantified in term of global warming potential. The following table illustrate global warming potential of certain greenhouse gases

Table 1.1 -Global Warming Potentials

Greenhouse Gases	Global Warming Potential (10 decades average)
Carbon dioxide	1
Methane	22
Nitrous oxide	311
Perfluoroethane	11800
HFC-23	9300

(Source: IPPC,Climate Change 1995)

Even though is a mild greenhouse gas, Carbon dioxide accounts for 77.3% of total greenhouse gas being emitted (IPCC, 2007).

1.2 Sources of carbon dioxide emission

The annual global carbon dioxide emission amounts at about 34 billion tons. The largest emitters of carbon dioxide are (as per 2011 data): China (29 %), the USA (16 %), the European Union (11 %), India (6 %), the Russian Federation (5 %), and Japan (4 %) (Oliver et al., 2012). The global carbon dioxide emission can be classified into seven groups on the basis of attributed activities. These groups are (IPCC, 2007)

A. **Energy Supply** (27 %) – For electricity generation, fossil fuels such as natural gas, oil and coal are used in thermal power plant which is the largest source of carbon dioxide emission in environment.

B. **Industry & Factories** (18 %) – The emission of carbon dioxide from factories & industries has been due consumption of fossil fuels. Carbon dioxide has also been produced as one of the by-product in various metallurgical & chemical industries.

C. **Deforestation** (17 %) - Deforestation, clearing of land for agriculture, forest fires and decay of fertile soils also leads to rise in carbon dioxide level in environment.

D. **Agriculture** (13 %) – Carbon dioxide emission from agriculture sector mainly come from the poor management of agricultural land soils, land renunciation, raising livestock, biomass burning and rice cultivation.

E. **Transportatio**n (14 %) – Carbon dioxide emissions from this group mostly comes from use of fossil fuels for running automobiles.

F**. Commercial and Residential Buildings** (8 %) – The emission of greenhouse gas from this group arise from burning fuels for cooking food in homes or heating buildings in cold regions.

G**. Waste and Wastewater** (3 %)

1.3 Mitigation of carbon dioxide emission

1.3.1 Various mitigation techniques for carbon dioxide emission

To curtail emission of carbon dioxide, a wide range of fixing techniques, both short & long term can be used. These solutions are broadly classified into following groups:

1. **Use of non-convectional sources of energy -** Fossil fuels contributes 83 % of global energy demand. Fossil fuels are the biggest source of anthropogenic carbon dioxide emission accounting for 74 % of global emission (IPCC, 2001). By moving on to renewable energy resources, a paramount reduction in carbon dioxide emission can be achieved. The non-convectional source of energy includes wind, solar, tidal, nuclear, biomass energy.

2. **Energy conservation-** Energy demands by various stratums of society and economy, in large are culpable reason for utilisation of fossil fuels which further leads to carbon dioxide emission. Adoption of high energy efficient technologies and judicious energy utilisation & conservation practices in transportation; urban development planning and building structural design will reduce emission of carbon dioxide.

3. **Carbon capture and sequestration-** This technique involves capturing carbon dioxide from an abundant source for example thermal power plant and further sequestration it deep below earth in geological structures. Almost 80% to 90% of emitted carbon dioxide can be capture and stored using present technological standards (IPCC, 2005).

4. **Utilization of free carbon dioxide-** Carbon dioxide has a great variety of industrial and domestic use. Various applications & uses of carbon dioxide can be grouped together into two basis division: physical and chemical. Physical applications can be listed as uses in enhanced oil recovery (EOR), beverage manufacturing, fire extinguisher, supercritical carbon dioxide extraction etc. It can be observed these applications of carbon dioxide do not at first hand minimise the emission of carbon dioxide in environment in most of the cases. Chemical application comprises of use of carbon dioxide as a raw material for production of valuable commodity. Chemical applications directly contribute to minimising emission of carbon dioxide in environment. .

1.3.2 Chemical conversion of carbon dioxide into value added products

Carbon based organic compounds contributes for 37 % of overall chemical production (Friedlingstein et al, .2010). For manufacturing of most of organic chemicals, industries have been using petroleum based carbon as initial raw material. Carbon dioxide emitted from numerous sources can become low cost source of carbon required by organic industry (Aresta and Fortis, 1987).

Carbon dioxide can act as a major feed stock for a huge number of value added chemicals such as methanol, formaldehyde, di-methyl ether, formic acid, MTBE, di-methyl carbonate, higher alcohols, methane, polycarbonates, carbon monoxide etc.

Carbon dioxide is quite stable compound due to its linear & Centro-symmetric molecular structure. As a consequence, carbon dioxide is nearly inert and most of its chemical reactions are thermodynamically unfavourable or unfeasible. Following hurdle can be resolved by using appropriate catalyst & suitable operating conditions. In today scenario, transformations of carbon dioxide into fuel and valuable commodities have achieved wide acclaim (Hu et al., 2013; Olah et al., 2009; Wang et al., 2011; Xiaoding and Moulijn, 1996). The following table lists the standard Gibbs free energy change ∆G and standard enthalpy change ∆H values for various reactions of carbon dioxide.

Table 1.2 Enthalpy and Gibbs free energy changes (Xiaoding and Moulijn, 1996)

Reactions	$\Delta G°$	$\Delta H°$
$CO_2(g) + H_2(g) \rightarrow HCOOH(l)$	-31	+34.1
$CO_2(g) + 2H_2(g) \rightarrow HCHO(g) + H_2O(l)$	-11.6	+46.5
$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l)$	-137.7	-10.5
$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(l)$	-259.9	-132.5
$CO_2(g) + CH_4(g) \rightarrow CH_3COOH(l)$	-13.2	+58.7
$CO_2(g) + C_6H_6(l) \rightarrow C_6H_5COOH(l)$	-21.5	+30.4
$CO_2(g) + CH_4(g) + H_2(g) \rightarrow CH_3CHO(l) + H_2O(l)$	-14.7	+74.1
$3CO_2(g) + CH_4(g) \rightarrow 4CO\ (g) + 2H_2O(l)$	+235.2	+209.3
$2CO_2(g) + 6H_2(g) \rightarrow CH_3OCH_3(g) + 3H_2O(l)$	-264.3	-38.1

It can be observed from the table 1.2, hydrogenation reactions of carbon dioxide are generally more feasible thermodynamically, and hence it is more suitable for practical application.

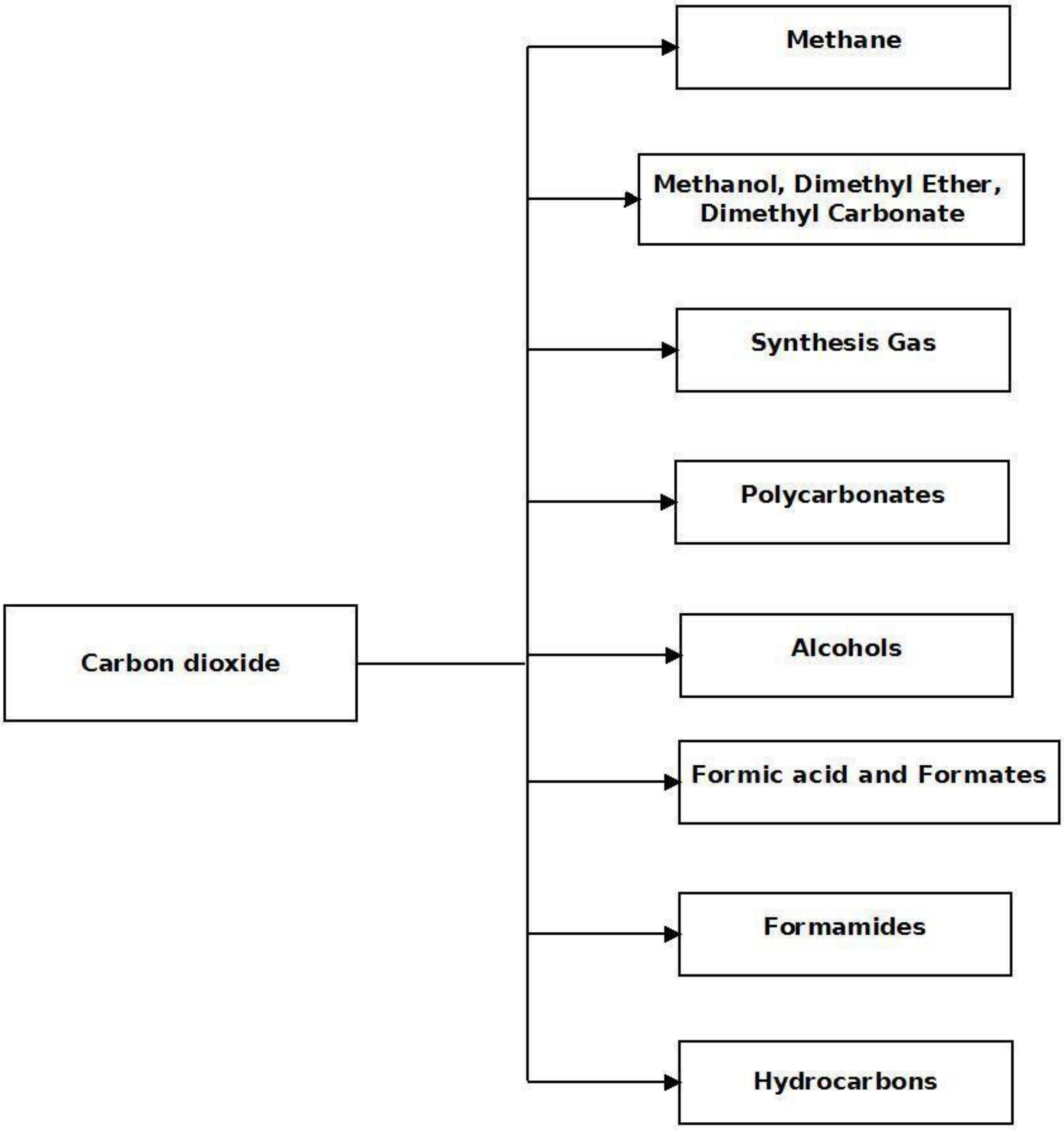

Figure 1.2 Products manufactured from carbon dioxide

1.4 Advantages of using methanol

Non-convectional sources of energy comprise of solar, wind, hydro & geothermal as well nuclear energy which are playing an increasing role in the global energy spectrum, generate primarily electricity. Even though electrical form of energy is efficient way to transmit it over a short stretch, its storage has always been a huge hurdle. Compressed air storage, flywheels, pumped hydro and batteries are available but they have their own limitations. Solar and wind are prominent renewable sources of energy, but their inconsistent & intermittent nature are major hurdle for their widespread usage. Solar based devices generate much low power output under cloudy sky and zero output at night. Similarly to solar energy, wind energy too has problem of inconsistent velocity and direction of wind. For a recognisable contribution toward energy demand or electricity production, a non-convectional source of energy must produce a stable output which has to be achieved by evening out its production fluctuations. The production of electrical power is mainly governed the market demand of electricity. Intermittent renewable energy sources don't seem to fit the adjusting electricity demand. Storing surplus electrical power and utilizing it when demanded is therefore required. A promising solution may be by storing excess electrical energy in the form of chemical energy in chemical compounds such as CH_3OH, H_2, CH_4 and higher hydrocarbons. These compounds can then be hoarded & transported and used subsequently to produce electricity or in other uses such as transportation, cooking, etc.

Hydrogen is one of the components that are obtained during electrolysis of water. Electrolysis of water is one of the techniques to convert electrical energy into chemical energy. Other techniques such as photochemical splitting, thermal splitting are new ways for splitting water into H_2 and O_2. Since long time, technique of electrolysis has been used due to its high conversion efficiency of 75 % to 80 %. Great efforts are invested to achieve higher efficiency.

Hydrogen is environmental friendly and excellent fuel since only product formed on combustion is water. Therefore, H_2 can be an attractive future energy storage media. The term "Hydrogen economy" is coined out based on concept of recycling of water to generate hydrogen. On practical grounds, use of H_2 has a many limitation and hurdle. H_2 is a highly explosive & flammable gas as well as it is a low density gas which requires high pressure for compression & storage. H_2 has high diffusivity and it can pass through most of the metals and leak out. Due to various safety drawbacks, use of H_2 has not gained much popularity.

Storage of chemical energy in form of chemical seems to be much fruitful, if chemical storage media is in liquid state rather in gaseous state. Liquid state of chemical storage media facilities its easy storage & transport. There is a need to replace liquid phase fossil fuel by a renewable and sustainable liquid fuel. Among various liquid fuels, methanol has one of the promising attributes as a fuel.

Methanol is an efficient fuel due to its high octane rating. It is a good substitute for as well as additive for motor spirit in IC engine. Methanol has various advantages attributes which make it an excellent energy carrier. Methanol can also be used as a fuel with little modification in diesel engine. It is also being used a fuel in direct methanol fuel cells. Direct methanol fuel cells convert chemical energy stored in methanol into electrical energy at normal conditions. Through dehydration of methanol, di-methyl ether can also be produced. Methanol is the most direct and simplest feedstock for producing DME. DME exist normal in gaseous phase, but it can be easily liquefied under moderate pressure. Dimethyl ether is a good substitute for diesel due to its high cetane rating. For electrical power generation in gas turbines, both methanol, & di-methyl ether can be used as a fuel. Technological advancement has led to development of various fuel conversion techniques such as methanol to gasoline process developed by Mobil. Methanol is also a common feedstock for various industrial chemicals such as HCHO, CH_3COOH and MTBE. Ethylene & propylene can also be manufactured through methanol to olefins process (MTO). Ethylene & propylene is the most key feed stock for polymer industry. Various other hydrocarbons can be obtained through conversion of methanol via advance techniques.

Methanol is a major organic feedstock compound for chemical industry. The annual global production of methanol is nearly 65 million tonnes. Due to economical constrain, methanol is manufactured from naphtha, natural gas or coal. It is also possible to produce methanol from organic material such as biomass and in coming future, carbon dioxide may also become a major feedstock for producing methanol. The concept of methanol economy is based on the theory of anthropogenic carbon cycle which can be used to harness its virtues for methanol production. Methanol has potential to become a renewable fuel and feedstock for major synthetic product which is derived from fossils fuels.

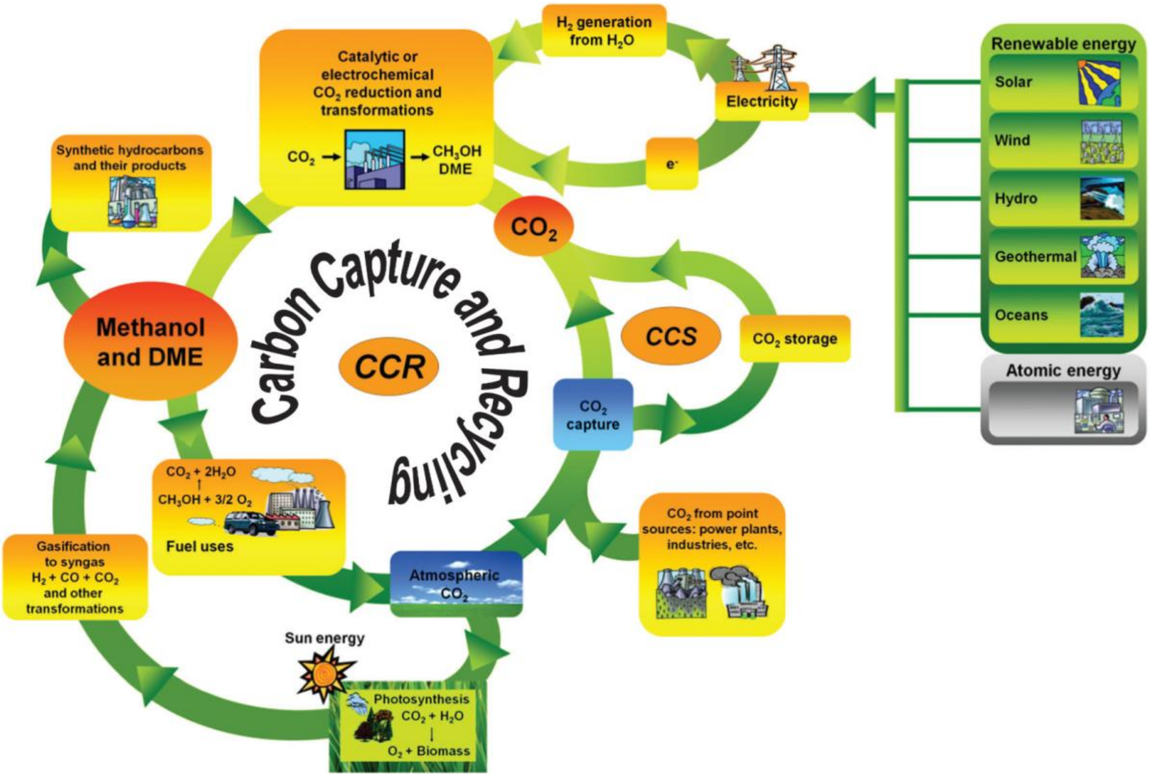

Fig. 1.3 Anthropogenic carbon cycle within the Methanol Economy
(Source: Olah et al. 2009)

CHAPTER 2

LITERATURE REVIEW

The following literature review consists of two sections. The former section involves the literature review of numerous chemical reactions of carbon dioxide being studied for practical use & application as part for mitigation of carbon dioxide emission. The later section deals with thermodynamic analysis of carbon dioxide conversion to methanol.

2.1 Review of Carbon dioxide utilization techniques

Huge amount of literature exists with regards to numerous carbon dioxide utilization techniques for carbon dioxide mitigation. Discussion on all the techniques being researched upon for carbon dioxide mitigation would be unworkable. Thus research work which have reviewed and compiled techniques are studied & discussed in this part.

Xiadong and Moulijn (1996) covered a considerable range of chemical conversion processes of carbon dioxide. Different chemical routes covered in their research work comprises of reduction of carbon dioxide, reactions with chemical species having activated hydrogen atoms, poly-carbonates formation, chemical reaction involving epoxides, chemical reaction with ethers & alcohols, chemical reactions with sulfur compounds, chemical reaction with N_2 compounds, and bioconversion. They also studied the utilization of carbon dioxide as a weak acid and a mild oxidizing agent. They commented that to somewhat reduce emission of carbon dioxide via chemical conversion techniques, focus should be on manufacturing of bulk chemicals commodities. They concluded that the most important use of carbon dioxide conversion are manufacturing of CH_3OH, Di-methyl ether, MTBE & Di-methyl Carbonate for their major role as motor sprit additives and standalone fuels

Olah et al. (2009) targeted on the technique of carbon dioxide recycling in proposed Methanol economy. Methanol economy is an idea in which CH_3OH replace convectional fossil fuel as means of raw material & fuel for industry and domestic sectors. They have covered various methods that can be used to produce methanol, subsequently DME, from CO_2. The methods described are catalytic hydrogenation, Carroll's process and electrochemical production. They have also given a brief description of various methods for capture of CO_2 for utilization purpose and production of hydrogen for methanol synthesis.

Wang et al. (2011) in their work have carried out critical review of advancements in various catalytic hydrogenation of CO_2. Hydrogenation forms the thermodynamically most favourable group of reactions being studied of chemical conversion of CO_2. The hydrogenation reaction covered by them include reverse water gas shift reaction, synthesis of hydrocarbon, synthesis of methanol, methanation, synthesis of dimethyl ether, synthesis of higher alcohols, synthesis of formic acid and formate, and synthesis of formamides. The emphasis of the study has been largely on reaction mechanism, catalytic activity, and reactor design.

Hu, et al. (2013) provides a comprehensive review of techniques based on thermal, electrochemical and photochemical conversion. They summarize the advantages and disadvantages of different methods of conversion of carbon dioxide being pursued to day. In their work, they have focused on reaction mechanism, thermodynamics and catalyst. They have covered a range of products starting from simple molecule (e.g. CO) to higher hydrocarbon polymers. They have given special focus on conversion CO_2 to CO using reduction, electro-catalysis and plasma. Other techniques covered include conversion to Syngas, HCOOH, HCHO, CH_3OH and long chain hydrocarbons, polymer and oxygenates.

2.2 Thermodynamic analysis of CO_2 conversion to methanol

Skrzypek et al. (1989) studied the effects of the initial pressure, temperature and feed composition, on the equilibrium conversions and concentrations of the components were examined for methanol synthesis from carbon dioxide and hydrogen. The two reaction systems $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$; $CO_2 + H_2 \rightarrow CO + H_2O$ were analysed. From a thermodynamic aspect, direct methanol synthesis from carbon dioxide and hydrogen is quite promising for industrial applications. The goal of this work was to determine the effects of the main process parameters such as pressure, temperature and initial feed composition on the equilibrium conversions and concentrations of components in the two reaction systems.

Shen et al. (2000) examined the thermodynamics involved in synthesis of methanol and dimethyl ether from CO_2 and H_2 in gas phase. Assuming methanol and dimethyl ether as their main product, both of the parallel reaction systems (including side reactions) were compared in terms of their yield and selectivity of desired product. The analysis was carried out using equilibrium constant method. The equilibrium constant and fugacities for both systems were calculated using empirical relations. Analysis investigated the effects of temperature, pressure and initial feed composition on the equilibrium conversion of CO_2 and yields of the desired products. Study concluded that formation of DME allows for higher yield and selectivity than methanol.

Jia et al. (2006) carried out a comparative thermodynamic study of CO and CO2 hydrogenation for production of DME & methanol. The analysis was done using equilibrium constant method. The equilibrium constant was calculated using Equilibrium Calculator, non-commercial software. Fugacity coefficients were calculated using SRK equation of state. The study concluded that CO hydrogenation may obtain higher yield than CO2 hydrogenation but is not suitable due to low efficiency of carbon utilization.

Fornero et al. (2011) simulated the production of methanol via the catalytic hydrogenation of carbon oxides in a reacting system that included the recycling of non-condensable gases (H_2, CO_2 and CO) to evaluate the CO_2 capture capability of the process. As a first step, the asymptotic responses of the system 'operating in thermodynamic equilibrium' (i.e., overall recoveries of CO_2 and H_2, CH_3OH selectivity and productivity) were analysed for various industrial conditions of pressure (3–5 MPa), temperature (508–538K), feed composition (H_2/CO_2 = 1.5/1 to 4/1) and mole recycle ratio (R) with respect to the molar feed flow rate. Then the performance of two catalysts (a novel one, $Pd–Ga_2O_3/SiO_2$ and a commercial $CuO/ZnO/Al_2O_3$type) in an ideal isothermal, isobaric, pseudo homogeneous fixed-bed reactor was studied for a broad range of W/FCO_2 ratios. It was found that, whereas the 'reactor in equilibrium' would allow up to 100% CO_2 capture, the capture values upon using these catalysts were significantly lower. Nevertheless, such recoveries always increased whenever R was raised, which implies that catalyst development efforts in this field should prioritize achievement of the highest catalytic activity (i.e., specific productivity) rather than attempt catalyst selectivity improvements.

Machado et al. (2014) studied two processes to meet the demand for methanol production with focus in the reduction of carbon dioxide (CO_2) emission and operating costs.

The first was the conventional process of methanol synthesis from syngas. The new process is the hydrogenation of CO_2 for methanol production. This new process can be considered a green chemical process because it uses CO_2 as raw material contributing to the mitigation of CO2 (major greenhouse gas). The simulation of this processes were carried out using the Aspen- Hysys software to assess energy consumption and CO2 emissions in addition to process conditions. The influence of various process conditions as pressure, H_2/CO_2 ratio and $(H_2-CO_2)/(CO_2+CO)$ were analysed from different parameters as selectivity to methanol, CO and CO2 conversion, methanol production. In all cases studied the processes were evaluated at 245 °C to produce 465 kta of methanol for define the behaviour of the operation conditional, to compare the energy consumption and the CO_2 emission of the two process.

Swapnesh et al. (2014) performed thermodynamic analysis of dimethyl ether and methane synthesis from carbon dioxide hydrogenation, & dry reforming of methane using the technique of Gibbs free energy minimization. The effects of pressure, temperature, and initial feed composition on conversion, selectivity, and yield were investigated for each chemical reaction system. Low temperature, high pressure and high H_2/CO_2 ratio favoured dimethyl ether production. The yield of methane during carbon dioxide methanation increased at lower temperature, higher pressure, and H_2/CO_2 ratio. The yield of synthesis gas improved at higher temperature. Comparison of the three processes demonstrated that the CO_2 conversion was highest during CO_2 methanation reaction if the fraction of CO_2 mol in the feed was less than 0.3. Above this value in the feed, dry reforming allowed the highest CO_2 conversion.

Iyer et al. (2015) studied the effect of feed composition on synthesis of methanol from a feed mixture comprising of primarily CO, H_2 and CO_2. The performance characteristic of reactor under single and two phase conditions were analysed using thermodynamic approach. The Gibbs free energy minimization approach was implemented for this purpose. The effect of all possible combinations of feed gas compositions on reactor performance encompassing both single and two phase regions were analysed for isothermal and adiabatic operation under single and two phase conditions. First, a rate based approach was compared with an equilibrium approach for methanol synthesis using Aspen Plus. The conditions under which the predictions from both the approaches agree were established. Under these conditions, the thermodynamic model is then used to predict the influence of feed composition on the reactor performance viz. reactor outlet temperature, conversion of CO, conversion of CO_2 and conversion of CO + CO_2.

2.3 Dry reforming of methane

Amin and Yaw (2007) carried out the thermodynamic analysis of CO_2 reforming of methane coupled with partial oxidation of methane. The analysis was done by Gibbs free energy minimization using Lagrange's multiplier method. The study assumed ideal behaviour of gases for its calculation. The study concluded that optimal equilibrium conditions for the coupled reaction systems are: CH_4:CO_2:O_2 ratio within the range of 1:0.8:0.2–1:1:0.2 and a minimum requirement temperature of 1000 K.

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Li et al. (2008) carried out the thermodynamic analysis of CO_2 reforming of methane coupled with steam reforming of methane. The analysis was done by Gibbs free energy minimization using Lagrange's multiplier method. The study focused on CO_2 conversions, H_2 yield and coke deposition as a function of feed ratios, temperature and pressure.

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Sun et al (2011) performed thermodynamic analysis for the reforming of methane with carbon dioxide alone and with carbon dioxide and steam together (“mixed reforming”) using Gibbs free energy minimization. In the dry reforming process, a carbon formation regime is always present at a CO_2/CH_4 molar ratio of 1 for T = 700−1000 °C and p =1−30 bar, whereas carbon-free regime can be obtained at a CO_2/CH_4 molar ratio greater than 1.5 and $T \geq 800$ °C.

2.4 Research gap

It can be seen that Gibbs free energy minimization technique has not been used previously for thermodynamic analysis of methanol synthesis from carbon dioxide. This method, although, has been used previously for dry reforming of CH_4, however, effect of pressure was not studied. Similarly, comparative thermodynamic study of numerous possible processes available that can be used for mitigation of CO_2 emission and conversion of CO_2 into fuels and value added is not available. Considering these research gaps in the literature, this work focuses on comparative study of thermodynamics of the selected three chemical reaction systems.

CHAPTER 3

OBJECTIVE

The prime objective of this study focuses on conversion of CO_2 into methanol via hydrogenation of CO_2 and dry reforming coupled by methanol synthesis. One of the most peculiar characteristic of any chemical reaction system on industrial ground is its efficiency to maximise the amount of desired product. Degree or extent of conversion at equilibrium can be defined as peak possible conversion which could be obtained for a given pressure and temperature. It sets the boundary limit to the formation of desired products in reaction system. Therefore it is crucial to calculate the degree of conversion of initial reacting chemical species, selectivity and yield of desired chemical products, and understand the effect of operating parameters on conversion and yield. This helps in optimising economic feasibility or viability of a manufacturing process. Thermodynamic analysis of the processes helps in determining the optimum value of various operating parameters for a chemical system. The present study looks into thermodynamic attributes of different chemical processes being taken into consideration for conversion of carbon dioxide into methanol.

Objectives of the research work are:

- To execute thermodynamic analysis of the following mentioned chemical processes:
    1. Synthesis of methanol via carbon dioxide hydrogenation
    2. Dry reforming of methane.
    3. Synthesis of methanol using dry reforming product.
- To calculate the conversion of the initial reacting species, yield and selectivity to the desired products.
- To evaluate the effect of operating conditions such as reaction pressure and temperature and initial feed composition on conversion, yield and selectivity of the desired products.
- To evaluate the effect due to presence of carbon monoxide in initial feed on conversion of the reactants and yield of desired products.
- To perform a comparative study of the various all the thermodynamic attributes related for all major chemical processes taken into consideration.
- To comment on the most suitable chemical reaction systems for practical applications

CHAPTER 4
THEORY

4.1. Equilibrium

Thermodynamic analysis of chemically reacting systems mainly attributed with the state of the system at thermodynamic chemical equilibrium. Equilibrium is a core phenomenon of nature. In a plain context, equilibrium is defined as the state in which all acting influences are counter cancelled by others, leading to a stable, balanced, or invariable system. From thermodynamic aspect, for a system to be in absolute equilibrium, it must attain mechanical, thermal, physical and chemical equilibrium altogether. The internal energy of a system and its partial Legendre transforms, also acknowledged as thermodynamics potentials, play a vital part in thermodynamics analysis of a chemical reaction system. These functions represent the potential of the chemical system to do work. At the state of equilibrium, internal energy or any of its potentials is minimized for given reaction conditions.

The prime focuses of this study is on thermodynamic chemical equilibrium. Chemical equilibrium can be defined as the state in which rate of forward and backward reactions in a chemically reacting system become equal and the final composition of reacting system becomes invariable for a specified pressure & temperature. Gibbs free energy is used as a mathematical tool for estimating the thermodynamic potential of a chemical reaction system.

4.2 Gibbs free energy minimization

There are two approaches for performing thermodynamic analysis of a chemical system: Stoichiometric & non-stoichiometric. To use stoichiometric approach, it is requires to exactly know chemical species in the system and independent reactions taking place in the system. For complex reaction systems, application of stoichiometric approach becomes tedious because of involvement of large number of reactions. Equilibrium constant method cannot be applied to chemical reaction systems in which all the reactions involved taking place are not known. Non-stoichiometric approach or Gibbs free energy minimization requires only knowledge of chemical species involved in the reaction system for thermodynamic equilibrium calculations. As a result, non-stoichiometric methods can be applied with ease to any chemical reaction system irrespective of its complexity. The present study uses Non-stoichiometric approach thermodynamic analysis.

The total Gibbs free energy of a reaction system can be given as:

$$G_T = \sum_{I=1}^{N} n_i \mu_i \qquad (1)$$

For gaseous species,

$$\mu_i = G_i^0 + RT\ln(\hat{a}_i) = G_i^0 + RT\ln\left(\frac{\hat{\phi}_i y_i P}{P_o}\right) \qquad (2)$$

For condensed pure chemical species, activity is taken as unity, therefore

$$\mu_i = G_i^o \qquad (3)$$

For chemical reaction system, individual molecular species are not be conserved but total number of atoms of each element remains conserved. The conservation of atoms of elements can expressed as

$$E_j = \sum_{i=1}^{N} \beta_{ij} n_i \qquad j = 1,2,3 \ldots\ldots\ldots\ldots\ldots k \qquad (4)$$

At a fixed pressure & temperature, the total Gibbs free energy of a chemical reaction system is minimum at the state of equilibrium. Thus, the equilibrium chemical composition of reaction system can be estimated by minimizing the Gibbs free energy subject to constraints of conservation of atoms of each element. The solution involves calculation of standard chemical potential and fugacity of various reactions species at various pressures and temperature. The standard chemical potential or standard Gibbs free energy of formation of a substance is function of its temperature. It is can be calculated using the following expression

$$\frac{G_i^o}{T} = \frac{\Delta G_{298}^o}{298} - \int_{298}^{T}\left(\Delta H_{298}^o + \int_{298}^{T} \Delta C_{pi}^o \, dT\right)\frac{dT}{T^2} \qquad (5)$$

Where

$$\Delta C_{p,i}^o = C_{p,i}^o - \sum \nu_e C_{p,e}^o \qquad (6)$$

$\Delta C_{p,i}^o$ is the algebraic sum of the heat capacity of a compound and its elements and ν_e is the stoichiometric coefficient. It should be noted that choice of chemical species to present in reaction system is an important consideration in non-stoichiometric approach. It is important to include all the possible major products to get a practical composition profile for a chemical reaction system. Neglecting important side products may very well distort the equilibrium composition of the system.

4.3 Calculation of fugacity coefficients

The fugacity coefficients of each reaction species can be calculated in variety of ways. In present study, fugacity coefficients are computed using Soave-Redlich-Kwong (SRK) equation of state. The fugacity coefficients of various components in a mixture are calculated by the expression derived from SRK equation of state:

$$\ln\hat{\phi}_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) + \frac{a}{bRT}\left[\frac{b_i}{b} - 2\sqrt{\frac{a_i}{a}} \times \ln\left(\frac{Z+B}{Z}\right)\right] \tag{7}$$

where,

$$A = \frac{a_i P}{R^2 T^2} \tag{8}$$

$$B = \frac{b_i P}{RT} \tag{9}$$

Z is the compressibility factor calculated by solving the following expression

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \tag{10}$$

The a_i and b_i are the SRK parameters of species i given by the following expressions

$$a_i = \frac{0.427 R^2 T_{c,i}^2}{P_{c,i}} \tag{11}$$

$$b_i = \frac{0.08664 R T_{c,i}}{P_{c,i}} \tag{12}$$

The overall mixture parameters a and b depend on the composition of mixture and values of parameters of individual pure component. The mixture parameter is calculated by the mixing rules commonly used for cubic equation of state. The mixing rules are

$$a = \sum_{i,j} y_i y_j \sqrt{a_i a_j}(1 - K_{ij}) \tag{13}$$

$$b = \sum y_i b_i \tag{14}$$

Where K_{ij} = binary interaction parameter

Due to lack of experimental data in gas phase, all the binary interaction parameters are taken as zero.

4.4 Model solution

The total Gibbs energy function is minimized using in-built "**fmincon function"** available in MATLAB software. The fmincon function used for optimization of single or multivariable nonlinear expressions subject to various linear and nonlinear constraints. The fmincon function is based on sequential quadratic programming. Using MATLAB, it's possible to get solution in 1 step but use of fugacity, which is depends on the composition of the reaction mixtures, makes the solving procedure iterative.

The steps for the solution are

1. Temperature, pressure and feed composition for the process are initialized.
2. The molar standard Gibbs free energy of formation of each species is calculated.
3. Assuming the fugacity coefficient to be 1 for all the species, Gibbs free energy of the system was minimized using fmincon function to get a preliminary equilibrium composition.
4. Using equilibrium composition calculated in the above step, fugacity coefficients of the reaction species were calculated.
5. The step 3 was repeated using the fugacity coefficients as calculated in step 4.
6. The calculations were repeated until the composition converges.

CHAPTER 5

REACTIONS AND REACTION SPECIES

5.1 Synthesis of methanol via CO_2 hydrogenation

Methanol is the simplest alcohol. It is a clean colourless liquid that can be easily stored and transported. Methanol is an important chemical feedstock and a potential alternative fuel to diesel & motor sprit because of its better fuel characteristics. Methanol has quite high cetane number and it doesn’t produce smoke and NOx. Methanol is generally produced by hydrogenation of CO and CO_2. The methanol synthesis is catalysed by Cu based metallic catalysts while the dehydration is catalysed by acidic catalyst such as γ-Al_2O_3, HZSM-5 etc. Table 5.1 list the major and minor reactions involved in methanol synthesis via CO_2 hydrogenation. Based on these reactions, the species chosen for thermodynamic study of methanol synthesis are: CO_2, H_2, CH_3OH, CO, and H_2O.

Table 5.1 Major possible reactions in formation of methanol (C.V. Miguel et al.**)**

Reaction Number	Reaction	ΔH_{298} (kJ/mol)
P1	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	-49.4
P2	$CO_2 + H_2 \leftrightarrow CO + H_2O$	41.2
P3	$CO + 2H_2 \leftrightarrow CH_3OH$	-90.6

5.2 Dry reforming of methane

CO_2 reforming of CH_4 refers to reaction of CO_2 with CH_4 and synthesis gas is one of the products of this reaction. Synthesis gas is an important industrial chemical feedstock. Thus, dry reforming of methane provides an alternative way to produce synthesis gas, which is used in production of methanol, formaldehyde, higher hydrocarbons, fertilizers, medicine etc. and also used as fuel (J.H. Edwards and Maitra, 1995). Dry reforming is catalysed by Ni based catalysts supported by various metal oxides. Table 5.2 list the major and minor reactions involved in dry reforming of methane. Based on these reactions, the species chosen for thermodynamic study of dry reforming of methane are: CO_2, H_2, CH_4, CO, H_2O, C (solid carbon).

Table 5.2 Possible reaction in dry reforming of methane (J. H. Edwards and Maitra, 1995; Nikoo and Amin, 2011).   .

Reaction Number	**Reaction**	**ΔH_{298} (kJ/mol)**
Q1	$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2$	247
Q2	$CO_2 + H_2 \leftrightarrow CO + H_2O$	41
Q3	$2CO \leftrightarrow C + CO_2$	-172.4
Q4	$CH_4 \leftrightarrow C + 2H_2$	74.9
Q5	$CO + H_2 \leftrightarrow C + H_2O$	-131
Q6	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-165
Q7	$CO_2 + 2H_2O \leftrightarrow C + 2H_2O$	-90

5.3 Dry reforming coupled by methanol synthesis

Methanol can also be produced by using syngas ($CO+H_2$) as the feed stock. In this process the reaction P3 becomes the major methanol forming reaction. Thus, an indirect way to use CO_2 for methanol synthesis is utilizing it for dry reforming of methane, producing syngas, which in turn is used as feed for methanol production. The reactions and species remain the same as mentioned in section 5.1 and 5.2.

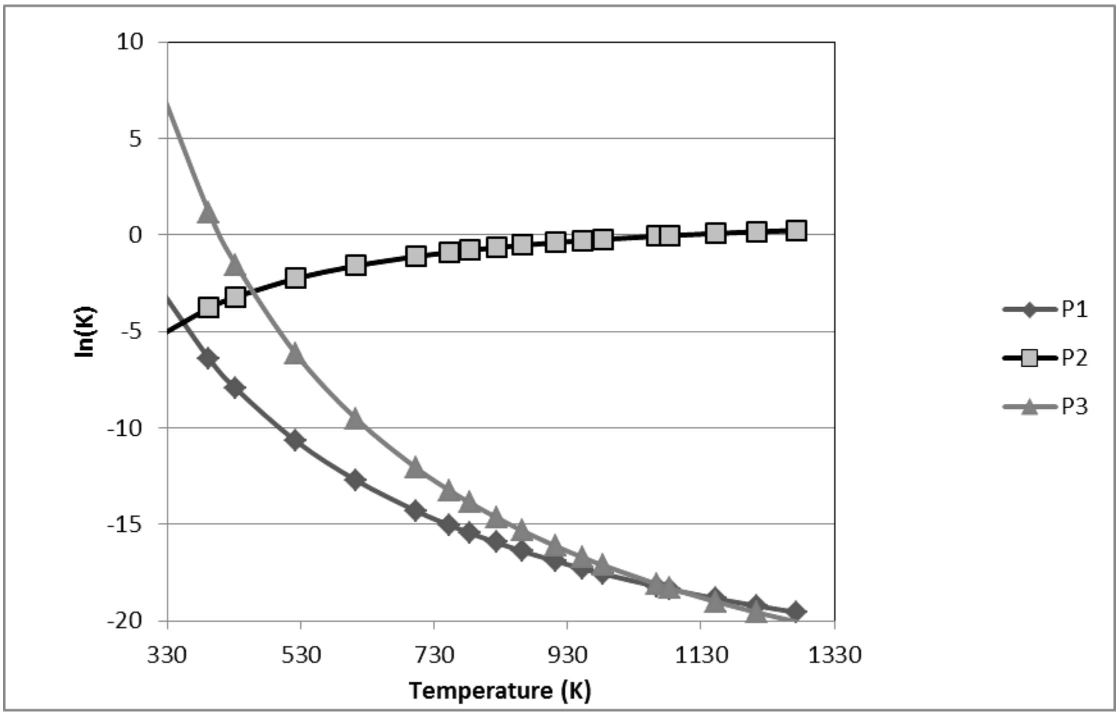

Figure 5.1 Effect of variation of temperature on equilibrium constants of reactions of methanol synthesis

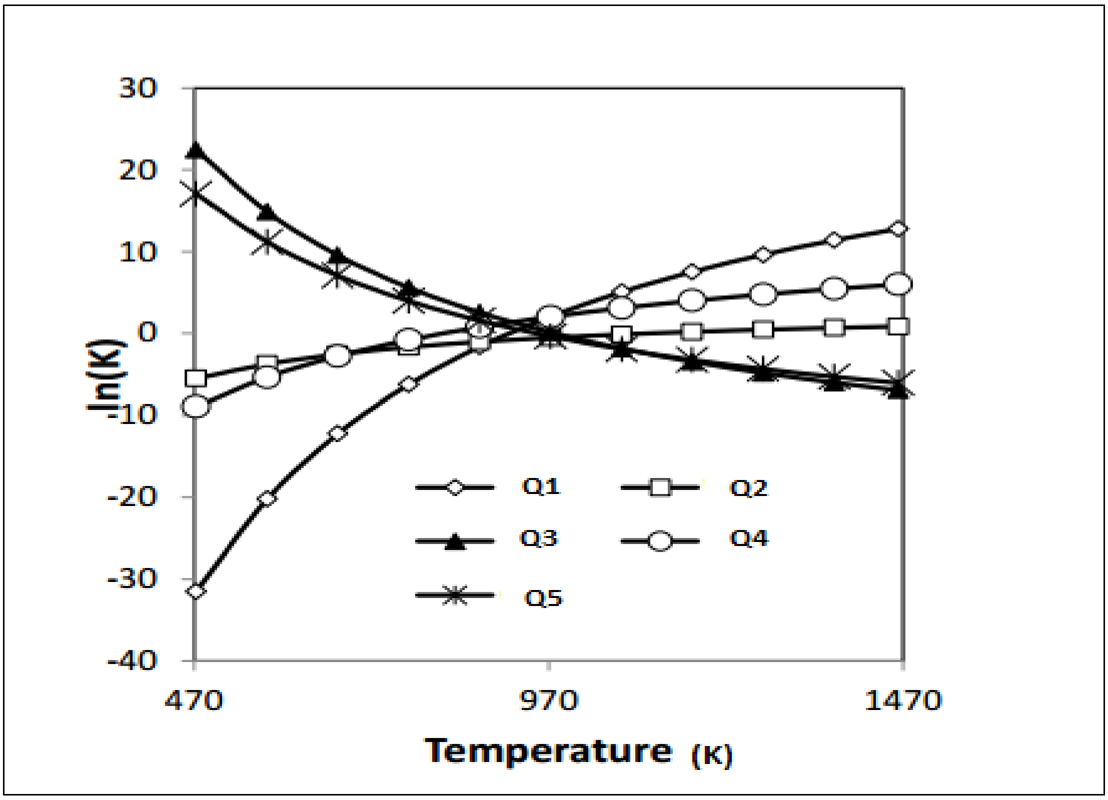

Figure 5.2 Effect of variation of temperature on equilibrium constants of reactions of dry reforming of methane

CHAPTER 6

RESULTS AND DISCUSSION

6.1 Synthesis of methanol by CO_2 hydrogenation

6.1.1 Effect of pressure and temperature

The Figure 6.1.1, 6.1.2 and 6.1.3 illustrates the effect of temperature and pressure on CO_2 conversion, methanol selectivity and methanol yield respectively. The feed ratio of H_2/CO_2 is kept at a constant value of 4 for the case. The equilibrium conversion of carbon dioxide first decreases & then increases with increase in equilibrium reaction temperature. Reaction P1 and P2 compete with each other for carbon dioxide. It can be seen from Figure 5.1 that the value of equilibrium constant for reaction P2 is greater than those of reaction P1 for all range temperature, reaction P1 tends to dominates over the reaction P2 up to the temperature of 500 ^oC. Thermodynamically the methanol synthesis from CO_2 is less favoured to that from CO. The initial decline in equilibrium conversion is due to the exothermic nature of reaction P1. For temperature beyond 450-500 ^oC, reaction P2 (reverse water gas shift reaction), an endothermic reaction, starts to dominate over reaction P1 and P2. This results in increase in CO2 conversion. The equilibrium constant of reaction P1 becomes negligible above 350 ^oC. It can be seen from the figure 6.1.1 that for temperatures above 500 ^oC, CO_2 conversion becomes independent of pressure. This happens because for temperatures above 500 ^oC, only reaction P2 consumes CO_2. Reaction P2 is neither a mole increasing nor mole reducing reaction, hence not affected by pressure.

The yield and selectivity of methanol decreases with increase in temperature as reaction P1 and P3 are exothermic in nature and P2 is endothermic. It can be seen from the figure 6.1.2 that pressure has positive effect on methanol selectivity & yield. Reaction P1 and P3 is mole reducing reaction, thus methanol formation is favoured by high pressure. It should be noted that pressure does not have any effect on reaction P2. It can be seen from Figure 6.1.2 that selectivity of methanol over carbon monoxide shows a trend similar to that of methanol yield. The selectivity of methanol decreases rapidly with increasing temperature, as a result it will be not easy to obtain pure methanol from CO_2 hydrogenation.

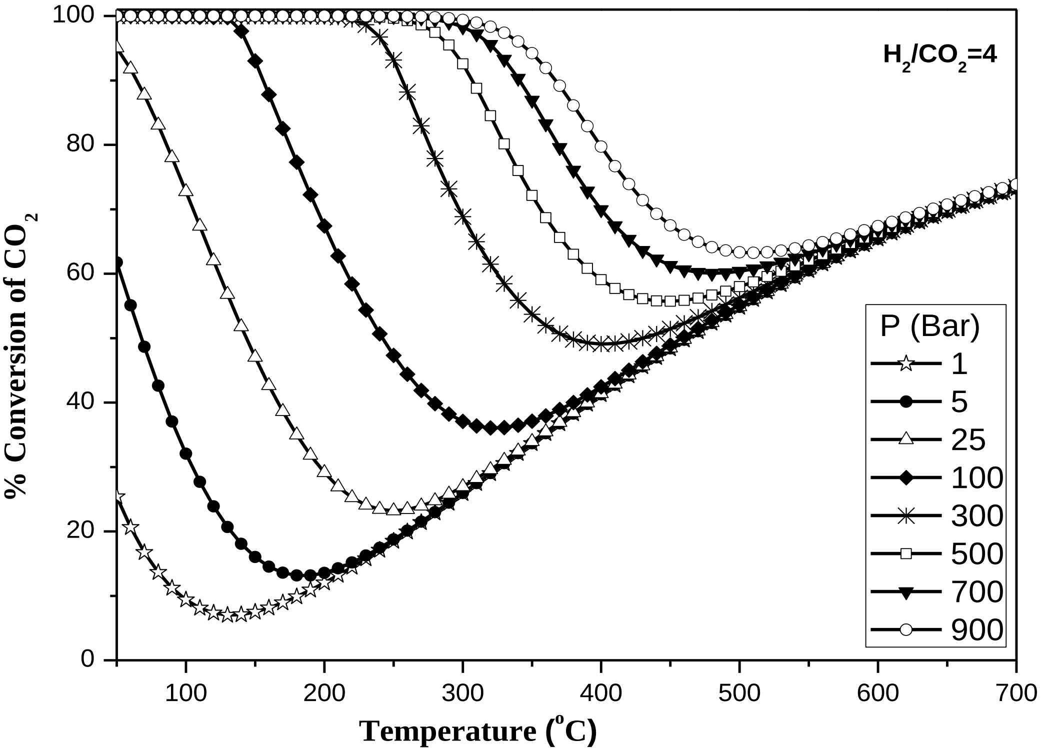

Figure 6.1.1 Influence of temperature and pressure on CO_2 conversion in Methanol synthesis

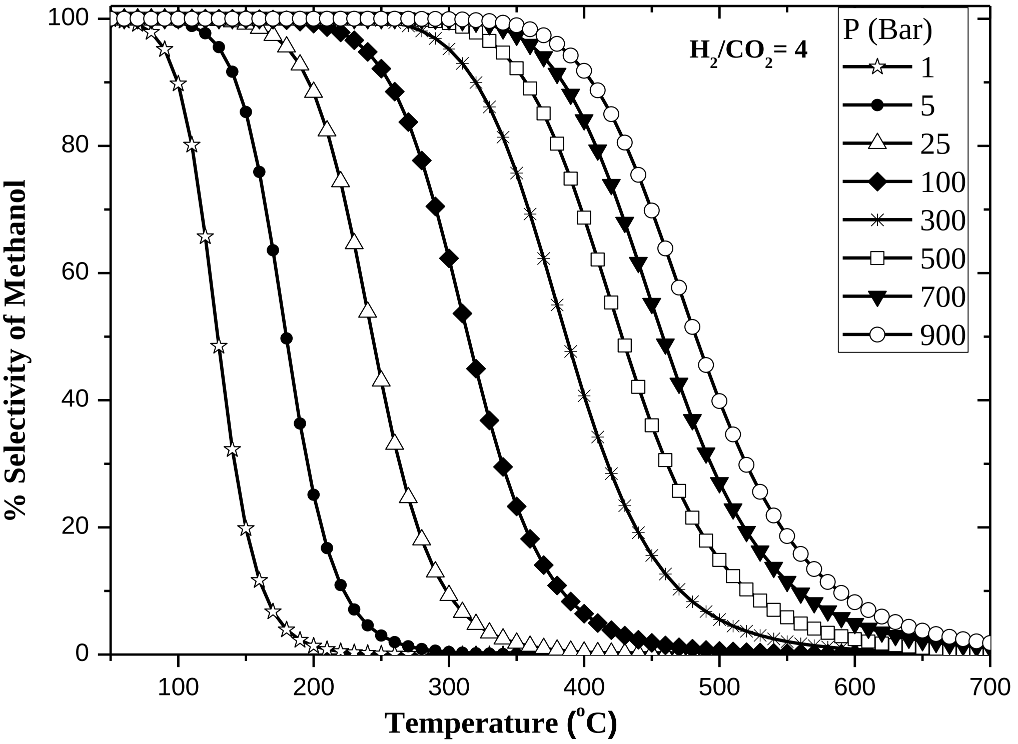

Figure 6.2 Influence of Temperature and Pressure on Methanol selectivity in direct methanol synthesis

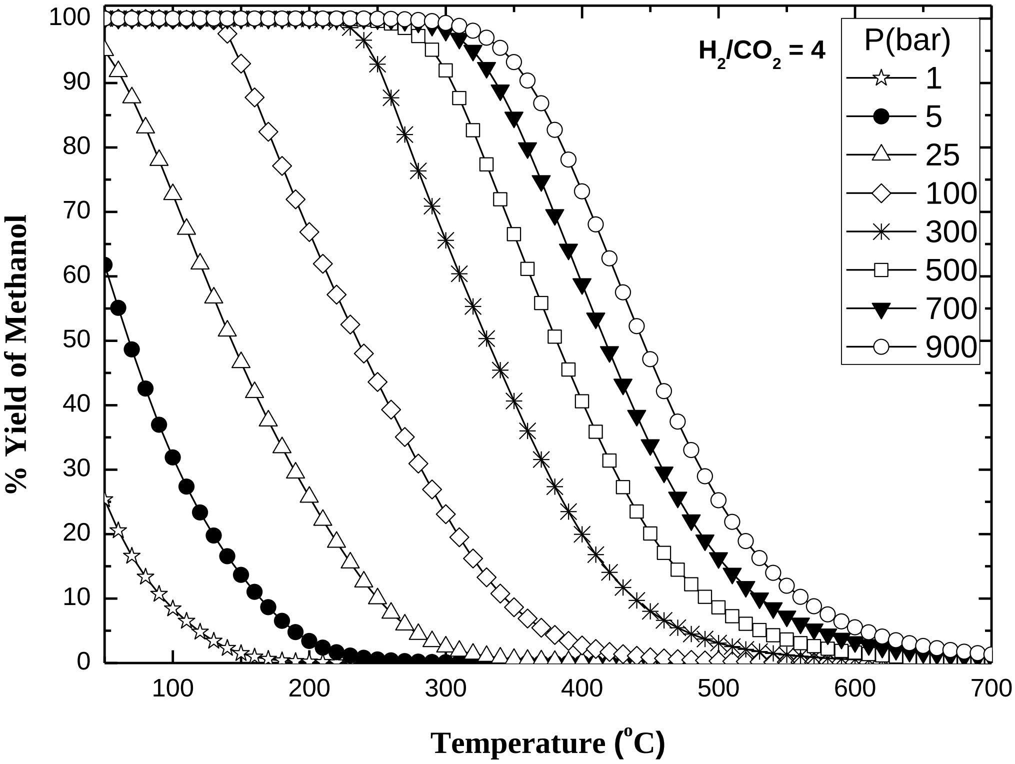

Figure 6.3 Influence of Temperature and Pressure on Methanol Yield in direct methanol synthesis

6.12 Effect of feed composition

The feed to methanol process consists of CO_2 and H_2. The feed composition is generally varied in terms of H_2/CO_2 ratio. The figure 6.1.4, 6.1.5, 6.1.6 depicts the effect of feed composition on CO_2 conversion, methanol selectivity and methanol yield respectively. H_2/CO_2 ratio is taken as the basis. It can be observed that high H_2/CO_2 ratio favours CO_2 conversion and methanol yield. For H_2/CO_2 ratio greater than 3, CO_2 act as the limiting reagent, resulting in enhanced conversion of CO_2. Also the increased availability of hydrogen shifts the reactions in forward direction.

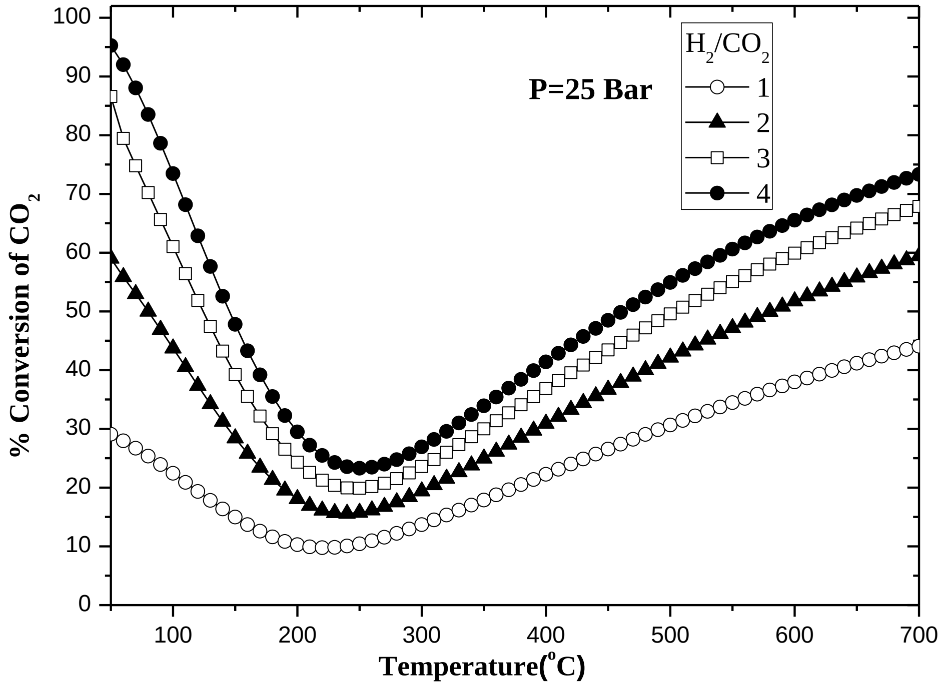

Figure 6.1.4 Influence of H_2/CO_2 ratios on CO_2 conversion in methanol synthesis in methanol synthesis

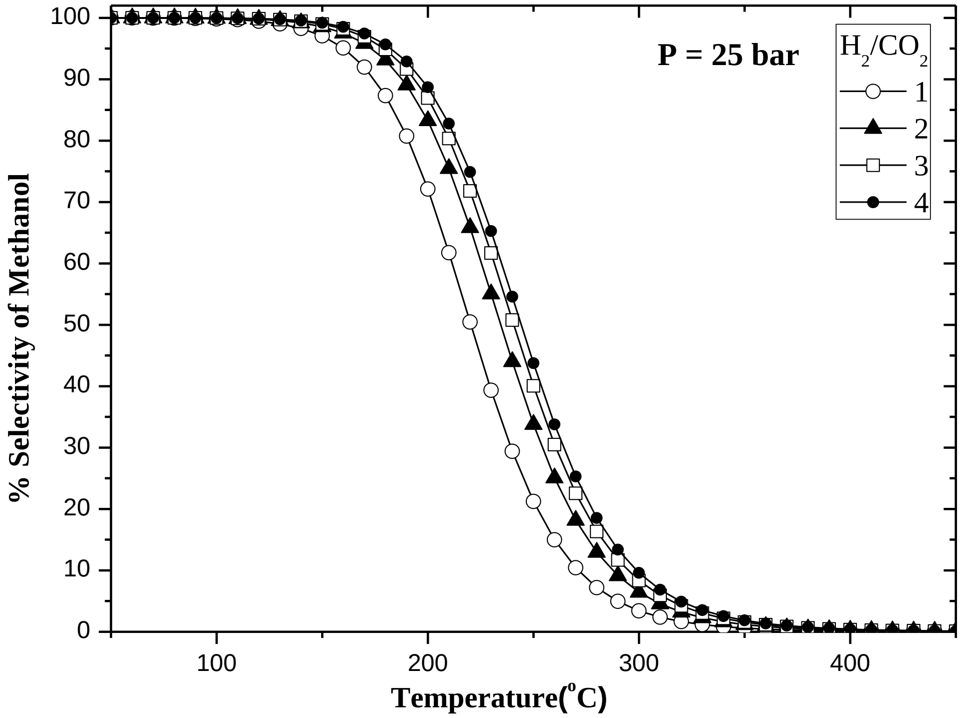

Figure 6.1.5 Influence of H_2/CO_2 ratios on Methanol selectivity in methanol synthesis

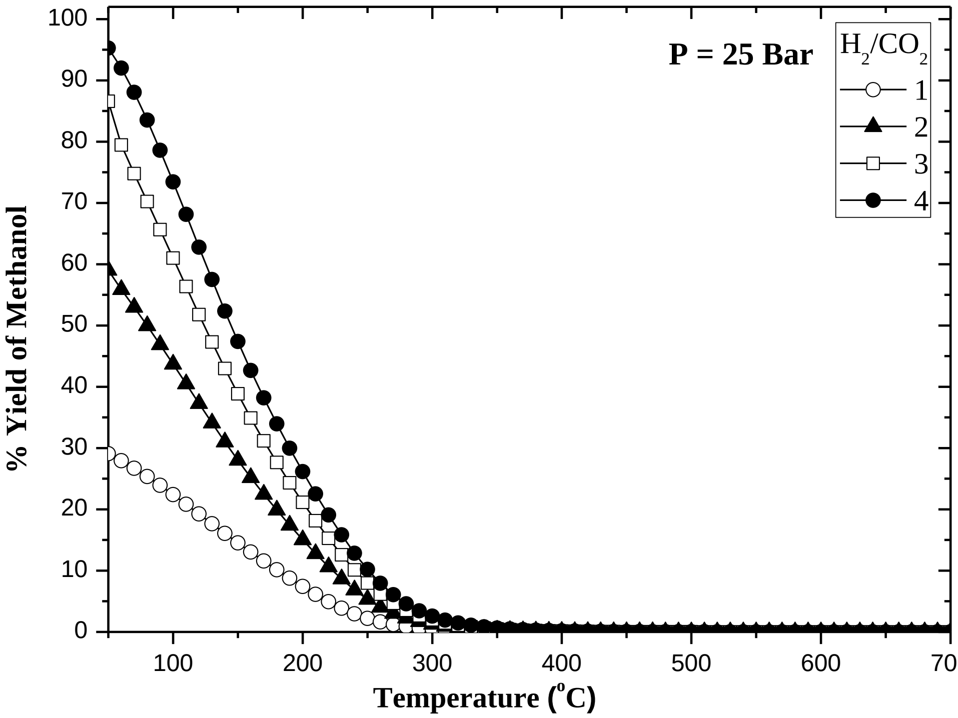

Figure 6.1.6 Influence of H_2/CO_2 ratios on Methanol Yield in methanol synthesis

6.1.3 Effect of CO in feed

CO_2 emissions from various sources often contain carbon monoxide in varying amounts. Thus, it is important to ascertain the effect of CO on methanol synthesis from CO_2 hydrogenation. Figure 6.1.7 and 6.1.8 illustrates the effect of CO in feed on CO_2 conversion and methanol yield respectively. The H_2/CO_2 of the feed is kept at 4. It can be seen from figure 6.1.7 that presence of CO depresses the CO_2 conversion. The reduction in CO_2 conversion increases with increase in CO concentration. Hydrogenation of CO to methanol is more favourable to Hydrogenation of CO_2 to methanol. This results reduced availability of hydrogen for CO_2 causing the observed reduction in CO_2. For high CO concentrations, CO_2 conversion may also become negative, implying more CO_2 is being formed than being consumed. This excess CO_2 is result of water gas shift reaction (reverse P2) at lower temperature. Methanol yield increases with increasing CO concentration for temperature higher than 150 °C. This happens because hydrogenation of CO produces larger amount of methanol than hydrogenation of CO_2 does.

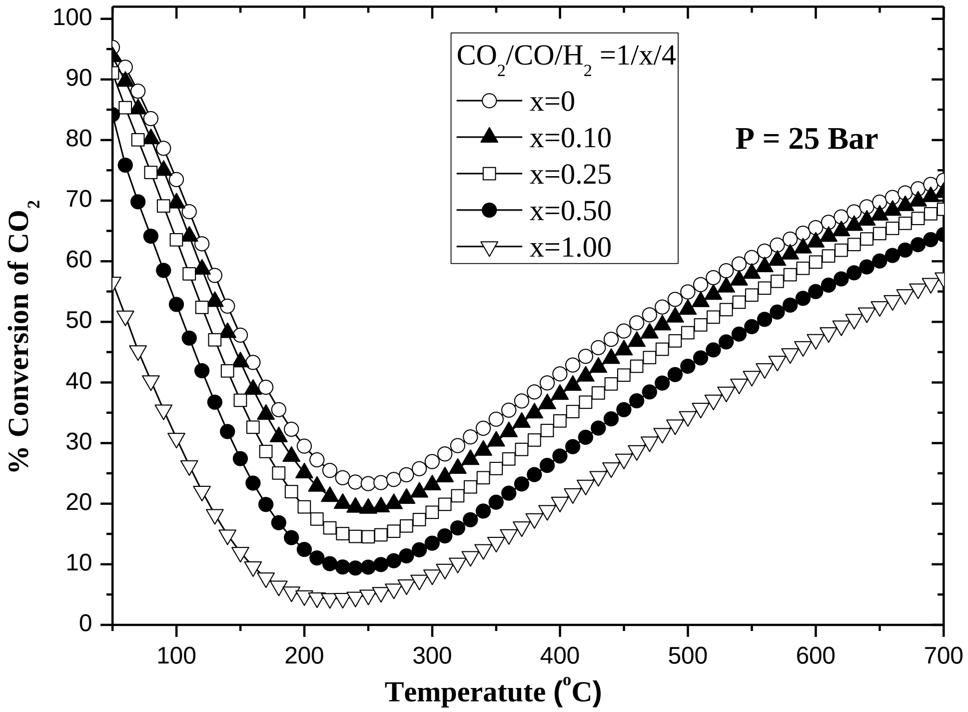

Figure 6.1.7 Effect of presence of CO in feed on CO$_2$ conversion in dirct methanol synthesis

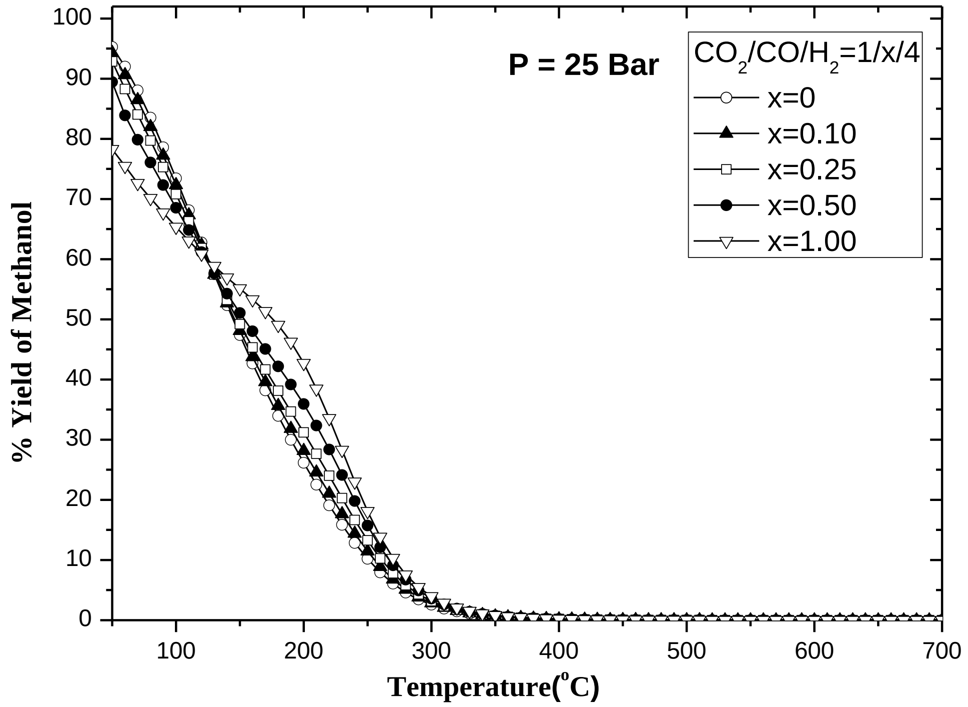

Figure 6.1.8 Effect of presence of CO in feed on Methanol yield in direct methanol synthesis

6.2 Dry Reforming of Methane

6.2.1 Effect of temperature and pressure

Figure 6.2.1 - 6.2.5 shows the effect of pressure and temperature on conversion, yield, H_2/CO ratio and coke deposition. It can be observed from figure 6.2.1 that the conversion of carbon dioxide first decreases and then increases with increase in temperature. Reaction Q1 and Q2 are endothermic in nature and these two reaction have very low equilibrium constants at lower values temperatures, thus they do not contribute to consumption of CO_2 (see figure 5.2). Conversion of carbon dioxide at temperature lower than 600 ^oC is mainly due to reaction Q5 and Q7. Formation of water &coke leads to predominance nature of reaction Q5 & Q7 at lower values of temperature. The initial decline up to the temperature of 600-550 ^oC is due to the exothermic nature of reaction Q5 and Q7. Beyond these temperatures, reactions Q1 and Q2 start to dominate over coking reactions. The subsequent increase in conversion of CO_2 is due to the endothermic nature of reactions Q6 and Q7. Pressure has both positive as well as negative effects on CO_2 conversion depending on the value of temperature. High pressure has a positive effect on CO_2 conversion at lower values of temperature while low pressure has a positive effect on carbon dioxide conversion at higher values of temperature. Both reaction Q1 and reaction Q2 are moles increasing chemical reactions, thus it is expected carbon dioxide conversion will be favoured by low pressure. The expected effect is observed at temperatures above 600 ^oC but not at lower temperature. This happens because at lower temperatures reaction Q5 and Q7, which are favoured by high pressure, are largely responsible for conversion of CO_2. Both H_2 and CO yield increase with increase in temperature and decrease with increase in pressure. This is expected as both reactions Q1 and Q2 are endothermic and mole increasing. It can be seen from Figure 6.2.4 that the H_2/CO ratio varies widely over the studied temperature range. Ideally the reforming should result in H_2/CO ratio of unity as evident from reaction Q1 but reaction Q3 and Q5 consumes CO at low temperatures; thereby, making the H_2/CO ratio greater than 1. As the temperature increases, coke formation diminishes and H_2/CO ratio starts to approach unity. At temperatures above 1000 ^oC, the H2/CO ratio drops below unity as reaction Q2 starts to dominate over reaction Q1, effectively increasing the CO content and reducing the H_2 content. Pressure does not have any significant effect on H_2/CO ratio. Reaction Q5 and Q7 are largely responsible for formation of coke in the systems. Figure 6.2.5 illustrates that the coke formation increases with increase in pressure and decreases with an increase in temperature. This is because both reaction Q5 and Q7 are volume reducing and exothermic.

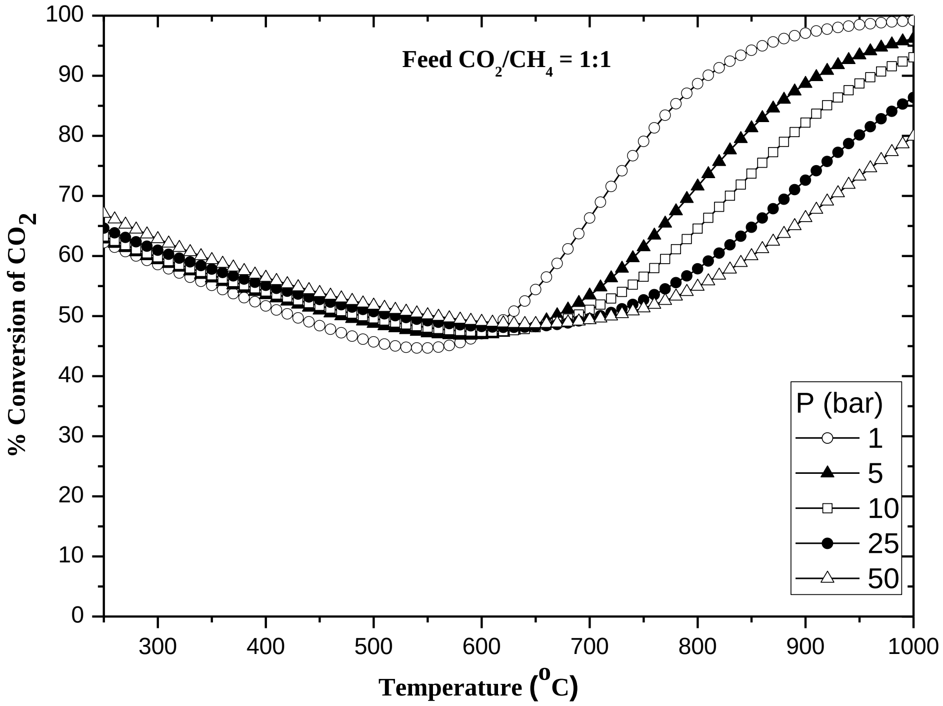

Figure 6.2.1 Influence of Temperature and Pressure on CO_2 conversion in dry reforming of methane

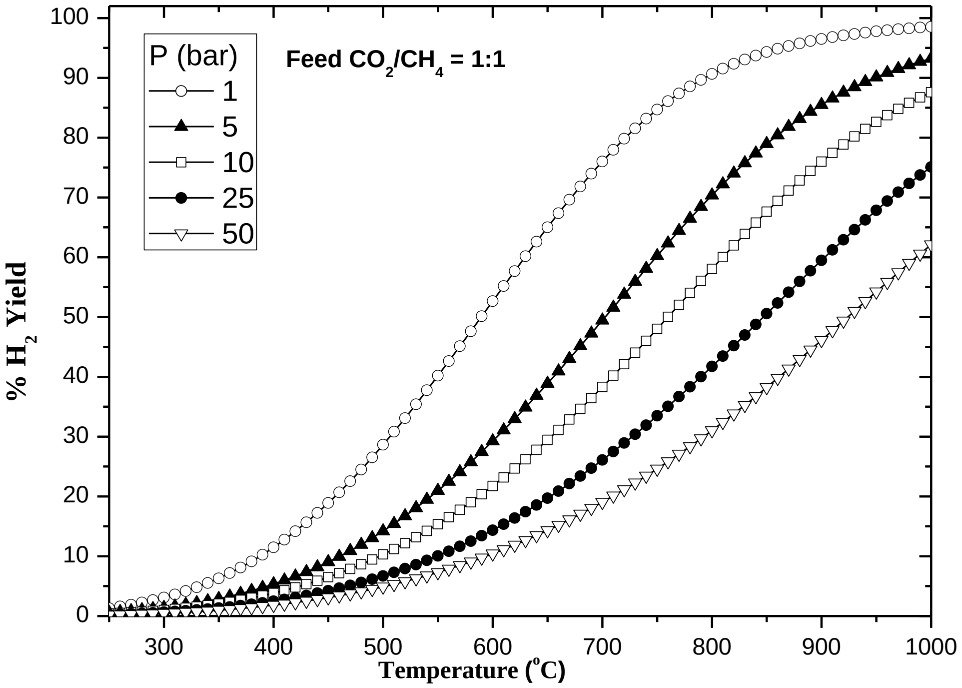

Figure 6.2.2 Influence of Temperature and Pressure on hydrogen yield in dry reforming of methane

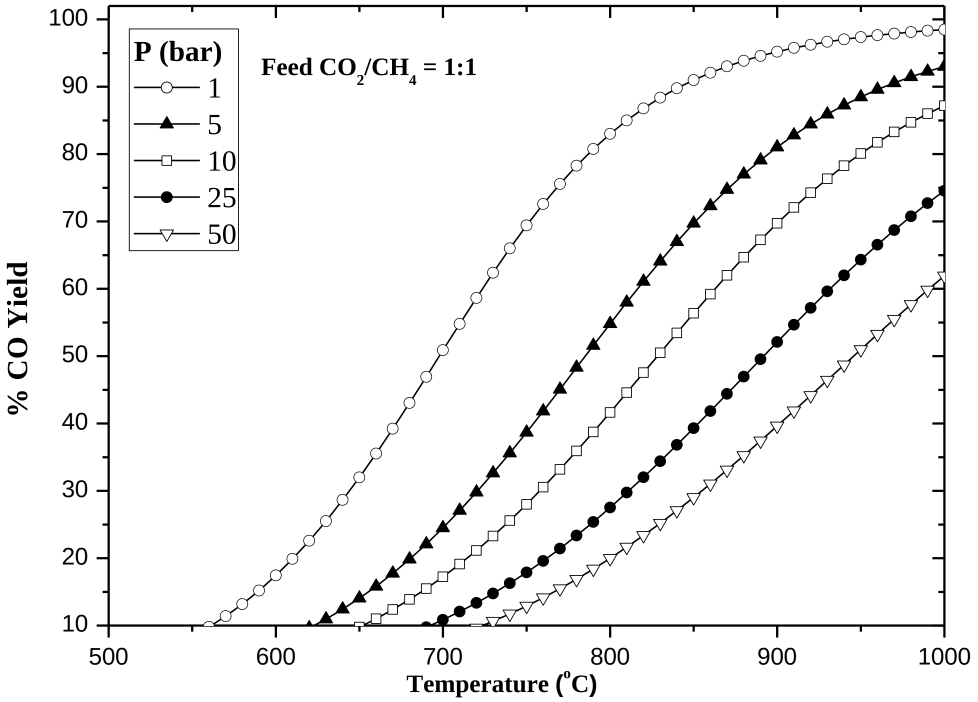

Figure 6.2.3 Influence of Temperature and Pressure on CO yield in dry refrorming of methane

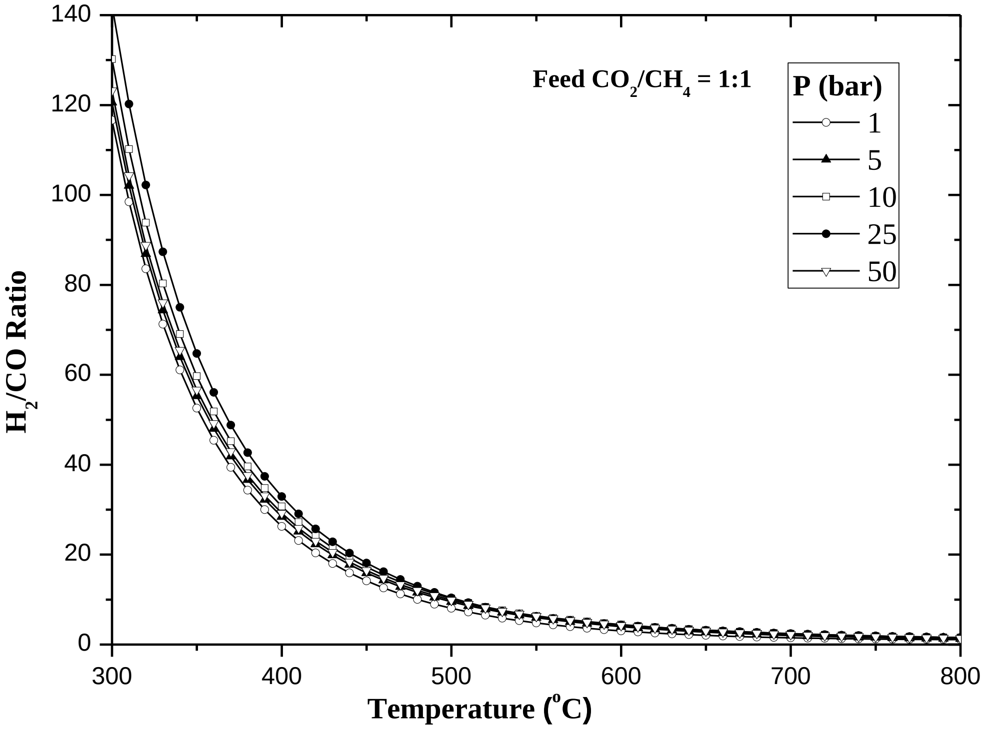

Figure 6.2.4 Influence of Temperature and Pressure on H_2/CO ratio in dry reforming of methane

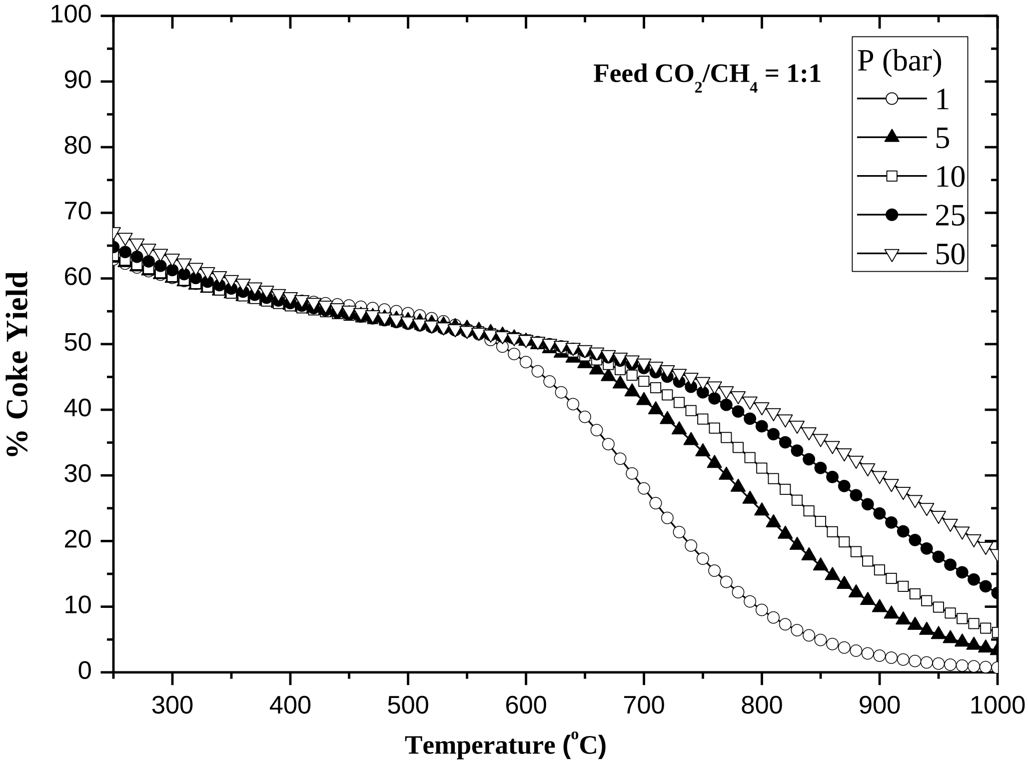

Figure 6.2.5 Influence of Temperature and Pressure on coke deposition of methane

6.2.2 Effect of CO_2/CH_4 ratio

Figure 6.2.6 - 6.2.9 illustrates the effect CO_2/CH_4 ratios on CO_2 conversion, CO yield, H_2/CO equilibrium ratios and coke formation at 25 bar. From Figure 6.2.6, it can be concluded that the carbon dioxide conversion is favoured by low CO_2/CH_4 ratios. For CO_2/CH_4 ratios less than unity, carbon dioxide is the limiting reagent. As a result it is consumed in reaction to maximum possible extent. For CO_2/CH_4 ratios greater than unity, methane becomes the limiting reagent; thereby, limiting the conversion of CO_2.Variation of mole ratio CO_2/CH_4 in feed has nearly no effect on carbon dioxide conversion over a long observed range of temperature.

CO_2/CH_4 ratios show both positive & negative impact of CO yield depending upon whether CO_2/CH_4 ratio is less than or greater than unity as show in figure 6.2.7. For CO_2/CH_4 ratios less than unity, CO yield increases with an increase in CO_2/CH_4 ratio as CO_2 is the limiting reagent. Any incremental addition of carbon dioxide at CO_2/CH_4 ratios less than unity is largely consumed resulting in higher carbon monoxide yield. For CO_2/CH_4 ratios greater than 1, CO yield decreases with an increase in CO_2/CH_4 ratio. In case of CO_2/CH_4

ratios greater than 1, CH_4 is the limiting reagent in reaction system. Thus any addition of carbon dioxide does not increase the moles of carbon monoxide formed, instead it effectively reduces the yield of the carbon monoxide.

It can be seen from figure 6.2.8 that low CO_2/CH_4 ratios results in higher H_2/CO ratios. Reaction B2 consumes H_2 and produces CO. With increase of CO_2/CH_4 ratio, more CO_2 becomes available for reaction Q2. This effectively reduces moles of H_2 formed and increases the moles of CO formed; thereby, reducing the H_2/CO ratio. Coke formation is favoured by low CO_2/CH_4 ratio (see figure 6.2.9).

Coke formation for feed ratio CO_2/CH_4 greater than 1, drops to zero at higher values of temperature as the primary coke forming reactions (Q5, Q7, and Q3) are exothermic in nature. Methane cracking (reaction Q4), even though endothermic, is not plausible at higher temperatures because CH_4 is the limiting reagent. On the other hand, nearly constant amount of coke deposits remain for feeds with CO_2/CH_4 ratios less than 1. This happens because of methane cracking, which becomes plausible at higher temperatures. Calculations and trends as observed in the present study are in agreement with simulation results reported by Nikoo and Amin et al., 2011 and Sun et al., 2011.

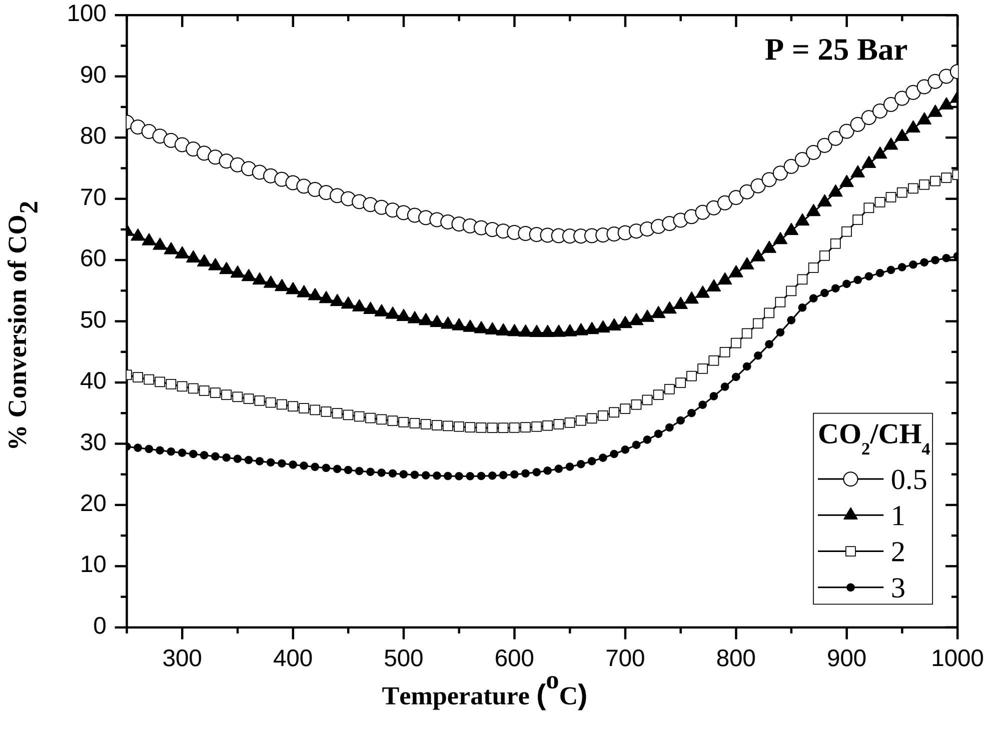

Figure 6.2.6 Influence of CO_2/CH_4 ratios on CO_2 conversion in dry reforming of methane

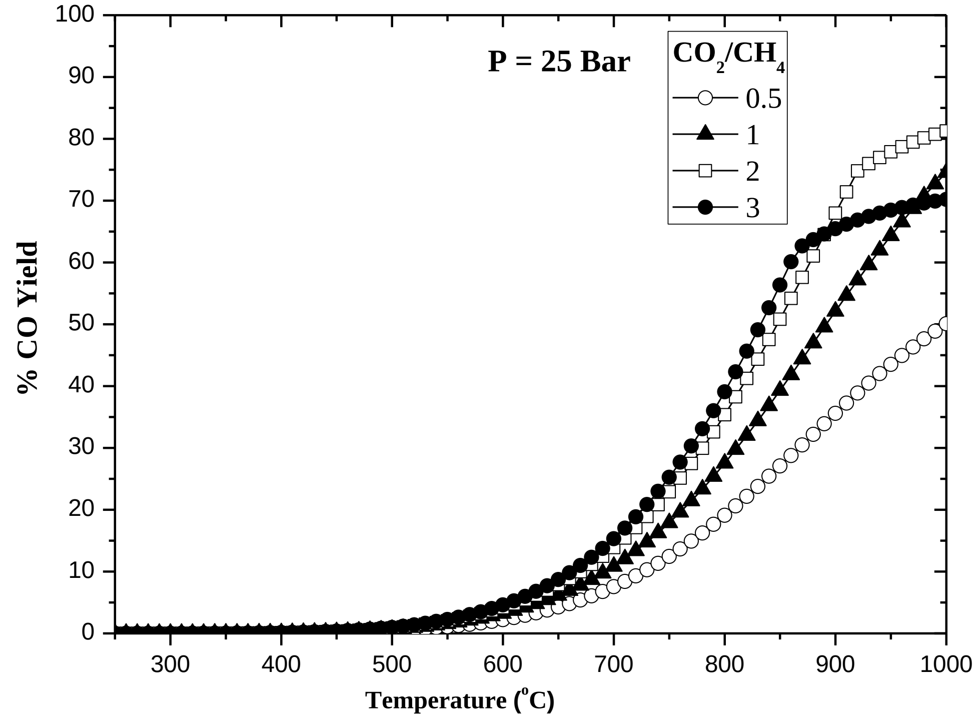

Figure 6.2.7. Influence of CO_2/CH_4 ratios on CO yield in dry reforming of methane

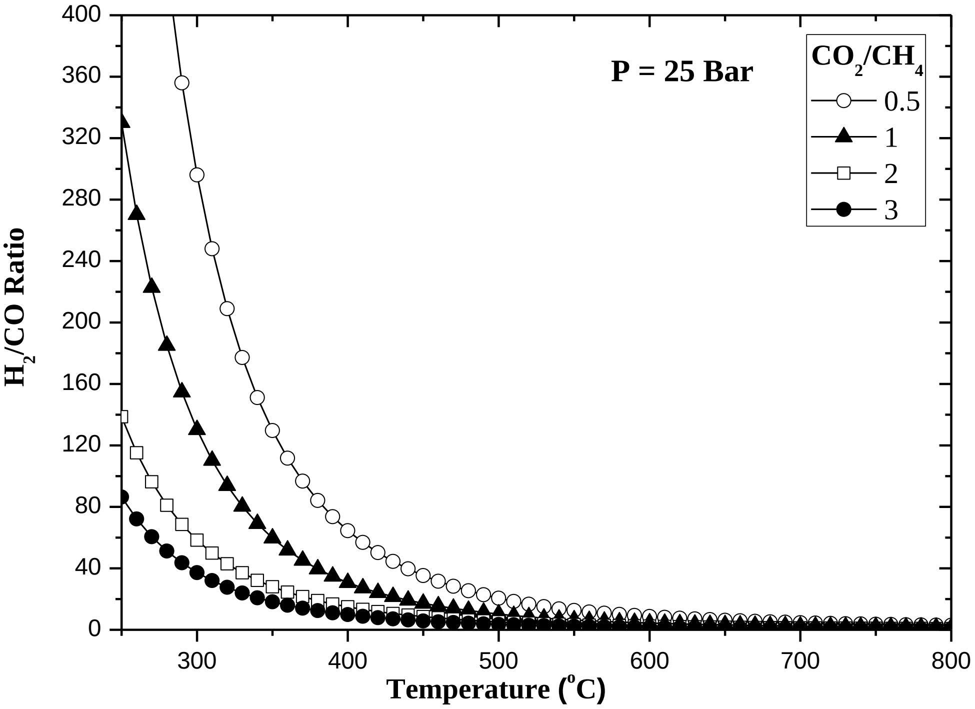

Figure 6.2.8 Influence of CO_2/CH_4 ratio on H_2/CO ratios in dry reforming of methane

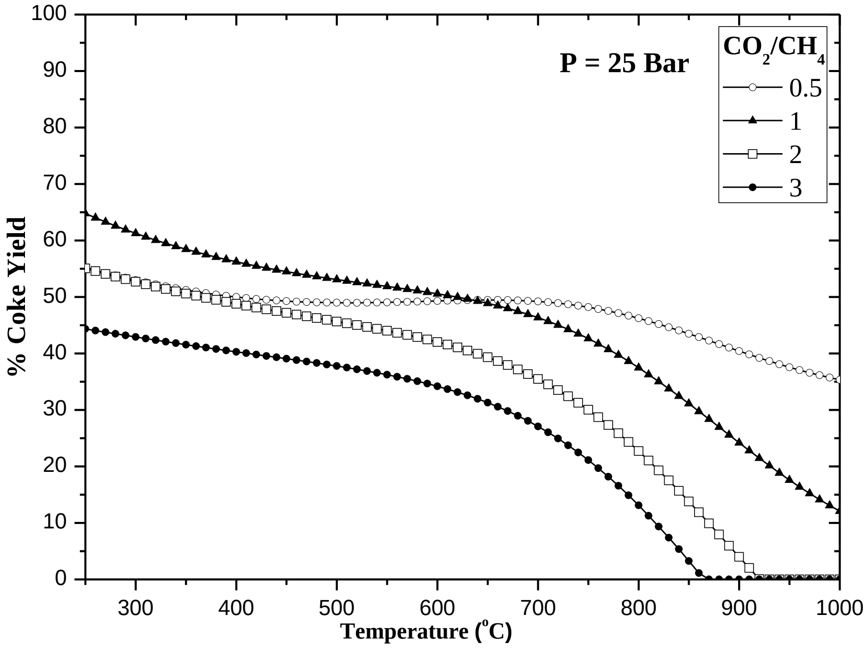

Figure 6.2.9 Influence of CO_2/CH_4 ratio on coke yield in dry reforming of methane

6.2.3 Effect of presence of CO in reaction feed

Figure 6.2.10 depicts the effect of CO on CO_2 conversion. Since CO is one of main product of reaction system, presence of CO reduces carbon dioxide conversion. Presence of CO in feed doesn't have any major effect on H_2 and CO yields.

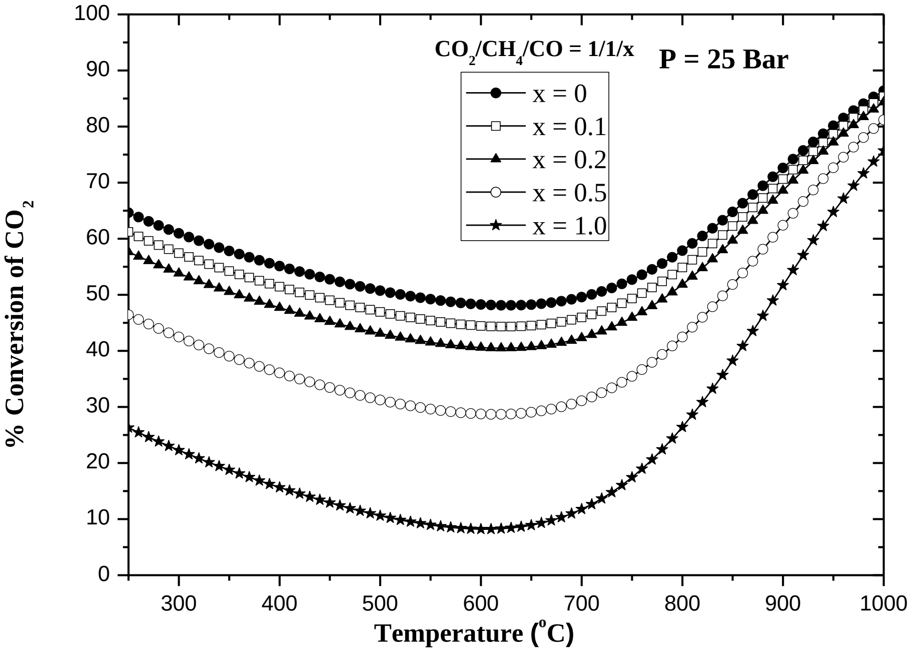

Figure 6.2.10 Effect of presence of CO on CO_2 conversion in dry reforming of methane

6.3 Methanol synthesis from dry reforming product

6.3.1 Effect of temperature and pressure

The analysis of dry reforming coupled with methanol synthesis is done in two steps. The output from analysis of dry reforming is taken as the feed to methanol synthesis. Water and coke formed in dry reforming are not taken in feed for methanol. Figure 6.3.1 and 6.3.2 show the effect methanol synthesis temperature on overall CO_2 conversion and methanol yield. They also depict the effect of dry reforming temperature on overall CO_2 conversion and methanol yield. Pressures for dry reforming and methanol synthesis are taken as 1 bar and 100 bar respectively. Feed with CO_2/CH_4 ratio of 1 is taken for calculations. For methanol synthesis temperatures below 270 ^oC, low temperature feeds from dry reforming have higher CO_2 conversions but opposite trend is observed beyond 270 ^oC. Low temperature feed contain only unreacted CO_2 with trace amount of CO and H_2 (see Table 6.1). As a result, very less variation in CO_2 conversion for low temperature feed is observed. High temperature feeds contain only CO and H_2 but water gas shift reaction at low temperature causes in significant formation of CO_2, resulting in low CO_2 conversion. It can be seen from figure 6.3.2 that methanol yield decrease with increasing temperature. This happens because synthesis of methanol from CO is exothermic in nature. High dry reforming temperature also favours methanol yield because higher dry reforming temperature leads to increased availability of CO and hydrogen. Dry reforming is favoured by low pressure. As a result, low pressure feeds in dry reforming have better CO_2 conversion and methanol yield (see figure 6.3.3 and 6.3.4). Figure 6.3.7 and 6.3.8 show the effect of methanol synthesis pressure and temperature on overall CO_2 conversion and methanol yield. Methanol synthesis pressure has nearly no effect on overall CO_2 conversion but methanol yield increases with methanol synthesis pressure (see Figure 6.3.5 & 6.3.6)

Table 6.1 Dry Reforming Product composition

(P = 1 bar & Feed CO_2 = 1 mole & H_2 = 1 mole)

Temperature (°C)	CO_2	H_2	CH_4	CO	H_2O	C(Solid)	H_2/CO
500	0.543	0.573	0.292	0.073	0.843	1.094	7.84
600	0.529	1.053	0.177	0.348	0.592	0.944	3.021
650	0.456	1.300	0.126	0.640	0.448	0.778	2.031
700	0.337	1.520	0.085	1.017	0.308	0.560	1.494
800	0.113	1,813	0.037	1.660	0.113	0.190	1.092

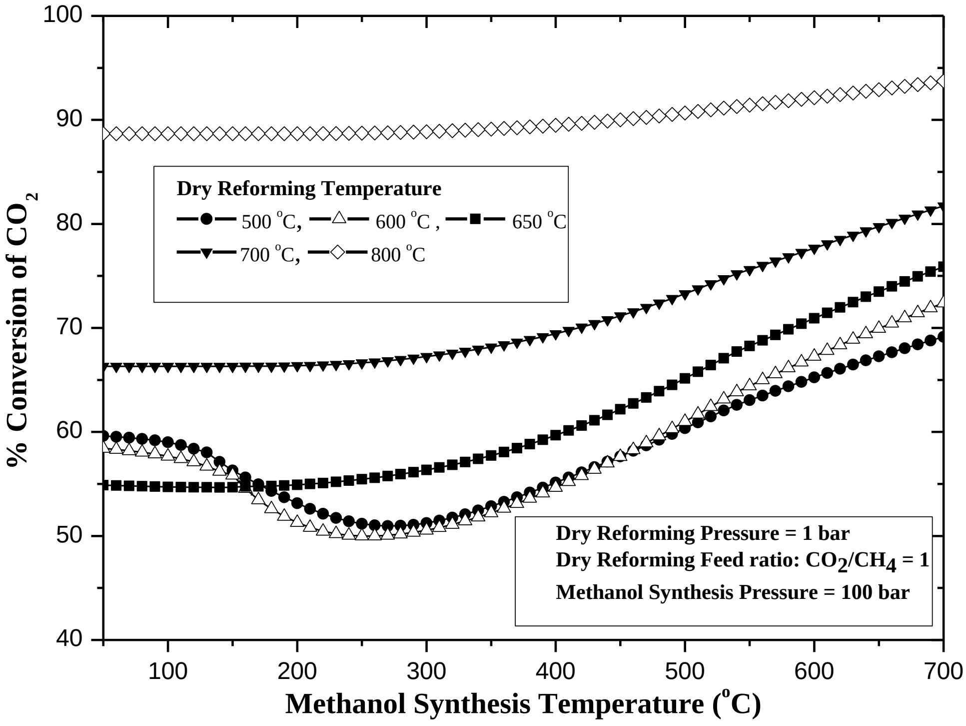

Figure 6.3.1 Effect of Dry reforming temperature & Methanol synthesis temperature on overall CO_2 Conversion

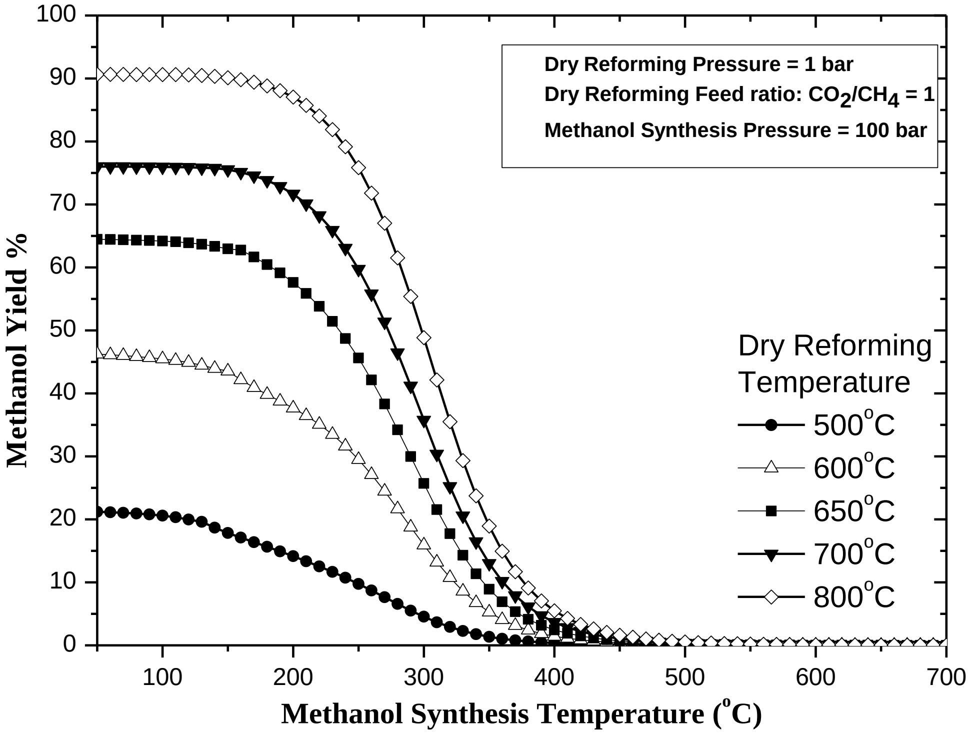

Figure 6.3.2 Effect of Dry reforming temperature & Methanol synthesis temperature on Methanol Yield

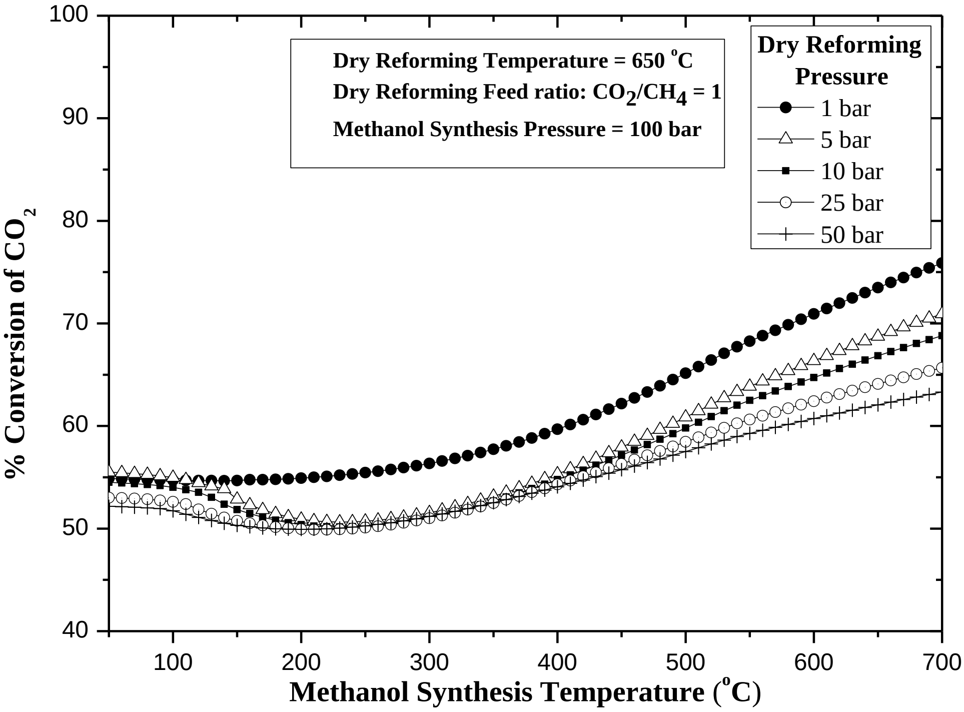

Figure 6.3.1 Effect of Dry reforming temperature & Methanol synthesis temperature on overall CO_2 Conversion

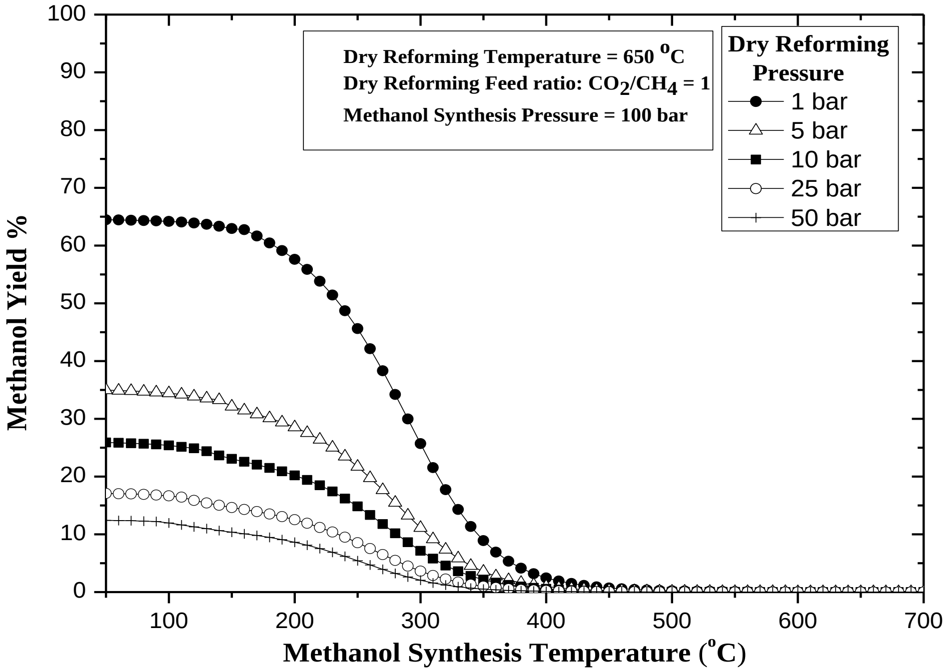

Figure 6.3.4 Effect of Dry reforming pressure & Methanol synthesis temperature on Methanol yield

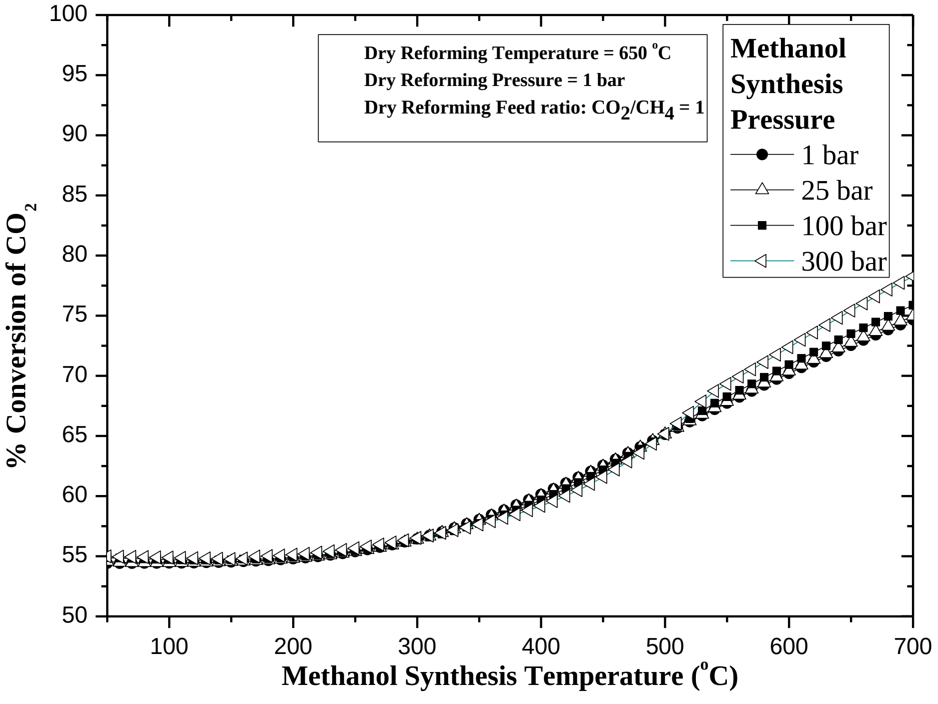

Figure 6.3.5 Effect of Methanol synthesis Pressure & Temperature on overall CO_2 Conversion

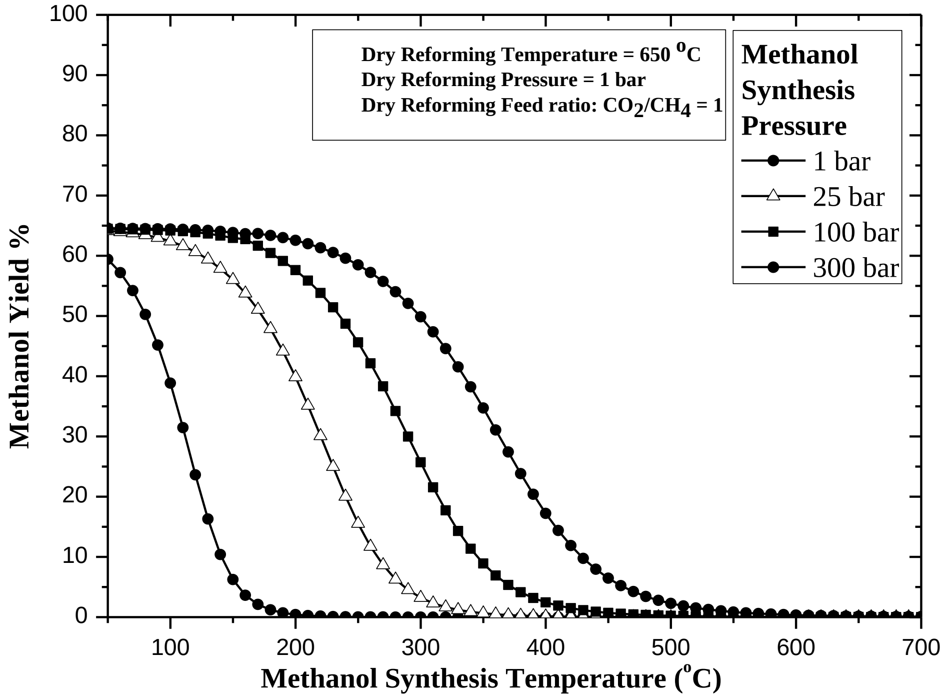

Figure 6.3.6 Effect of Methanol synthesis Pressure & Temperature on methanol Yield

6.3.2 Effect of feed composition

Methanol synthesis via CO hydrogenation is favoured by high H_2/CO ratios. Dry reforming produces syngas at H_2/CO ratio of 1. H_2/CO ratios>1 are observed for at lower dry reforming temperatures but they are accompanied by low CO yield and coke formation (see Table 6.1). As a result, overall methanol yield from high H_2/CO (low temperature methanol synthesis operation) ratio feed is less than yield form feed with H_2/CO ratios of 1. H_2/CO ratios can also be changed by changing the feed to dry reforming. It can be seen from figure 6.2.8 that low CO_2/CH_4 ratio results in higher H_2/CO ratio but our analysis shows that CO_2/CH_4 ratio of 1s gives the best methanol yield.

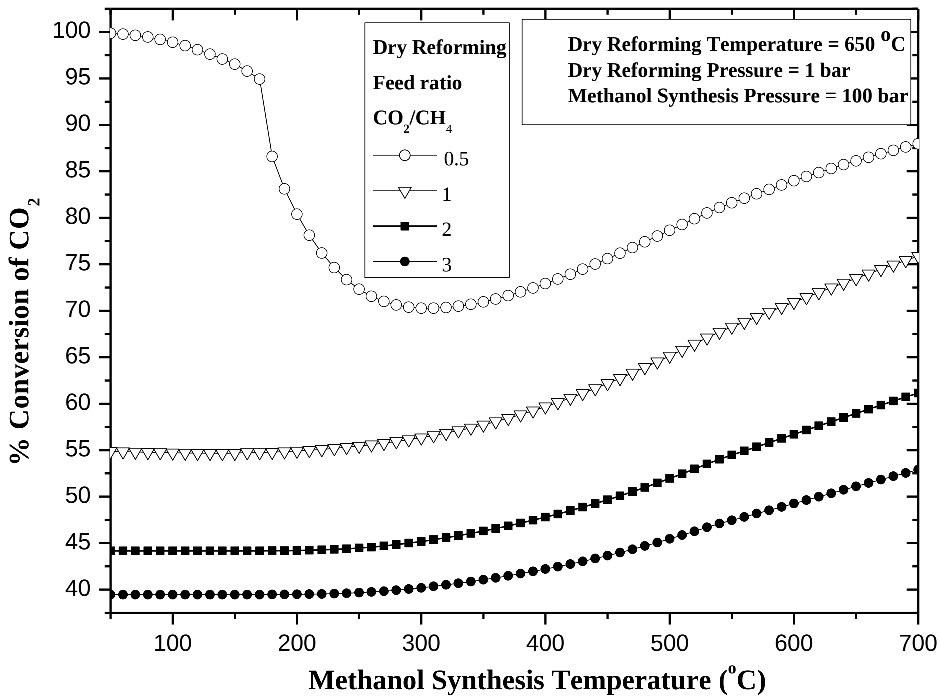

Figure 6.3.7 Effect of Dry Reforming Feed Composition & Methanol synthesis Temperature on % CO_2 Conversion

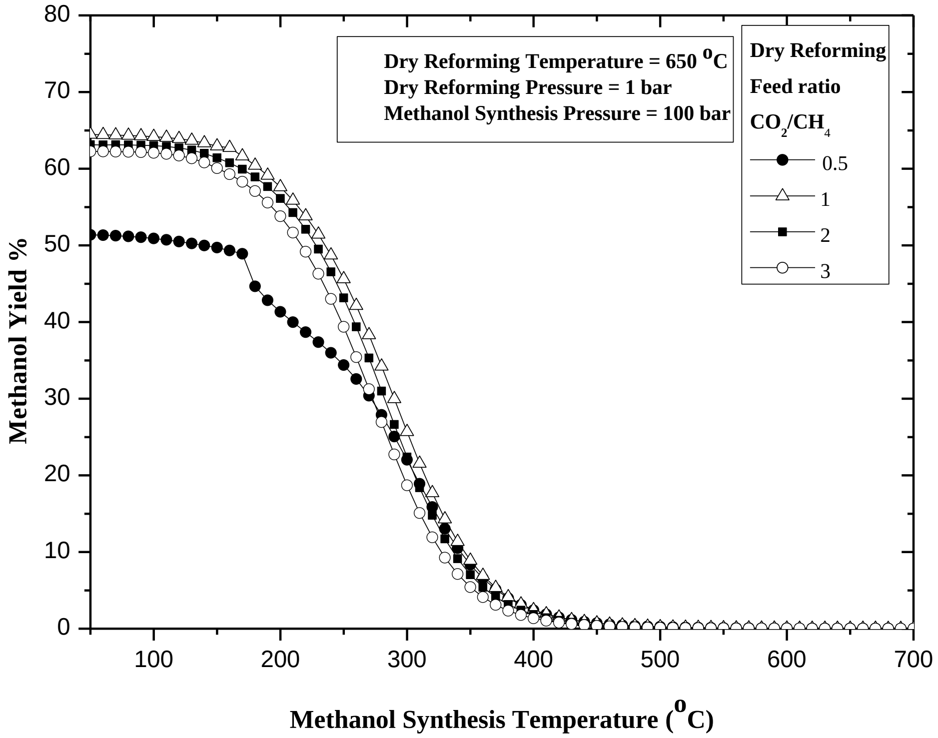

Figure 6.3.8 Effect of Dry Reforming Feed Composition & Methanol synthesis Temperature on Methanol Yield

CHAPTER 7

CONCLUSION

Detailed thermodynamic study of three systems: synthesis of methanol from CO_2, dry reforming of methane and methanol synthesis using dry reforming product was performed in the present study. Influence of temperature, pressure, feed compositions and presence of CO in feed were investigated in terms of their impact on conversion, selectivity and yield. It was found that methanol synthesis via CO_2 hydrogenation is favoured by low temperature, high pressure and high H_2/CO_2 ratio. For dry reforming, high temperature & low pressure are more favourable. Methanol synthesis using dry reforming product is favoured by high dry reforming temperature, low dry reforming pressure, high methanol synthesis pressure and low methanol synthesis temperature.

Methanol synthesis from dry reforming product shows better methanol yield than synthesis of methanol from direct CO_2 hydrogenation but the CO_2 conversion is better for synthesis of methanol from direct CO_2 hydrogenation. Synthesis of methanol from direct CO_2 hydrogenation requires very high pressure conditions which is not good from economical point of view. Higher methanol yield can be obtained at lower methanol synthesis pressure for methanol synthesis from dry reforming product. No external pure valuable hydrogen is required for producing methanol for the process of methanol synthesis from dry reforming product. It is a major benefit of methanol synthesis from dry reforming product over methanol synthesis via direct hydrogenation of carbon dioxide. Although methanol synthesis from dry reforming product yields better results, it has technological hurdles like removal of intermediate by product removal like water and coke.

Thermodynamic analysis of chemical reaction system represents only one of the aspects related to the chemical process. Other important factors such as kinetics, economic feasibility etc also play a major role in deciding the final application of any process at practical level.

REFERENCES

Amin, N.A.S., Yaw, T.C., *"Thermodynamic equilibrium analysis of combined carbon dioxide reforming with partial oxidation of methane to syngas"* Int. J. Hydrogen Energy *32,* **(2007)** 1789–1798. doi:10.1016/j.ijhydene.2006.12.004

An, X., Zuo, Y., Zhang, Q., Wang, D., Wang, J., *"Dimethyl ether synthesis from CO_2 hydrogenation on a CuO - ZnO - Al_2O_3- ZrO_2 / HZSM-5 bifunctional catalyst".* Ind. Eng. Chem. Res. *47,* **(2008)** 6547–6554.

Arcoumanis, C., Bae, C., Crookes, R., Kinoshita, E., *"The potential of di-methyl ether (DME) as an alternative fuel for compression-ignition engines: A review".* Fuel *87,* **(2008)**1014–1030. doi:10.1016/j.fuel.2007.06.007

Aresta, M., Forti, G., *"Carbon Dioxide as a Source of Carbon";* NATO ASI Series **(1987),** D; Reidel: Dordrecht, The Netherlands,

Climate Change **1995**, *"The Science of Climate Change. Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change"* [Filho, L. G., Callander, B. A., Kattenberg, A. and Maskell K.] Cambridge University Press, Cambridge,United Kingdom, and New York, NY, USA.

Edwards, J.H., Maitra, A. M.,. *"The chemistry of methane reforming with carbon dioxide and its current and potential applications".* Fuel Process. Technol. 42, **(1995)** 269 – 289. doi:10.1016/0378-3820(94)00105-3

Friedlingstein, P.; Houghton, R. A.; Marland, G.; Hackler, J.; Boden, T. A.; Conway, T. J.; Canadell, J. G.; Raupach, M. R.; Ciais, P.; Quéré, C. L. *"Update on CO2 emissions".* Nature Geosci. 3, **(2010)** 811–812.

Fornero EL, Chiavassa DL, Bonivardi AL, Baltanás MA. *"CO_2 capture via catalytic hydrogenation to methanol: Thermodynamic limit vs.'kinetic limit'"*. Catalysis today. **(2011)** Aug 25;172(1):158-65.

Honisch, B., Ridgwell, A.,. *"The Geological Record of Ocean Acidification. Science".* 335, 1058–1063. 61 **(2012)**

IPCC, 1995 : Climate change 1995*: "The science of climate change: contribution of working group I to the second assessment report of the Intergovernmental Panel on Climate Change"* (Vol. 2). Cambridge University Press.

Hu, B., Guild, C., Suib, *S.L.,." Thermal, electrochemical, and photochemical conversion of CO_2 to fuels and value-added products".* J. CO2 Util. 1, 18–27 **(2013)**. doi:10.1016/j.jcou. 2013.03.004

Iliuta, I., Larachi, F., Fongarland, P.,. *"Dimethyl ether synthesis with in situ H2O removal in fixed-bed membrane reactor: model and simulations".* Ind. Eng. Chem. Res. 49, **(2010)** 6870–6877. doi:10.1021/ie901726u

IPCC, 2001: Climate Change 2001: *"Synthesis Report. A contribution of working groups I, II, and III to the third assessment report of the Intergovernmental Panel on Climate Change"* [Watson, R.T. and the Core Writing Team (eds.)]. Cambridge University Press, Cambridge, United Kingdom, and New York, NY, USA.

IPCC, 2005: *"IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change"* [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)] . Cambridge University Press, Cambridge, United Kingdom and NewYork, NY, USA, 442 pp.

IPCC, 2007: *Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, Pachauri, R.K and Reisinger, A.(eds.)]. IPCC, Geneva, Switzerland, 104 pp..*

Iyer, S. S., Renganathan, T., Pushpavanam, S., Kumar, M. V., & Kaisare, N. *"Generalized thermodynamic analysis of methanol synthesis: Effect of feed composition".* Journal of CO2 Utilization, 10, **(2015)** 95-104.

Jia, G., Tan, Y., Han, Y.,. *"A Comparative Study on the Thermodynamics of Dimethyl Ether Synthesis from CO Hydrogenation and CO_2 Hydrogenation".* Ind. Eng. Chem. Res. 45 **(2006)** 1152–1159.

Li, Y., Wang, Y., Zhang, X., Mi, Z. *"Thermodynamic analysis of autothermal steam and CO_2 reforming of methane".* Int. J. Hydrogen Energy 33, **(2008)** *2507–2514.* doi:10.1016/j.ijhydene. 2008.02.051

Machado CF, de Medeiros JL, Araújo OF, Alves RM.*" A comparative analysis of methanol production routes: synthesis gas versus CO_2 hydrogenation".* In Proceedings of the 2014 International Conference on Industria l Engineering and Operations Management Bali, Indonesia **(2014)** Jan 7 (pp. 7-9).

Moradi, G.R., Ahmadpour, J., Yaripour, F., Wang, J., *"Equilibrium calculations for direct synthesis of dimethyl ether from syngas".* Can. J. Chem. Eng. 89, **(2011)** 108–115. doi:10.1002/cjce.20373

Nikoo, M.K., Amin, N. A. S.,. *"Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation".* Fuel Process. Technol. 92, **(2011)** 678–691. doi:10.1016/j.fuproc.2010.11.027

Olah, G. a, Goeppert, A., Prakash, G.K.S, *"Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons"*. J. Org. Chem. 74, **(2009)**. 487–98. doi:10.1021/jo801260f

Shen, W.-J., Jun, K.-W., Choi, H.-S., Lee, K.-W.,. *"Thermodynamic investigation of methanol and dimethyl ether synthesis from CO_2 Hydrogenation"*. Korean J. Chem. Eng. 17, **(2000)** 210–216. doi:10.1007/BF02707145

Sun, Y., Ritchie, T., Hla, S.S., McEvoy, S., Stein, W., Edwards, J.H.,. *"Thermodynamic analysis of mixed and dry reforming of methane for solar thermal applications"*. J. Nat. Gas Chem. 20, **(2011)** 568–576. doi:10.1016/S1003-9953(10)60235-6

Swapnesh, A., Srivastava, V. C., & Mall, I. D. *"Comparative Study on Thermodynamic Analysis of CO_2 Utilization Reactions"*. Chemical Engineering & Technology, 37(10) **(2014)**., 1765-1777.

Wang, W., Wang, S., Ma, X., Gong, J.,. *"Recent advances in catalytic hydrogenation of carbon dioxide". Chem. Soc. Rev. 40,* **(2011)** *3703*–27. doi:10.1039/c1cs15008a

Xiaoding, X., Moulijn, J.A.,. *Mitigation of CO_2 by chemical conversion : plausible chemical reactions and promising products.* Energy. Fuel 10, **(1996)** 305–325.

Zhang, H., Li, M., Xiao, P., Liu, D., Zou, C.J.,. *"Structure and catalytic performance of Mg-SBA-15-supported nickel catalysts for CO_2 reforming of methane to syngas"*. Chem. Eng. Technol. **(2013)** n/a–n/a. doi:10.1002/ceat.201300006