THERMODYNAMIC ANALYSIS OF CARBON DIOXIDE UTILIZATION REACTIONS

A DISSERTATION

Submitted in the partial fulfillment of the
requirements for the award of the degree
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in
CHEMICAL ENGINEERING
(With Specialization in Hydrocarbon Engineering)

By
ANANG SWAPNESH

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE-247667 (INDIA)
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DECLARATION

I hereby declare that the work being presented in the dissertation titled "Thermodynamic Analysis of Carbon Dioxide Utilization Reactions" in partial fulfillment 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 the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my work carried out during the period from May 2013 to May 2014 under the supervision of Dr. I. D. Mall, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India. The matter presented in this dissertation has not been submitted by me for the award of any other degree of this or any other institute.

.

(Anang Swapnesh)

Date:

CERTIFICATE

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

(Dr. I. D. Mall)
Professor, Department of Chemical Engineering
Indian Institute of Technology Roorkee
Roorkee
Date:

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Abstract

Carbon dioxide (CO_2), a greenhouse gas, is considered to be largely responsible for phenomena of global warming. Over the last 2 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 DME from CO_2 hydrogenation, synthesis of methane from CO_2 hydrogenation, dry reforming of methane and synthesis of DME using dry reforming product was performed using 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 temperature, pressure and feed composition on conversion, selectivity and yield were investigated for each process. Effect of fractional removal of products and effect of presence of carbon monoxide on conversion and yield were also studied. The conversion and product yields of the processes were compared to ascertain the suitable processes for practical application.

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Chapter 1 Introduction

1.1 Introduction

The environmental degradation and climate change is one of the burning issues of industrial age. CO_2, a greenhouse gas, is considered to be the prime contributor to the greenhouse effect which causes global warming and climate changes. Other environmental concerns that are attributed to high atmospheric concentration of CO_2 are acid rains and ocean acidification (Honisch and Ridgwell, 2012). Unlike other pollutants such as SO_2, H_2S, etc., CO_2 does not have immediate harmful effect on human population.

With the advent of industrial age, atmospheric concentration of CO_2 has risen continuously. This rise can be attributed to widespread use of fossil fuels. The atmospheric CO_2 concentration has increased from 316ppm in 1959 to 393.82 in 2012 (NOAA). The following figure depicts the increase of atmospheric CO_2 concentration over time.

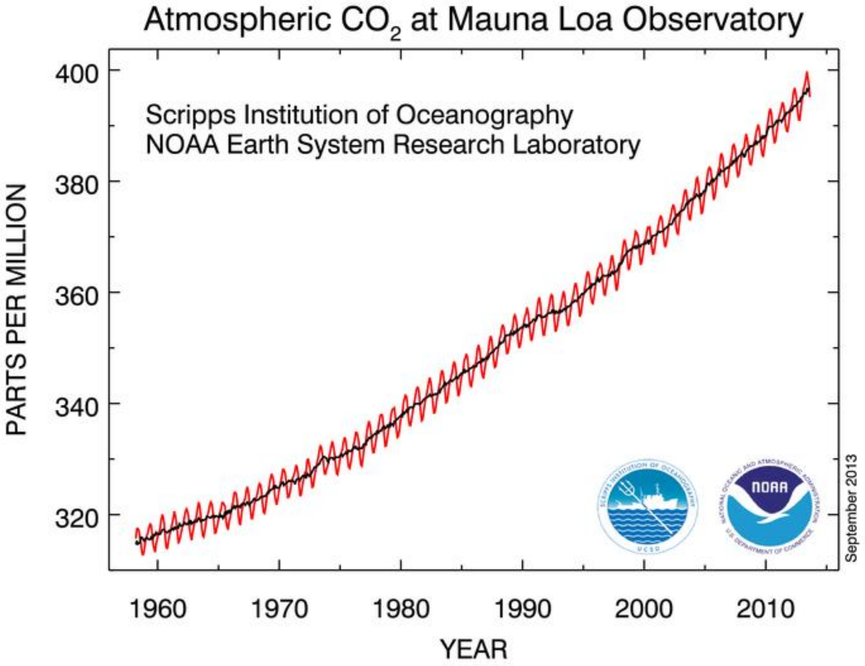

Figure 1.1- Carbon dioxide in atmosphere

(Source:http://www.esrl.noaa.gov/gmd/webdata/ccgg/trends/co2_data_mlo.png)

Other greenhouse gases such as chloro fluro carbon (CFC), NO_x, CO, etc. exhibit stronger greenhouse effect compared to CO_2 (*Climate Change*, 1995). The relative strength of greenhouse effect is measured in term of global warming potential. The following table shows GWP of certain greenhouse gases

Table 1.1 -Global Warming Potentials

Greenhouse Gases	Global Warming Potential (100 year average)
CO_2	1
Methane	21
Nitrous oxide	310
Perfluoroethane	11700
HFC-23	9200

(Source: Climate Change 1995)

Despite being a weak greenhouse gas, CO_2 is the major contributor to global warming as it accounts for 77% of total greenhouse gas emitted (IPCC, 2007).

1.2 Sources of CO_2 emission

The global CO_2 emission stands at about 34 billion tons per annum. The largest emitters are (as per 2011 data): China (29%), the United States (16%), the European Union (11%), India (6%), the Russian Federation (5%), and Japan (4%) (Oliver et al., 2012). The global emission can be divided to 7 categories based on the type of activity that lead to it. These categories are (IPCC, 2007)

1. **Energy Supply** (26%) – Use of fossil fuels such as coal, natural gas, and oil in thermal power plant for production of electricity is the largest source of CO_2 emission.
2. **Industry** (19%) - CO_2 emissions from industry is primarily from use of fossil fuels. Other sources include production of CO_2 as a byproduct in various chemical and metallurgical processes.
3. **Forestry** (17%) - This category primarily include CO_2emissions from deforestation, land clearing for agriculture, and fires or decay of peat soils.
4. **Agriculture** (14%) - Emissions from agriculture mostly come from the management of agricultural soils, livestock, rice cultivation, and biomass burning.

5. **Transportatio**n (13%) - CO_2 emissions from this category mostly comes from use of fossil fuels as the energy source.
6. **Commercial and Residential Buildings** (8%) - Greenhouse gas emissions from this category arise from burning fuels for heat in buildings or cooking in homes.
7. **Waste and Wastewater** (3%)

1.3 Mitigation of CO_2 Emission

1.3.1 Summary of mitigation techniques

A wide variety of solutions, both long term and short term, are available for reduction of CO_2 emission. These techniques are broadly classified into following categories

1. **Use of Alternate Energy Sources-** Fossil fuels are the prime source of energy (86%) in the world today. It is also the largest source of anthropogenic CO_2 emission accounting for 75 % of total emission (IPCC, 2001). A large reduction in CO_2 emission can be achieved by switching to energy sources which are renewable and do not emit CO_2. The alternate energy sources include nuclear, wind, solar, tidal, biomass energy.
2. **Energy Conservation-** Consumption of energy in forms fossil fuels across the sectors of economy and society is largely responsible for emissions. Adoption of energy efficient technologies and energy conservation practices in transport, urban planning and building design will reduce CO_2 emission.
3. **Carbon Capture and storage-** This method reduce CO_2 emission by capturing carbon dioxide from large point sources such as power plants and subsequently storing it away safely in geological formation. At current technological level, it is possible to capture approximately 80-90% of emitted CO_2 (IPCC, 2005).
4. **Utilization of CO_2 being emitted -** CO_2 has a number of useful industrial and domestic applications. All the application of CO_2 can be classified into 2 categories: Physical and Chemical. Physical applications include uses in enhanced oil recovery, beverage industry, supercritical CO_2 extraction etc. It should be noted that these applications do not directly reduce the emission in most of the cases. Chemical application involves use of CO_2 as a raw material

for production of useful products. Chemical applications directly contribute to reduction of CO_2 emission.

1.3.2 Chemical conversion of CO_2 into value added products

Carbon based organic compounds account for 34% of total chemical production (Friedlingstein et al, .2010). As of now, most of the organic chemical industries use petroleum based carbon as raw material. CO_2 emitted from various large point sources has immense potential to become a cheap source of carbon for organic chemical industry (Aresta and Fortis, 1987).

CO_2 can be converted into a large number of value added products such as methanol, dimethyl carbonate, dimethyl ether, higher alcohols, MTBE, formic acid, formaldehyde, formamides, polycarbonates, methane, carbon monoxide etc.

CO_2 is a stable compound because of its linear and centro-symmetric structure. As a result, it is inert and most of its reactions are thermodynamically unfavorable. It has become possible to overcome these issues by use of suitable catalyst and operating conditions. In recent times, conversion of CO_2 into fuel and value added products have gained popularity (Hu et al., 2013; Olah et al., 2009; Wang et al., 2011; Xiaoding and Moulijn, 1996). The following table shows the ΔG and ΔH values for reactions of CO_2

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

Reactions	ΔG°	ΔH°
$CO_2(g) + H_2(g) \rightarrow HCOOH(l)$	-31	+34.3
$CO_2(g) + 2H_2(g) \rightarrow HCHO(g) + H_2O(l)$	-11.7	+46.6
$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l)$	-137.8	-10.7
$CO_2(g) + 4H_2(g) \rightarrow CH4(g) + 2H_2O(l)$	-259.8	-132.4
$CO_2(g) + CH_4(g) \rightarrow CH_3COOH(l)$	-13.3	+58.8
$CO_2(g) + C6H_6(l) \rightarrow C_6H_5COOH(l)$	-21.6	+30.5
$CO_2(g) + CH_4(g) + H_2(g) \rightarrow CH_3CHO(l) + H_2O(l)$	-14.6	+74.4
$3CO_2(g) + CH_4(g) \rightarrow 4CO (g) + 2H_2O(l)$	+235.1	+209.2
$2CO_2(g) + 6H_2(g) \rightarrow CH_3OCH_3(g) + 3H_2O(l)$	-264.	-38.0

It can be observed from the table 1.2, hydrogenation reactions are generally more favorable thermodynamically, hence more suited for practical application

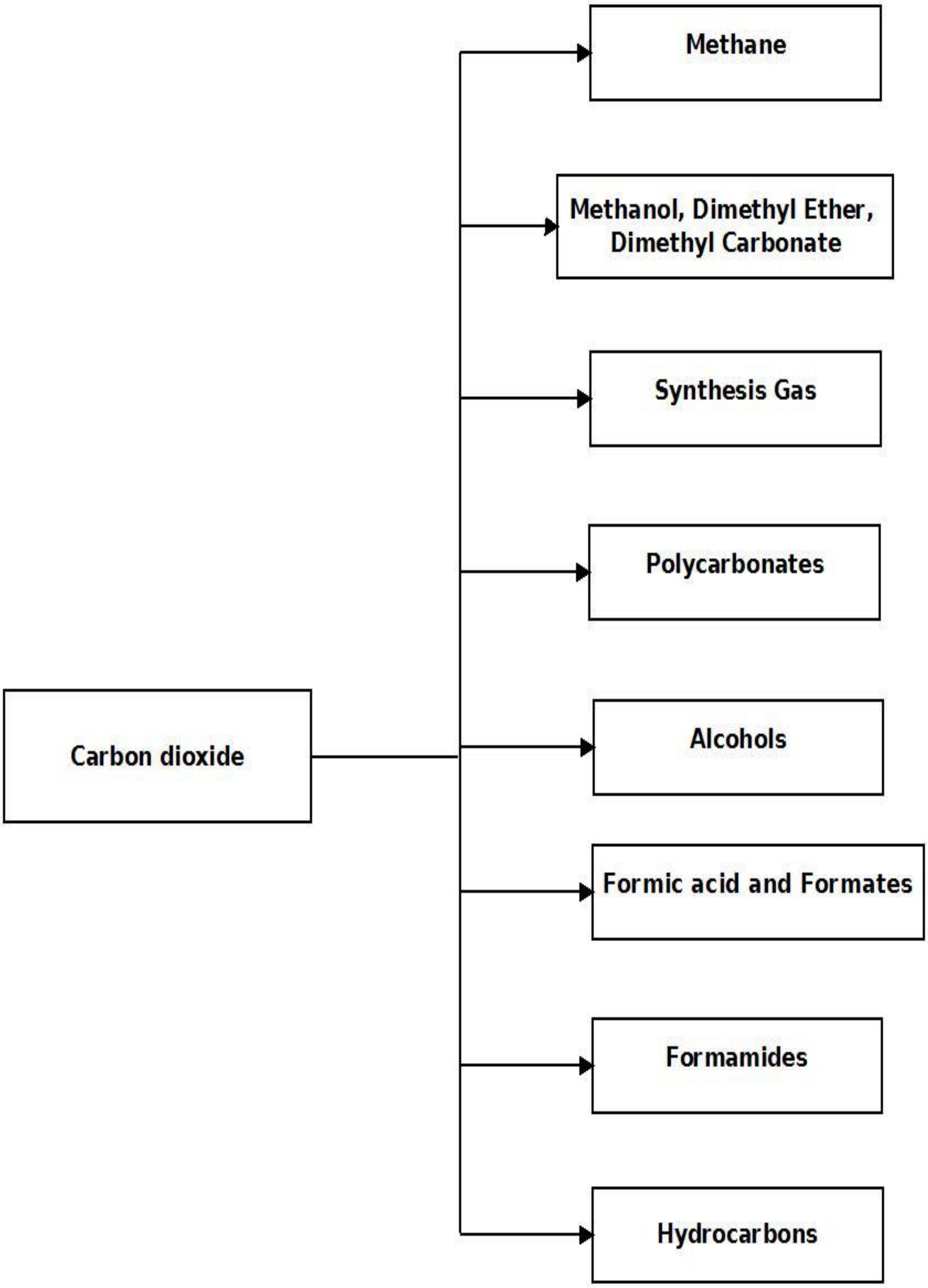

Figure 1.2-Products from Carbon dioxide

Chapter 2 Literature Review

The review is done in two parts. The first past deals with review of various reactions of CO_2 being considered for practical application as measure for mitigation of CO_2 emission. The second part deals with thermodynamic analysis of the selected systems for the present study.

2.1 Review of CO_2 utilization techniques

A large body of work exists regarding various CO_2 utilization techniques for carbon mitigation. It is impractical to discuss all of the techniques being researched upon. Thus only paper which have reviewed and summarized techniques are discussed in this section.

Xiadong and Moulijn (1996) covered a wide range of chemical conversion of CO_2. Various routes covered in their work include reduction of CO_2, reactions with Compounds Having Activated Hydrogen Atoms, production of polycarbonates, reaction with epoxides, reaction with alcohols and ethers, reaction with Nitrogen compounds, reactions with Sulfur Compounds and bioconversion. They also studied the use of CO_2 as a weak acid and an oxidizing agent. They commented that to significantly reduce CO_2emission through chemical conversion techniques, focus should be on production on bulk chemicals. They concluded that the most important application of CO_2 conversion are production are methanol, Dimethyl ether, MTBE and Dimethyl Carbonate for their increase role as gasoline additives and standalone fuels

Olah et al. (2009) focus on role on CO_2 recycling in proposed Methanol economy. Methanol economy is a concept in which methanol replace fossil fuel as means of raw material and 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 favorable 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 selected reactions

2.2.1 Synthesis of Dimethyl ether

Shen et al. (2000) examined the thermodynamics in synthesis of Dimethyl ether and methanol from CO_2 and H_2 in gas phase. Both of the reaction systems (including side reactions) were compared 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. Study concluded that DME allows for higher yield and selectivity than methanol.

Jia et al. (2006) carried out a comparative thermodynamic study of CO and CO_2 hydrogenation for production of DME. 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 CO_2 hydrogenation but is not suitable due to low efficiency of carbon utilization.

Moradi et al. (2011) analyzed the synthesis of DME from syngas on a bi-functional catalyst: $CuO/ZnO/Al_2O_3$. Study used a slurry bed reactor. The results from experimental setup were compared with results obtained from thermodynamic analysis. The analysis was done using equilibrium constant method. The equilibrium constant was calculated using Vant Hoff's equation. Fugacity coefficients were calculated using SRK equation of state. The parameters varied in the study were temperature, pressure and composition of feed ratio.

2.2.2 Methanation

Gao et al. (2012), in their work performed detailed analysis of methanation of CO_2 for production of synthetic natural gas using Gibbs free energy minimization technique. They investigated the effects of temperature, pressure, feed composition ratio, and the addition of other compounds (H_2O, O_2, CH_4, and C_2H_4) in the feed gas on conversion. They also compared the thermodynamic calculations with experimental data from literature.

Chen et al. (2013) carried out a comprehensive analysis of syngas methanation for production of synthetic natural gas with emphasis on carbon deposition tendencies on catalyst. Analysis was done using Gibbs free energy minimization technique. They investigated the effects of temperature, pressure, and feed composition ratio on conversion.

Beuls et al (2012) performed the methanation of CO_2 on Rh/γ-Al2O3 catalyst in a pulse reactor proposing a mechanism for adsorption and reaction of CO_2 on the catalyst. They performed the thermodynamic analysis of methanation of CO_2 and compared the results with experimental values. They also studied the effect of presence of oxygen on methanation.

Ocampo et al. (2009) investigated the $Ni–Ce_{0.72}Zr_{0.28}O_2$ catalysts containing up to 15 wt% Ni for carbon dioxide methanation. High CO_2 conversions were achieved at 350 and 400 °C, for all catalysts. They also performed the thermodynamic analysis of methanation of CO_2 and compared the results with experimental values.

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 behavior 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.

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.

Nikoo and Amin. (2011) carried out the analysis of CO_2 reforming of methane taking in account carbon deposit on catalyst. The analysis was done by Gibbs free energy. They investigated the effects of temperature, pressure, and feed composition ratio on conversion and carbon deposit.

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.

2.2.3 Research gap

It can be seen in Table 2.2 that Gibbs free energy minimization method has not been used previously for thermodynamic analysis of DME synthesis. This method, although, has been used previously for dry reforming of methane, however, effect of pressure was not studied. Similarly, comparative thermodynamic study of various 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, the present work focuses on comparative study of thermodynamics of the selected four processes.

Table 2.1- Review of CO_2 utilization techniques

Authors	Title	Brief Description
Xu and Moulijn. (1996)	Mitigation of CO_2 by Chemical Conversion: Plausible Chemical Reactions and Promising Products	Studied various routes to manufacture products such as acids, alcohols, esters, lactones, carbamates, urethanes, urea derivatives, various copolymers, and polymers from CO_2
Olah et al (2009)	Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons	Studied role of CO_2 recycling in Methanol economy
Wang et al (2011)	Recent advances in catalytic hydrogenation of carbon dioxide	Critical review of developments in field of catalytic hydrogenation of carbon dioxide. Focused on catalyst, reaction mechanism and rector design
Hu, et al (2013)	Thermal, electrochemical, and photochemical conversion of CO_2 to fuels and value-added products	Studied various routes to manufacture products such as formic acid, formaldehyde, CO, polycarbonates etc. from CO_2 using thermal, electrochemical, and photochemical methods

Table 2.2- Thermodynamic Analysis

Authors	Reaction System	Methodology of Analysis
Shen et al. (2000)	Synthesis of Dimethyl ether	• Equilibrium Constant Method • Equilibrium Constant calculated using empirical relations from Chinchen et al. (1982) • Fugacity coefficient calculated using empirical relations from Soave. (1972)
Jia et al. (2006)	Synthesis of Dimethyl ether	• Equilibrium Constant Method • Equilibrium Constant calculated using Equilibrium Calculator software • Fugacity coefficient calculated using SRK equation of state
Moradi et al. (2011)	Synthesis of Dimethyl ether	• Equilibrium Constant Method • Equilibrium Constant calculated using Equilibrium Calculator software • Fugacity coefficient calculated using SRK equation of state
Gao et al. (2012)	Methanation	Gibbs free energy minimization
Chen et al. (2013)	Methanation	Gibbs free energy minimization taking in account carbon deposition on catalysts
Beuls et al. (2012)	Methanation	Gibbs free energy minimization
Ocampo et al. (2009)	Methanation	Gibbs free energy minimization
Amin et al. (2007)	CO_2 reforming of Methane	Gibbs free energy minimization method
Li et al. (2008)	CO_2 reforming of Methane	Gibbs free energy minimization method
Nikoo et al. (2011)	CO_2 reforming of Methane	Gibbs free energy minimization taking in account carbon deposition on catalysts
Sun et al. (2011)	CO_2 reforming of Methane	Gibbs free energy minimization method

Chapter 3 Objective

The present study focuses on reactions for conversion of CO_2 into useful products. The major aspect of any reacting system for practical application is its efficacy to produce the desired product in maximum amount. Degree of conversion at equilibrium is the maximum possible conversion that can be achieved for a given temperature and pressure. It sets the upper limit on the production capacity. It is important to calculate the degree of conversion of reactants, selectivity of various products, yield of various products and the effect of operating conditions on conversion and yield for prediction of economic viability of a process. These required parameters are calculated by carrying Thermodynamic analysis of the processes under-study. The present study looks into thermodynamic aspects of various important processes being considered for conversion of CO_2 into useful products.

Objectives of the present study are as follows:

- To perform thermodynamic analysis of the following processes:
    1. Synthesis of dimethyl ether via CO_2 hydrogenation
    2. Synthesis of methane via CO_2 hydrogenation
    3. Dry reforming of methane
    4. Synthesis of DME using dry reforming product
- To calculate degree of conversion of the reactants, yield and selectivity of desired product.
- To study the effect of operating conditions namely pressure, temperature and feed composition on conversion, yield and selectivity of desired product.
- To study the effect of fractional removal of products on conversion of the reactants and yield of desired product.
- To study the presence of CO in feed on conversion of the reactants and yield of desired product.
- To compare the degree of conversion of the reactants, yield and selectivity of desired products for all the processes being analyzed in present study.
- To comment on suitability of the reaction systems for practical applications

Chapter 4 Theory

4.1 Equilibrium

Thermodynamic analysis of chemically reacting systems largely deals with the state of the system at chemical equilibrium. Equilibrium is one of the central concepts of science. In its most general form, equilibrium is defined as "the state in which all acting influences are canceled by others, resulting in a stable, balanced, or unchanging system". In thermodynamics, a system is in equilibrium when it attains thermal, mechanical and chemical equilibrium. . The internal energy and its partial Legendre transforms, also known as thermodynamics potentials, play an important role in thermodynamics analysis of process. These functions represent the potential of the system to do work. The state of equilibrium is the one in which internal energy or any of its potentials is **minimized** for given conditions.

The present study focuses on chemical equilibrium. Chemical equilibrium is defined as the state in which rate of forward and backward reactions in a chemically reacting system become equal and the composition of reacting system becomes constant for a specified temperature and pressure. The thermodynamic potential used for defining chemical equilibrium from mathematical perspective is Gibbs free energy.

4.2 Gibbs free energy minimization

There are two approaches for performing thermodynamic analysis: Stoichiometric and non-stoichiometric. Stoichiometric approach requires exact knowledge of chemical species in the system and independent reactions taking place in the system. Application of stoichiometric becomes tedious for complex systems involving a large number of reactions. Equilibrium constant method cannot be applied to systems whose all the reactions are not known. Non-stoichiometric approach, also known as Gibbs free energy minimization, requires only knowledge of chemical species in the system for thermodynamic equilibrium calculations. As a result, non-stoichiometric methods can be applied with ease to any system irrespective of its complexity. The present study uses Non-stoichiometric approach thermodynamic analysis.

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

$$G = \sum_{i=1}^{N} n_i \mu_i \tag{1}$$

For gaseous species,

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

For condensed pure species, activity is taken as 1, therefore

$$\mu_i = G_i^o \tag{3}$$

In a chemically reacting system, molecular species may not be conserved but number of atoms of various elements remains conserved. The conservation of elements can expressed as

$$E_j = \sum_{i=1}^{N} \beta_{ji} n_i \quad j = 1,2,3,.......k \tag{4}$$

The Gibbs free energy of a system, at a given temperature and pressure, is minimum for the state of equilibrium. Thus, the equilibrium composition can be estimated by minimizing the Gibbs free energy subject to constraints of conservation of elements. 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

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

where

$$\Delta C_{P,i}^o = C_{P,i}^o - \sum v_e C_{Pe}^o \tag{6}$$

$\Delta C_{P,i}^o$ is the algebraic sum of the heat capacity of a compound and its elements and v_e is the stoichiometric coefficient. It should be noted that choice of species present in system is an important consideration in non-stoichiometric approach. It is important to include all the possible major products to get a realistic composition profile for a process. 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:

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

where,

$$A = \frac{a_i P}{R^2 T^2} \quad (8)$$

$$B = \frac{b_i P}{RT} \quad (9)$$

Z is the compressibility factor calculated by solving the following expression

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

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

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

$$b_i = \frac{0.08664 R T_{c,i}}{P_{c,i}} \quad (12)$$

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

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

$$b = \sum y_i b_i \quad (14)$$

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 In-situ removal of products

In-situ removal of products is often used for enhancing the overall yield of reactions, which are limited by thermodynamics. In-situ removal of a species can be modeled by replacing the term for moles of species n_i with $n_i(1-f)$, where f is the fraction of species i being removed. Thus, the chemical potential of species i become

$$\mu_i = G_i^o + RT\ln\left(\frac{\hat{\phi}_i n_i (1-f)P}{n_T P_o}\right) \tag{15}$$

4.5 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 DME

Methoxymethane, commonly known as Di-methyl ether (DME), is the simplest ether. It is a clean colorless gas that can be easily liquefied and transported. DME is an important fuel additive and a potential alternative to diesel owing to its better fuel characteristics. It has high cetane number and it does not produce smoke and NO_x (Arcoumanis et al., 2008; Semelsberger et al., 2006). It is generally produced by a process involving 2 sequential reactions: synthesis of methanol followed by dehydration of methanol to DME. Methanol is generally produced by hydrogenation of CO and CO_2. The methanol synthesis is catalyzed by Cu based metallic catalysts while the dehydration is catalyzed by acidic catalyst such as γ-Al_2O_3, HZSM-5 etc. Table 5.1 list the major and minor reactions involved in DME synthesis via CO_2 hydrogenation. Based on these reactions, the species chosen for thermodynamic study of DME synthesis are: CO_2, H_2, CH_3OH, CO, H_2O, and CH_3OCH_3.

Table 5.1 Possible reactions in formation of DME (Iliuta et al., 2010; Jia et al., 2006)

Reaction Number	Reaction	ΔH_{298} (kJ/mol)
A1	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	-49.1
A2	$CO_2 + H_2 \leftrightarrow CO + H_2O$	41
A3	$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$	-37
A4	$CO + 2H_2 \leftrightarrow CH_3OH$	-90.6

5.2 Synthesis of Methane via CO_2 hydrogenation

Methane, the major component of natural gas, is an important industrial fuel. It is also used as fuel for gas turbine for production of electricity. In recent times, methane is also being considered for rocket fuel (Thunnissen et al., 2004). Methane is also a chemical feedstock, acting as a precursor for a large number of chemicals. Methane can be synthesized by hydrogenation of CO_2 over using a number of catalytic systems based on VIIIB metals (e.g., Ru and Rh) supported on various oxides (e.g., SiO_2, TiO_2, $Al_2 O_3$, ZrO_2). Ni based catalytic systems are also used. Table 5.2 list the major and minor reactions involved in methane synthesis via CO_2 hydrogenation. Based on these reactions, the species chosen for thermodynamic study of methane synthesis are: CO_2, H_2, CH_4, CO, H_2O, C (solid carbon).

Table 5.2 Possible reaction in methanation of CO_2 (Gao et al., 2012; Mills and Steffgen, 1974)

Reaction Number	Reaction	ΔH_{298} (kJ/mol)
B1	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-165
B2	$CO_2 + H_2 \leftrightarrow CO + H_2O$	41
B3	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-206.2
B4	$2CO \leftrightarrow C + CO_2$	-172.4
B5	$CH_4 \leftrightarrow C + 2H_2$	74.9
B6	$CO + H_2 \leftrightarrow C + H_2O$	-131
B7	$CO_2 + 2H_2 \leftrightarrow C + 2H_2O$	-90

5.3 Dry reforming of methane

CO_2 reforming of methane involves reacting CO_2 with methane to produce synthesis gas. Synthesis gas is one of the most important chemical feedstock. Thus, dry reforming provides an alternative approach to produce synthesis gas, which is used in production of methanol, higher hydrocarbons, fertilizers, etc. and also used as fuel (J.H. Edwards and Maitra, 1995). Dry reforming is catalyzed by Ni based catalysts supported by various metal oxides. Table 5.3 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 5.3 Possible reaction in dry reforming of methane (J. H. Edwards and Maitra, 1995; Nikoo and Amin, 2011)

Reaction Number	Reaction	ΔH_{298} (kJ/mol)
C1	$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2$	247
C2	$CO_2 + H_2 \leftrightarrow CO + H_2O$	41
C3	$2CO \leftrightarrow C + CO_2$	-172.4
C4	$CH_4 \leftrightarrow C + 2H_2$	74.9
C5	$CO + H_2 \leftrightarrow C + H_2O$	-131
C6	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-165
C7	$CO_2 + 2H_2 \leftrightarrow C + 2H_2O$	-90

5.4 Dry reforming coupled by DME synthesis

DME can also be produced by using syngas ($CO+H_2$) as the feed stock. In this process the reaction A4 becomes the major methanol forming reaction. Thus, an indirect way to use CO_2 for DME synthesis is utilizing it for dry reforming of methane, producing syngas, which in turn is used as feed for DME production. The reactions and species remain the same as mentioned in section 5.1 and 5.3.

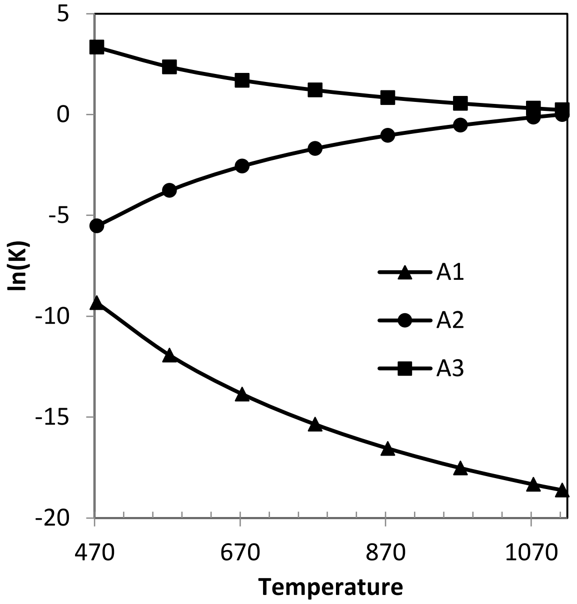

Figure 5.1 Effect of temperature on equilibrium constants of reactions of DME synthesis

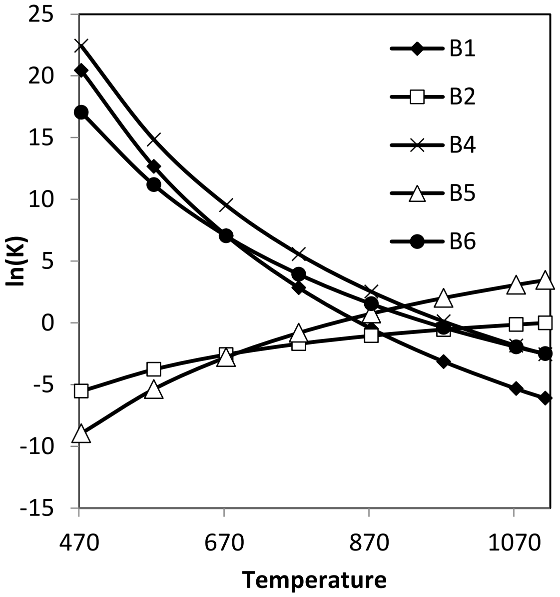

Figure 5.2 Effect of temperature on equilibrium constants of reactions of CO_2 methanation

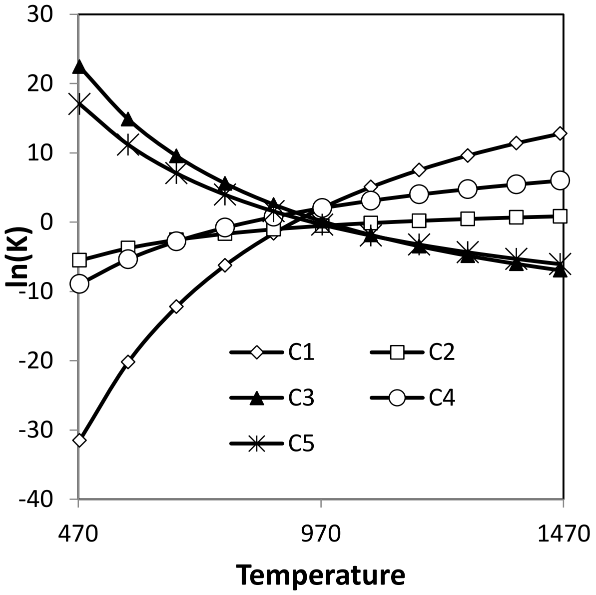

Figure 5.3 Effect of temperature on equilibrium constants of reactions of dry reforming of methane

Chapter 6 Results and Discussions

6.1 Synthesis of DME by CO_2 hydrogenation

6.1.1 Effect of pressure and temperature

The figure 6.1, 6.2 and 6.3 illustrates the influence of temperature and pressure on CO_2 conversion, DME yield and DME selectivity respectively. The H_2/CO_2 ratio of feed is kept constant at 3 for the study. The equilibrium conversion of CO_2 first increases and then decreases with increase in temperature. Reaction A1 and A2 compete with each other for CO_2. It can be seen from figure 5.1 that equilibrium constant values of reaction A2 is greater than those of reaction A1 for all temperature but when coupled with reaction A3, reaction A1 tends to dominates over the reaction A2 upto the temperature of 650 K. The initial decline in equilibrium conversion is due to the exothermic nature of reaction A1 and reaction A3. For temperature beyond 650 K, reaction A3 (reverse water gas shift reaction), an endothermic reaction, starts to dominate over reaction A1 and A2. This results in increase in CO_2 conversion. The equilibrium constant of reaction A1 becomes negligible above 650 K. It can be seen from the figure 6.1 that for temperatures above 650 K, CO_2 conversion becomes independent of pressure. This happens because for temperatures above 650 K, only reaction A2 consumes CO_2 . Reaction A2 is neither a mole increasing nor mole reducing reaction, hence not affected by pressure.

The formation of DME is a 2 step process involving formation of methanol from CO_2 followed by dehydration of methanol to form DME. The yield decreases with increase in temperature as both reaction A1 and A3 are exothermic in nature. It can be seen from the figure 6.2 that pressure has positive effect on DME yield. Reaction A1 is mole reducing reaction, thus methanol formation is favored by high pressure. This increased methanol formation in turn increases the formation of DME. It should be noted that pressure does not have any effect on reaction A3. It is only the synergic effect of increased methanol formation that increases the DME yield. It can be seen from figure 6.3 that selectivity of DME over methanol and Carbon monoxide shows a trend similar to that of DME yield. The selectivity of DME is not very high, maximum being only about 70 %. As a result it will be difficult to obtain pure DME from CO_2 hydrogenation.

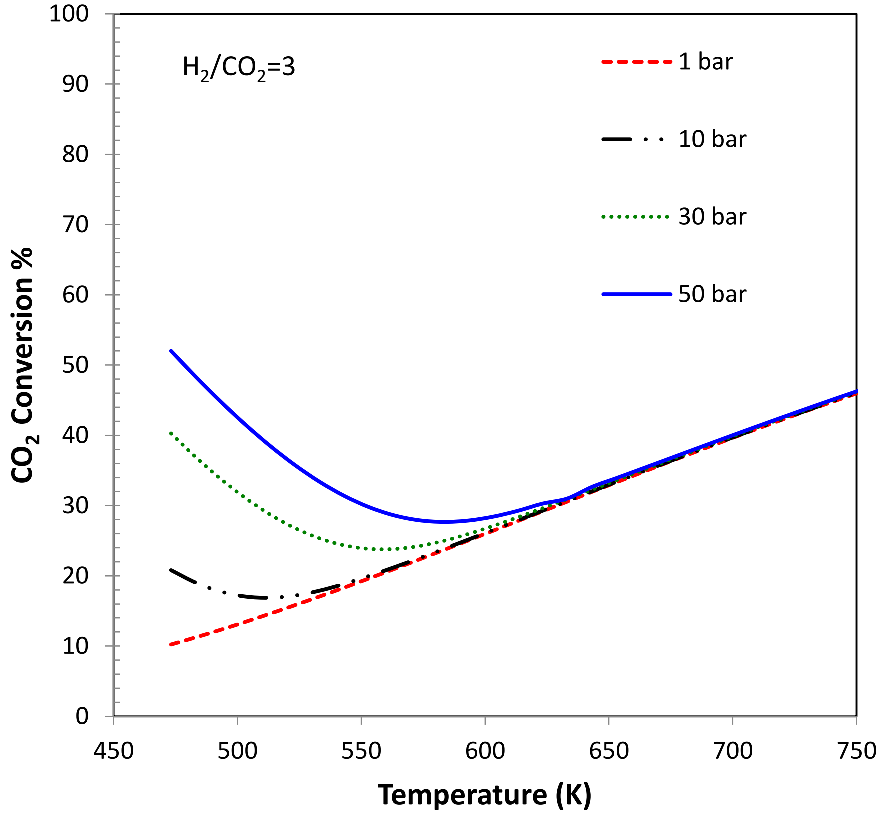

Figure 6.1 Influence of temperature and pressure on CO_2 conversion in DME synthesis

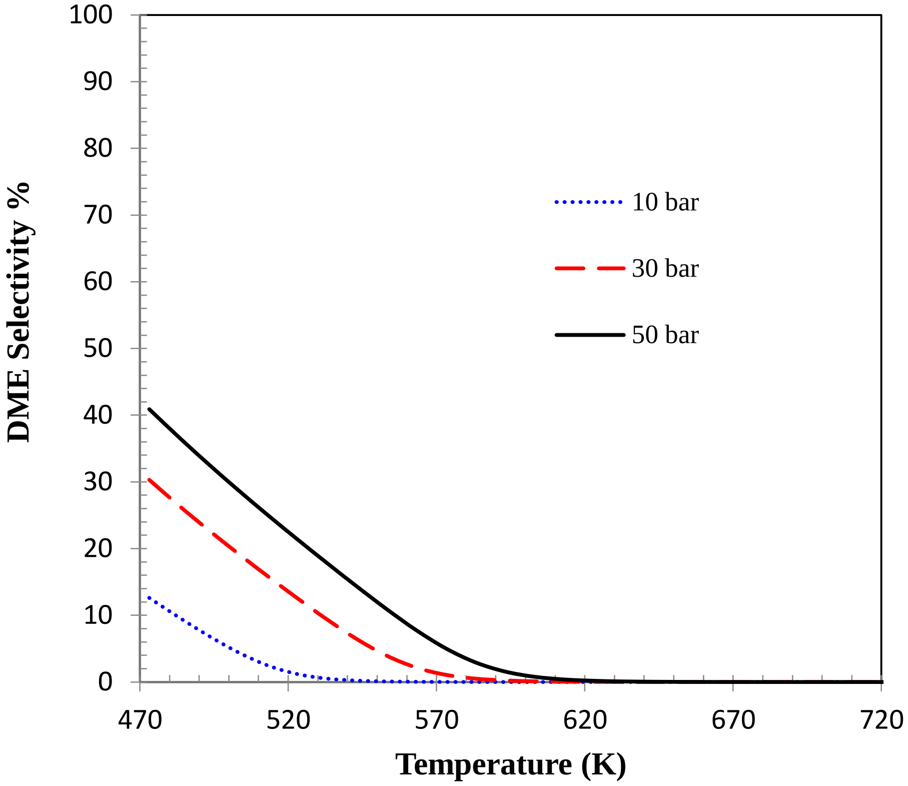

Figure 6.2 Influence of Temperature and Pressure on DME yield

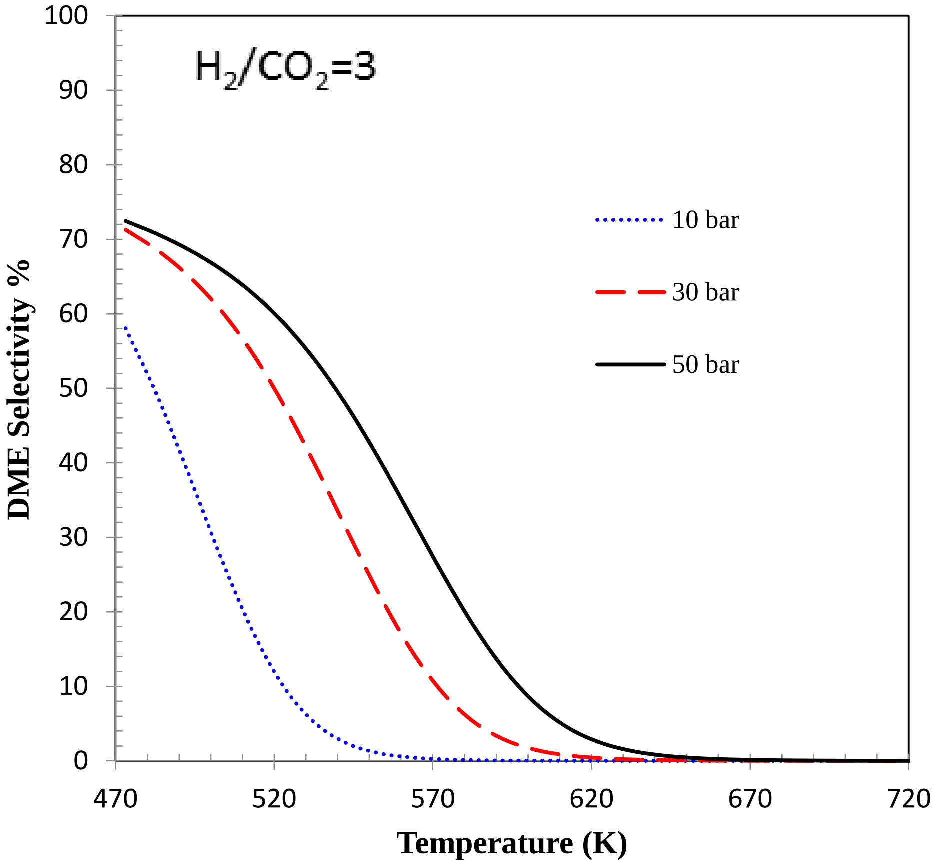

Figure 6.3 Influence of Temperature and Pressure on DME selectivity

6.1.2 Effect of feed composition

The feed to DME process consists of CO_2 and H2. The feed composition is generally varied in terms of H_2/CO_2 ratio. The figure 6.4, 6.5, 6.6 depicts the effect of feed composition on CO_2 conversion, DME yield and DME selectivity respectively. H_2/CO_2 ratio is taken as the basis. It can be observed that high H_2/CO_2 ratio favors CO_2 conversion and DME 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 avaialblity of hydrogen shitfts the rections in forward direction.

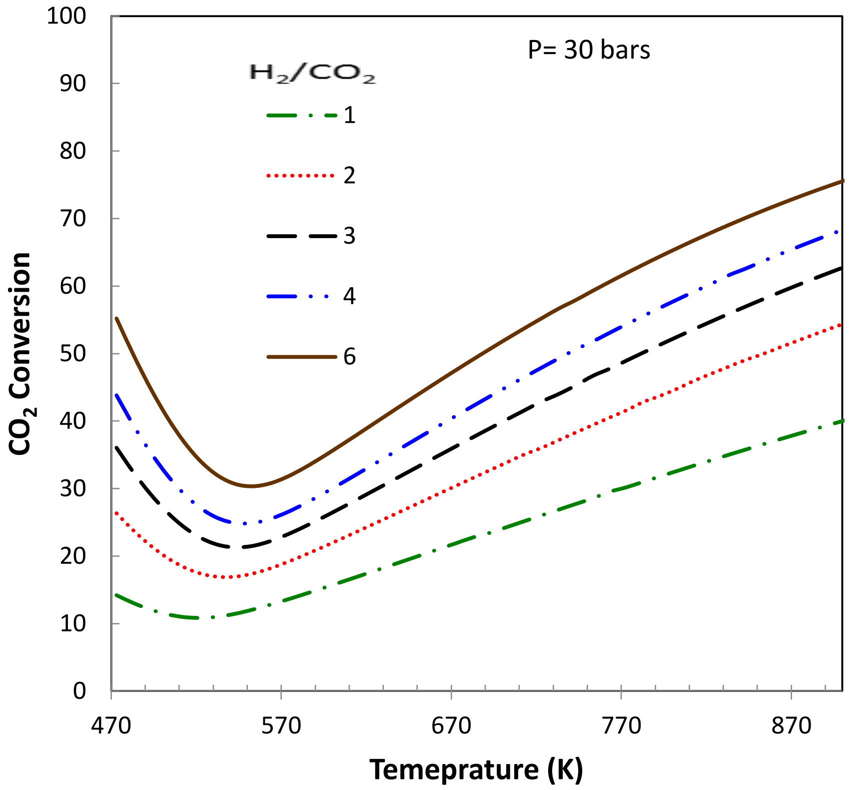

Figure 6.4 Influence of H_2/CO_2 ratios on CO_2 conversion in DME synthesis

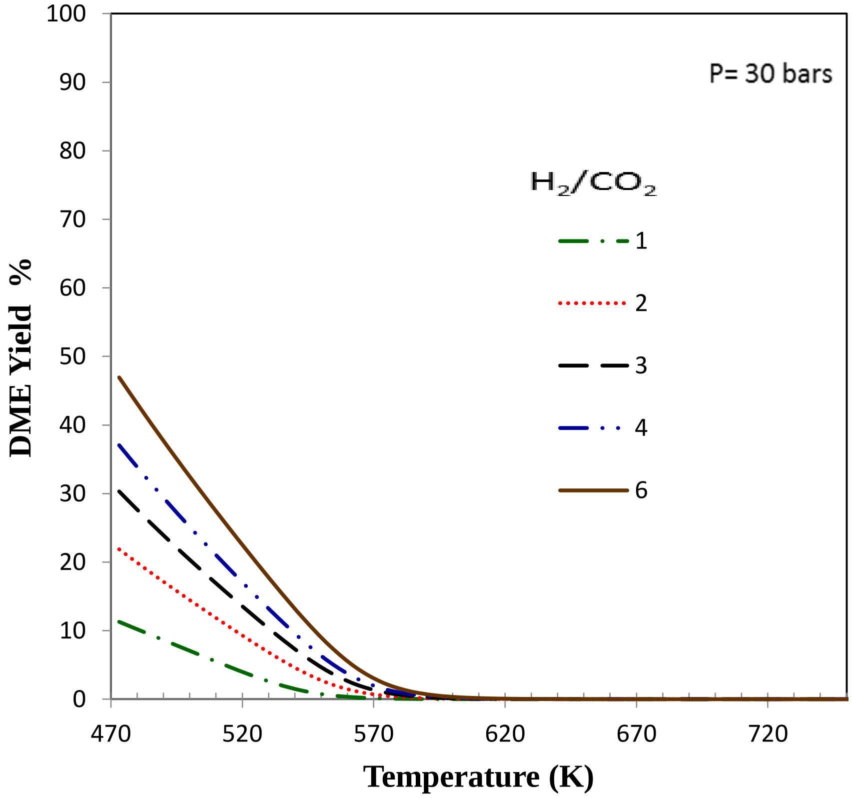

Figure 6.5 Influence of H_2/CO_2 ratios on DME yield

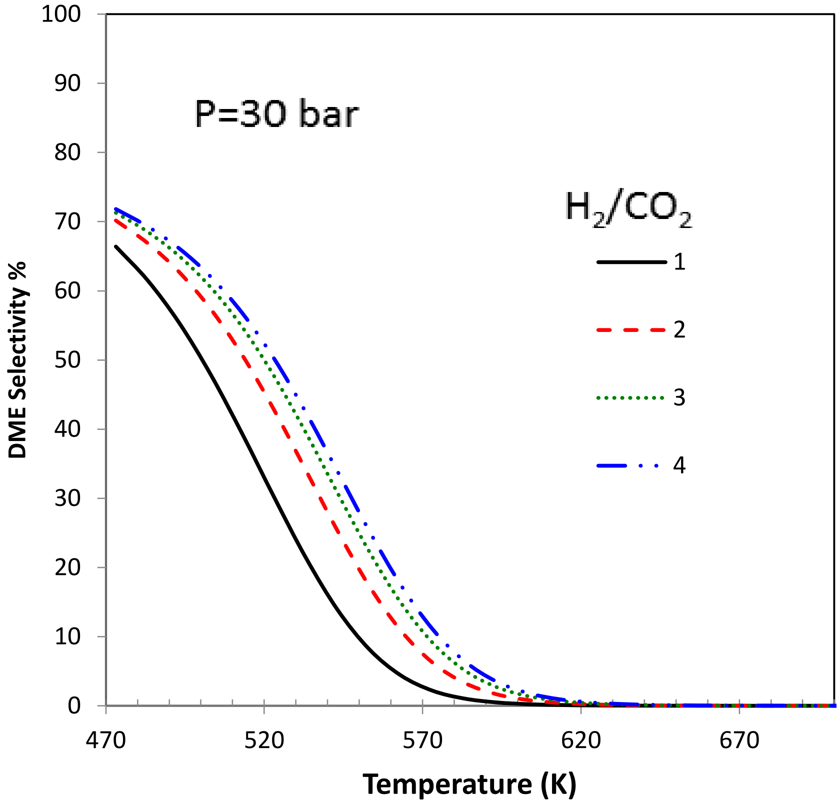

Figure 6.6 Influence of H_2/CO_2 ratios on DME selectivity

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 DME synthesis from CO_2 hydrogenation. Figure 6.7 and 6.8 illustrates the effect of CO in feed on CO_2 conversion and DME yield respectively. The H_2/CO_2 of the feed is kept at 3. It can be seen from figure 6.7 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 favorable 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 becomes negative, implying more CO_2 is being formed than being consumed. This excess CO_2 is result of water gas shift reaction (reverse A2) at lower temperature. DME yield increases with increasing CO concentration. This happens because hydrogenation of CO produces larger amount of methanol than hydrogenation of CO_2 does. This enhanced methanol formation in turn increases DME formation.

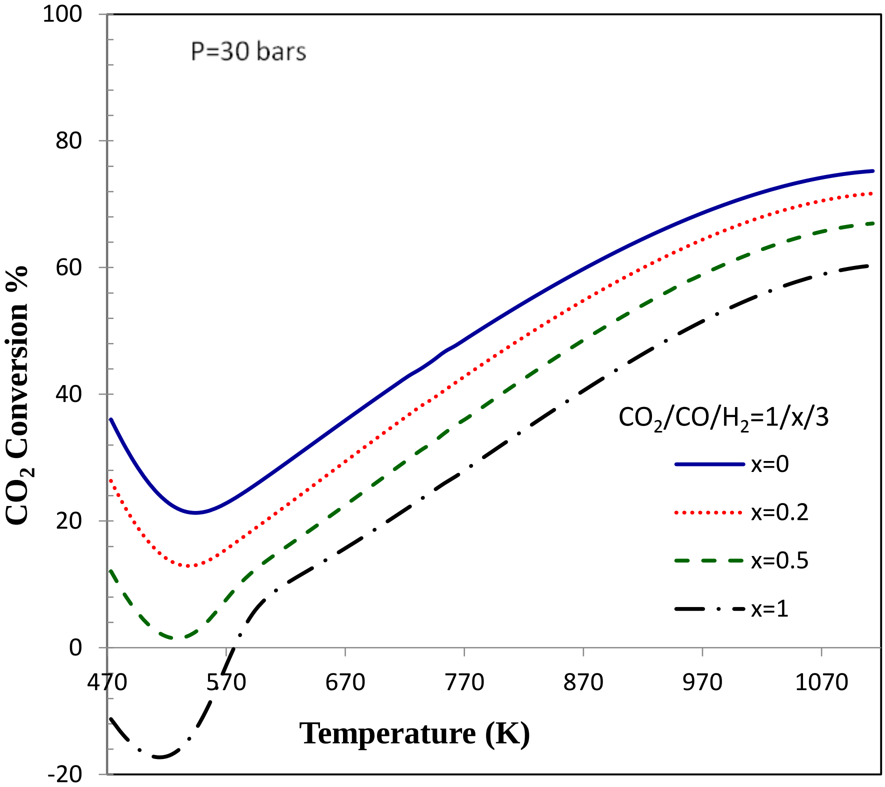

Figure 6.7 Effect of presence of CO in feed on CO_2 conversion

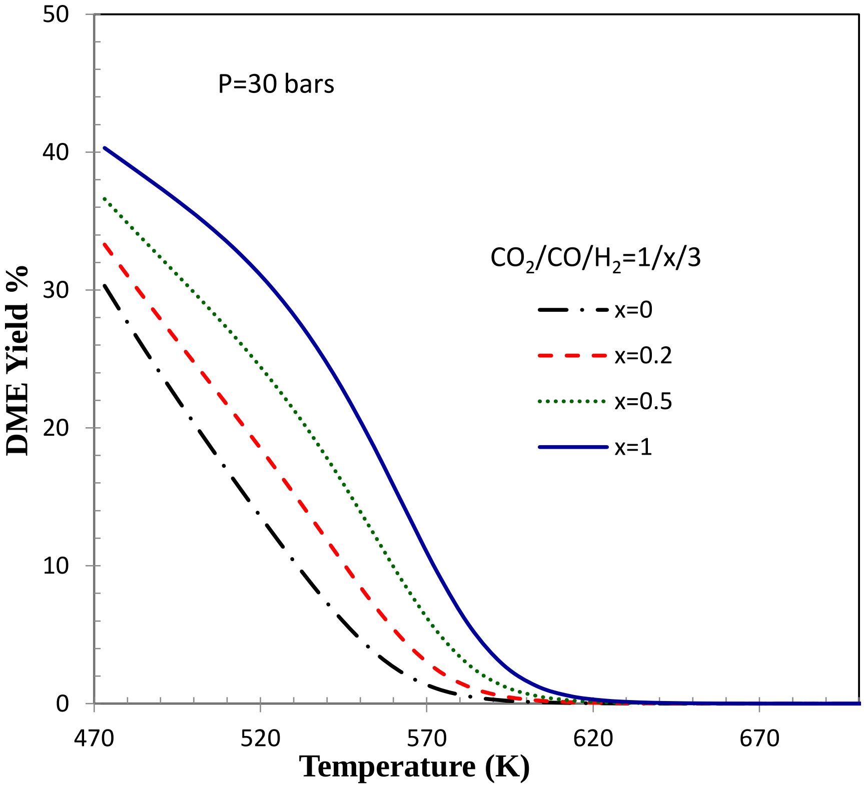

Figure 6.8 Effect of presence of CO in feed on DME yield

6.1.4 Effect of in-situ removal of water

Figure 6.1 and 6.2 shows that synthesis of DME from CO_2 hydrogenation gives low DME yield and CO_2 conversion. One of the ways to enhance the DME yield and CO_2 conversion is in-situ removal of products. There are 2 primary products of the process: water and DME. Figure 6.9 and 6.10 show the impact of removal water from reaction on DME yield and CO_2 conversion. As expected, the conversion and DME yield increases with increase in removal of water. Moreover, the effect of removal of water becomes more pronounced as the fraction of water being removed increases. Removal of water also enhances the reverse water shift reaction; thereby, increasing the CO_2 conversion at higher conversion at higher temperature. Irrespective of amount of water removed, DME yield becomes zero at temperatures above 600 K.

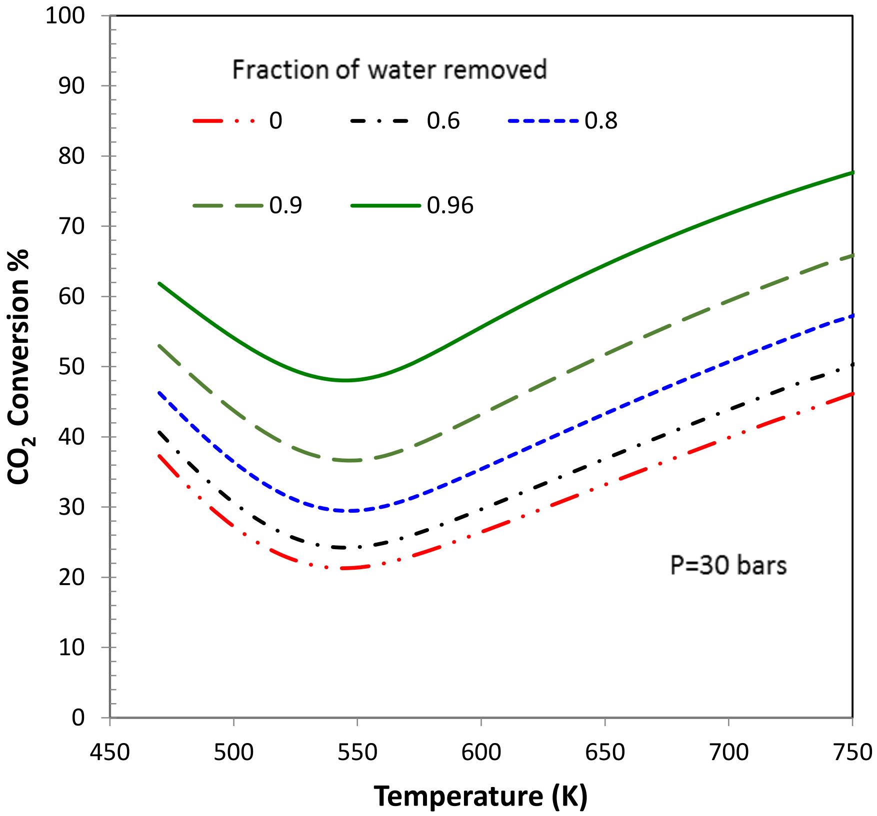

Figure 6.9 Effect of in-situ removal of water on CO_2 conversion

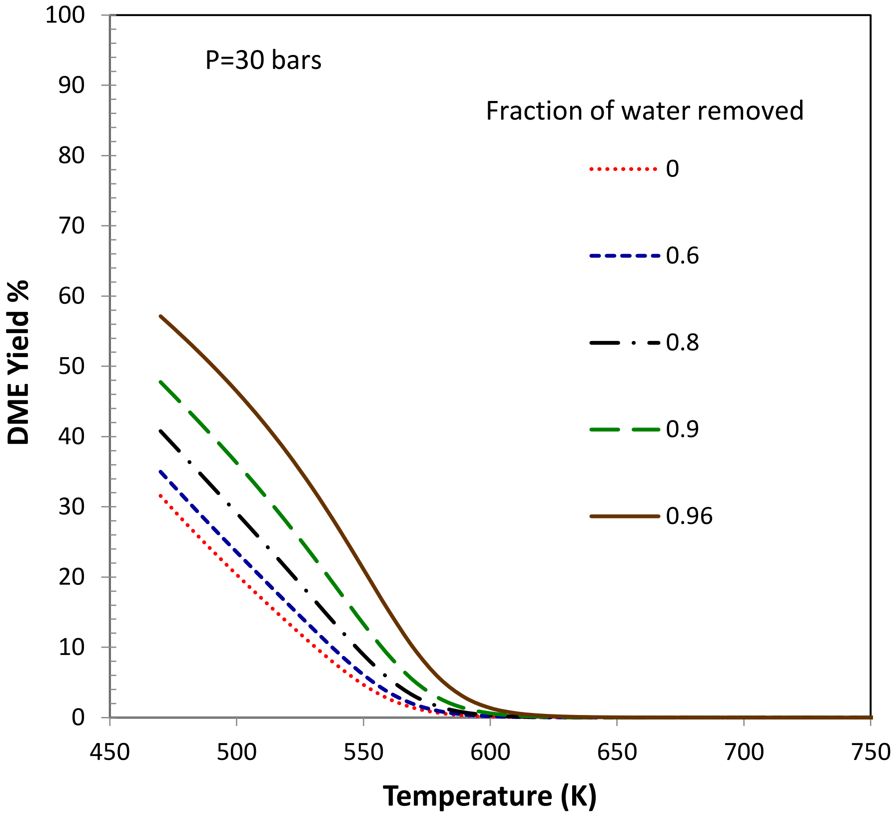

Figure 6.10 Effect of in-situ water removal on DME yield

6.1.5 Effect of in-situ removal of DME

In-situ removal of DME also enhances the DME yield and CO_2 conversion (see Figure 6.11 & 6.12) as DME removal shifts the reaction A3 forward. Removal of DME does not have any effect on CO_2 conversion at higher temperature as reaction A3 does not occur at high temperatures. It should be noted that observed increase in DME yield and CO_2 conversion due to in-situ removal of DME is less than the increase observed in case of in-situ removal of water. This is because removal of water enhances both reaction A1 and A3.

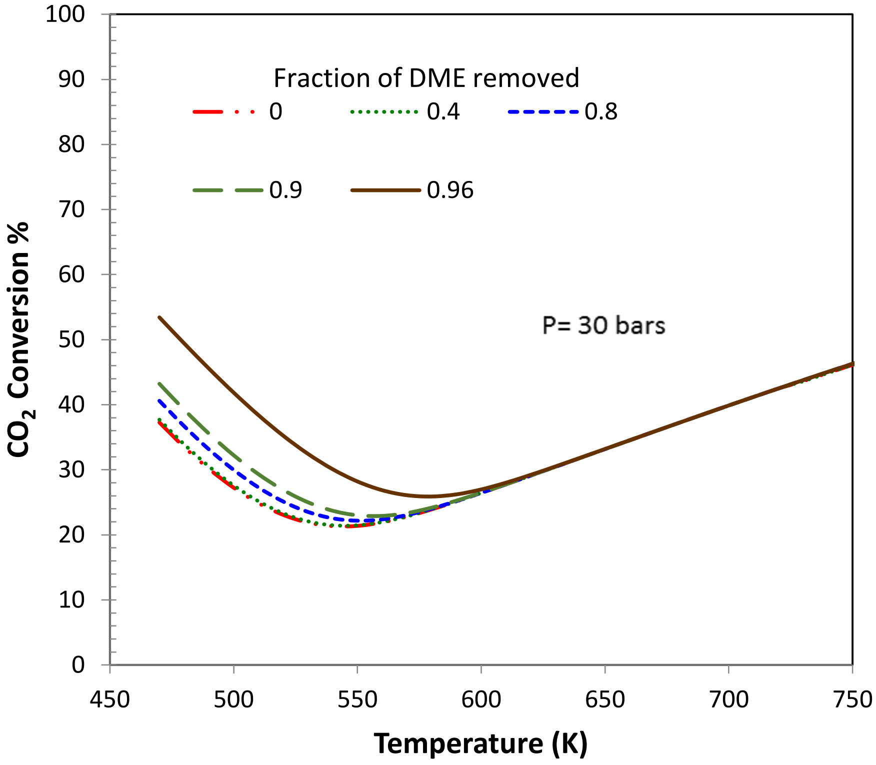

Figure 6.11 Effect of in-situ removal of DME on CO_2 conversion

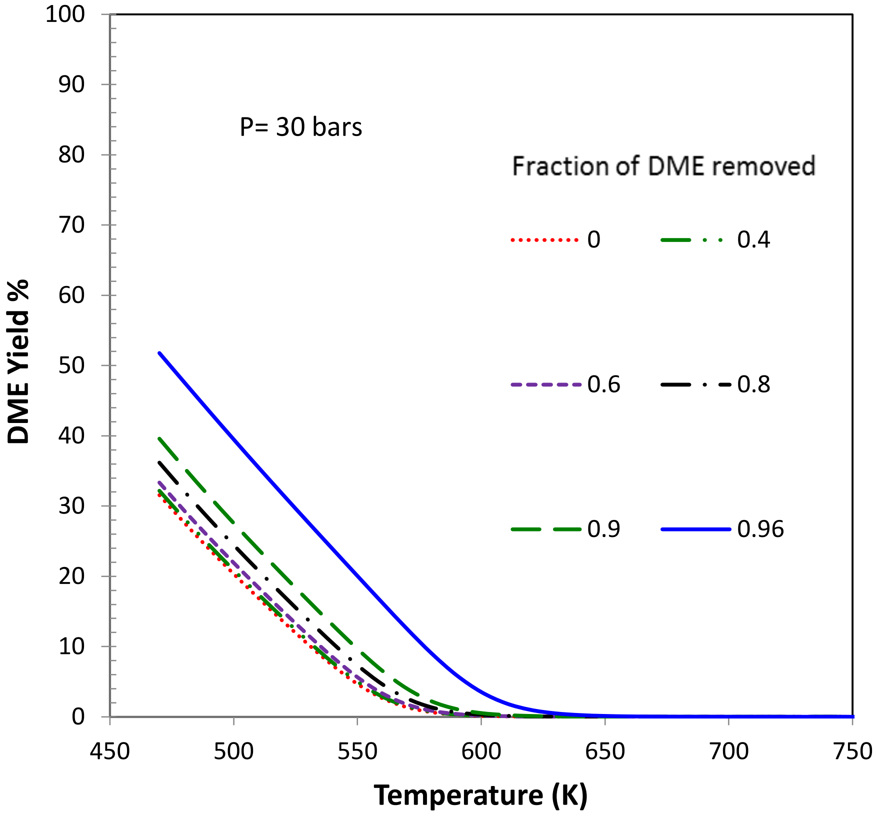

Figure 6.12 Effect of in-situ removal of DME on DME yield

6.2 Synthesis of Methane

6.2.1 Effect of temperature and pressure

Figure 6.13, 6.14 and 6.15 shows the effect of temperature and pressure on equilibrium CO_2 conversion, CH_4 yield and CH_4 selectivity respectively. The feed with CO_2/H_2 ratio of 4 was used for the calculations. It can be seen in figure 6.13 that the equilibrium conversion of CO_2, at constant pressure, first decreases and then increases with an increase in temperature. The initial decline in equilibrium conversion of CO_2 is due to exothermic nature of reaction B1. The equilibrium conversion increases gradually when temperature is raised beyond 850-950 K. This is happens because reaction B2 (reverse water gas shift reaction), an endothermic reaction, starts to dominate over reaction B1 at higher temperature (see Figure5.2), consuming more CO_2 in the process and enhancing the formation of CO. It can be seen from the Figure 6.13 that pressure has positive effect on equilibrium conversion of CO_2. This is expected as methanation is a mole reducing reactions which is favored at high pressure. The yield of methane decreases with an increase in temperature and decrease in pressure, which is in accordance in to the fact that methanation is an exothermic and molecule reducing reaction. Yield reduces further at higher temperature due to domination of reverse water-gas shift reaction. Thus irrespective of pressure, yield will decrease to zero at sufficiently high temperature. Figure 6.15 depicts the influence of temperature and pressure on selectivity of methane formation over carbon monoxide formation. .It can be seen that low temperature and high pressure favor methane formation. All trends and calculations performed in the present study agree with the simulations of Gao et al.(Gao et al., 2012) and Ocampo (Ocampo et al, 2009) .

It should be noted that no coke formation was observed in present study. Coke formation can be generally attributed to a set of 4 reactions consisting of reaction B4, B5, B6 and B7. Reaction B4 and B6 are exothermic reaction involving CO. They do not contribute to coke formation at lower temperatures because CO is not present at lower temperatures. Due to their exothermic nature, reaction B4 and B6 have very low equilibrium constants at higher temperature as shown in figure 5.2; hence, reaction B4 and B6 do not contribute to coke formation at higher temperatures, even though CO is available at those temperatures. The formation of water also suppresses coke formation. The methane cracking reaction (reaction B5), even though endothermic, does not contribute to coke formation because of the lack of CH_4 at higher temperatures.

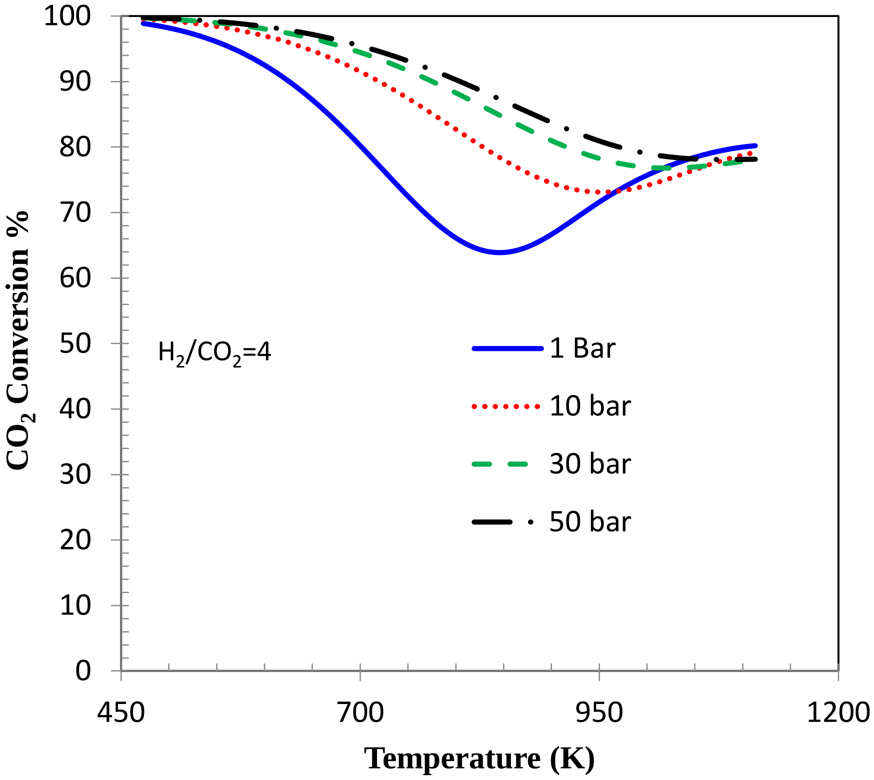

Figure 6.13 Influence of Temperature and Pressure on CO_2 conversion

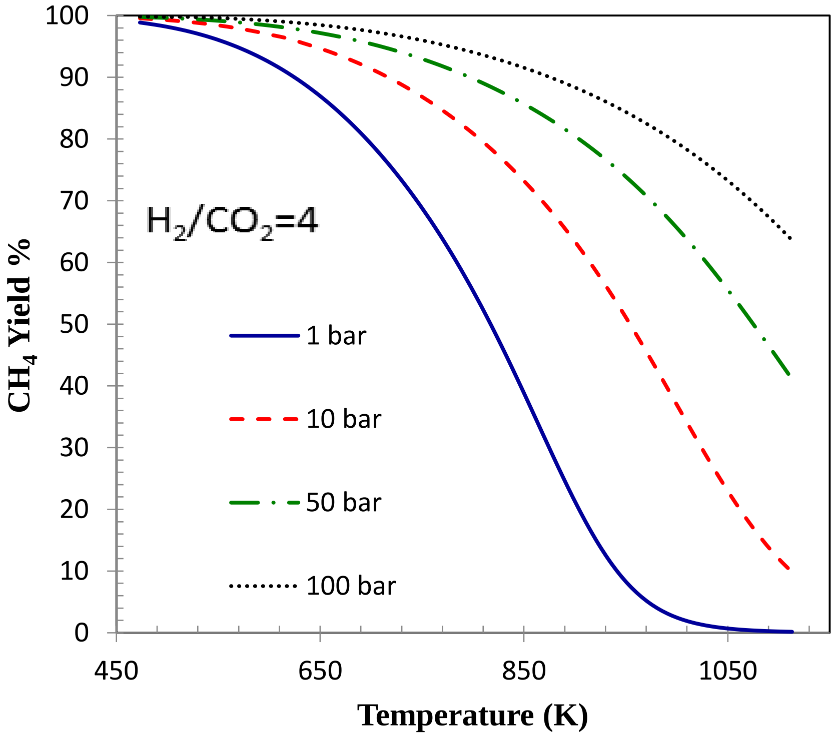

Figure 6.14 Influence of Temperature and Pressure on Methane Yield

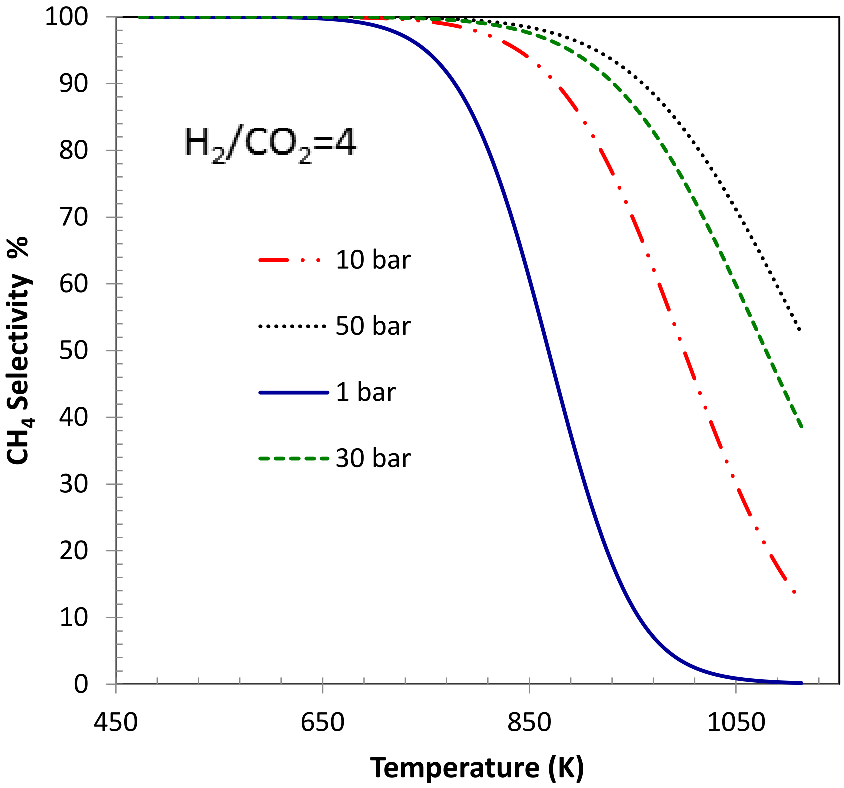

Figure 6.15 Influence of Temperature and Pressure on methane selectivity

6.2.2 Effect of H_2/CO_2 ratios

Figure 6.16, 6.17 and 6.18 shows the effect of feed composition on equilibrium CO_2 conversion, CH_4 yield and CH_4 selectivity. It can be observed from the Figure 6.16 that CO_2 conversion is favored by high H_2/CO_2 ratio. The conversions for feed with H_2/CO_2 ratio less than 4, are remarkebly low as compared to conversions for feed with H_2/CO_2 ratio equal to or greater than 4. For feed with H_2/CO_2 ratio less than 4, hydrogen act as the limiting reagent for the reaction B1. This keeps the conversion of CO_2 low at temperatures below 850 K. As the temperature increases over 850 K, reaction B2 starts to dominate. The reaction B2 is favorable at lower H_2/CO_2 ratio. This results in increase in CO_2. For ratios greater than or equal to 4, CO_2 is the limiting agent. CO_2 conversion is 100% initially but gradually decreases with an increase in temperature because of exothermic nature of methanation reaction B1. Figure 6.17 and 6.18 show that yield and selectivity of methane is favored by high H_2/CO_2 ratio. It can be seen from figure 6.19 that coke formation is observed only for H_2/CO_2 ratios less than 4. Lack of hydrogen suppresses the reaction B1 resulting in reduced water fromation. This allows reaction B7 to proceed in forward direction, resulting in coke formation. Water formation due to reaction B1 for H_2/CO_2 ratios greater than 4 supppresses coke formation.

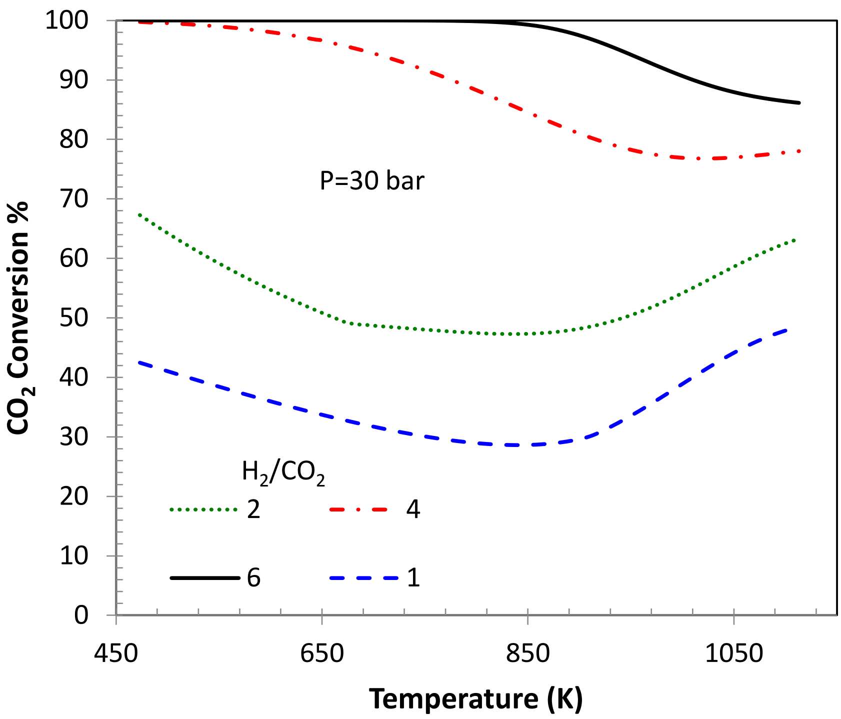

Figure 6.16 Influence of H_2/CO_2 ratios on CO_2 conversion

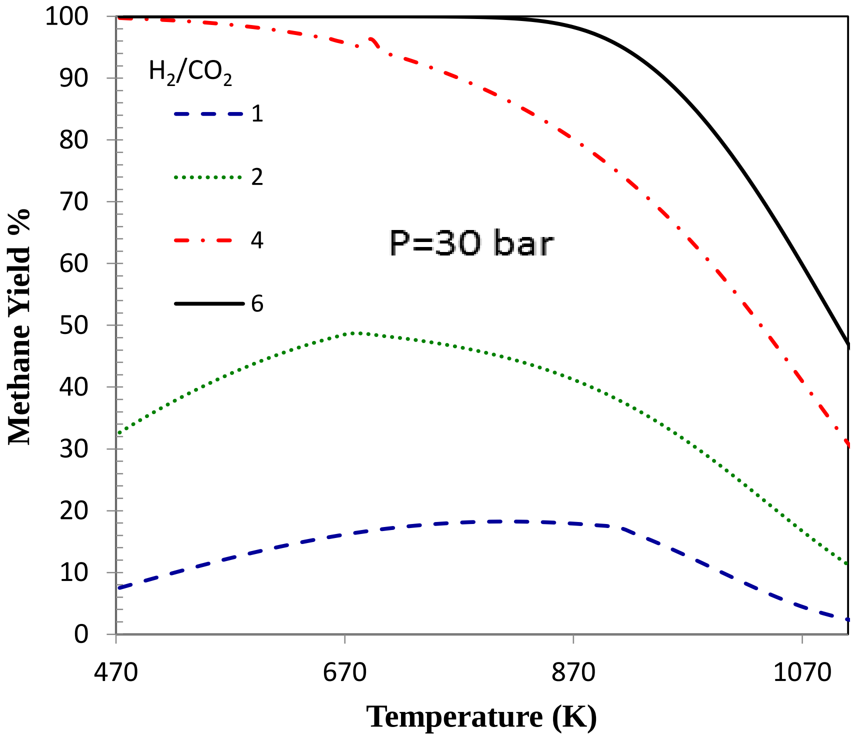

Figure 6.17 Influence of H_2/CO_2 ratios on methane yield

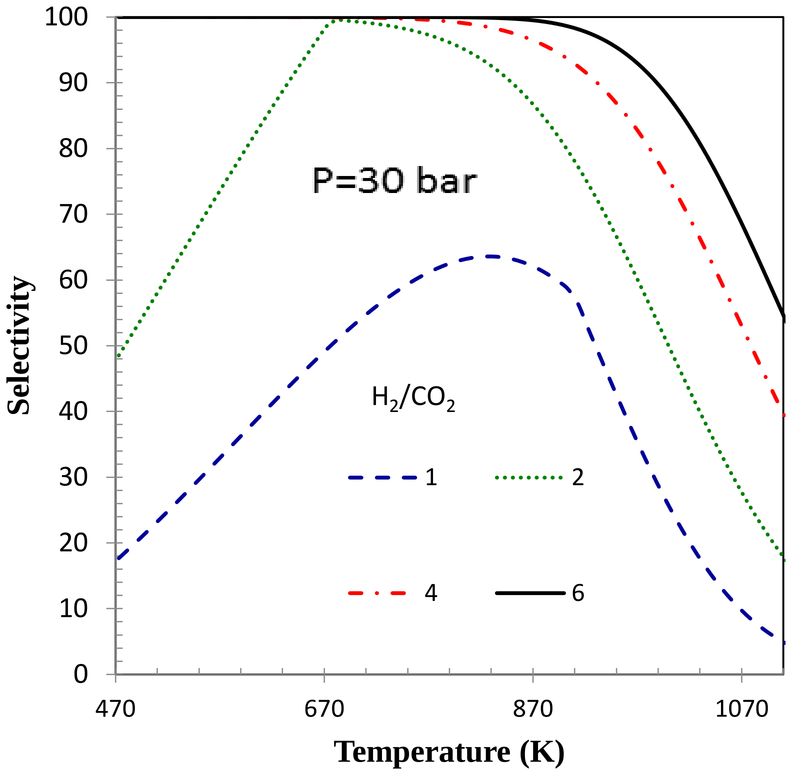

Figure 6.18 Influence of H_2/CO_2 ratios on methane selectivity

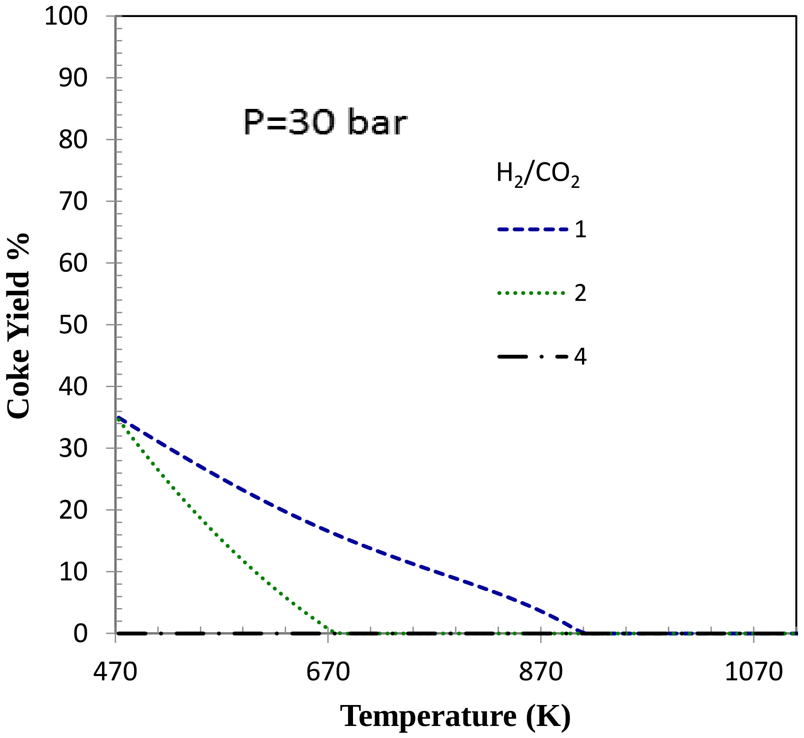

Figure 6.19 Influence of H_2/CO_2 ratios on coke formation

6.2.3 Effect of presence CO in feed

It can be seen from figure 6.20 that presence of CO depresses the CO_2 conversion. This happens because CO by reacting with hydrogen reduces the hydrogen available for CO_2 methanation. This reduces the CO_2 conversion. The variation of CO_2 conversion with respect to temperature remains same as in the case of no CO content in feed. Methane yield also decreases with increasing CO content (see figure 6.21). The decrease is more pronounced at lower temperature while at higher temperature, methane yield is nearly same irrespective of presence of CO content. In presence of CO, methane yield first increases and then decreases with temperature. The initial increase in methane yield is somewhat anomalous as both CO and CO_2 methanation are exothermic. This happens because presence of CO leads to coke formation, reducing the carbon available for methane formation. With increase in temperature, coke formation reduces, allowing more carbon to be available for methane formation.

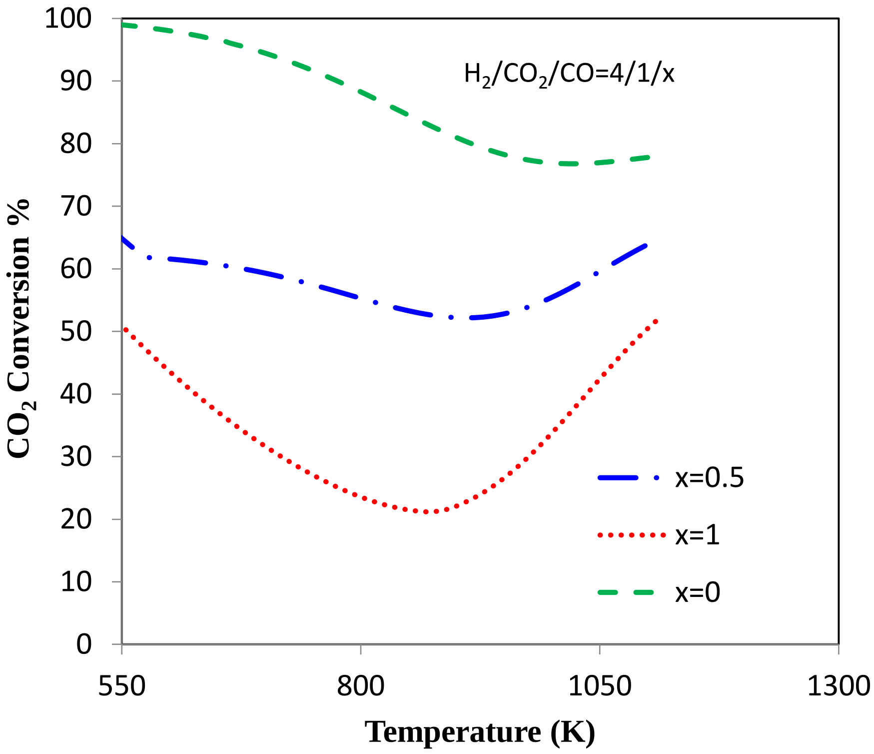

Figure 6.20 Effect of presence of CO in feed on CO_2 conversion

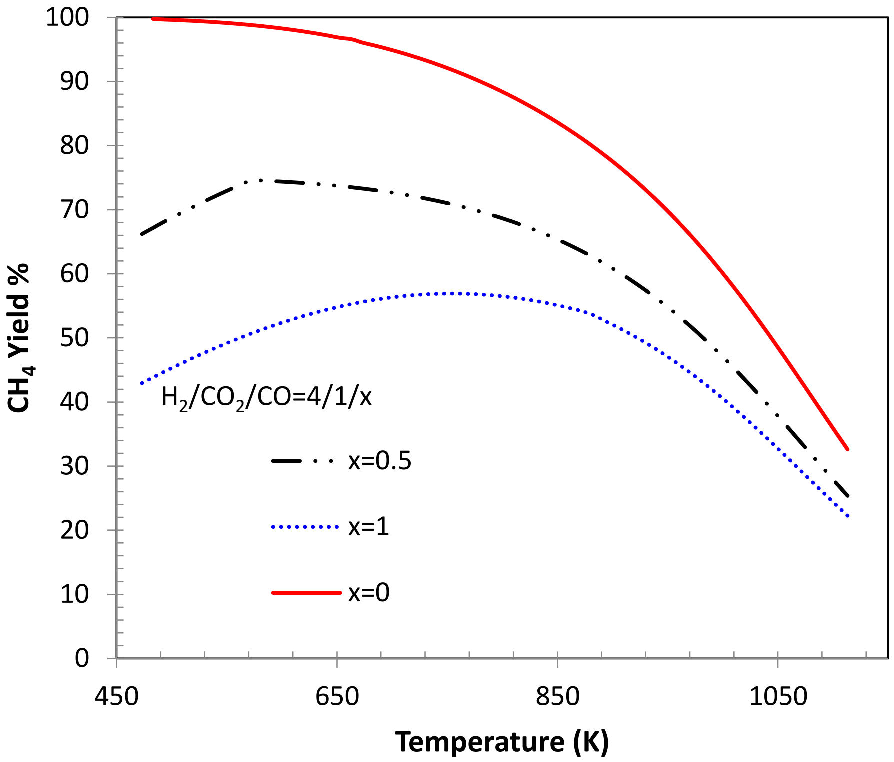

Figure 6.21 Effect of presence of CO in feed on methane yield

6.2.4 Effect of in-situ removal of methane

The methanation of CO_2 has results in nearly complete CO_2 conversion and 100% methane yield at low temperatures. But the methanation of CO_2 suffers from severe kinetic limitations because reduction of fully oxidized carbon is an eight electron process. As a result, often methanation has very low rate of formation. Thus a sufficiently active catalyst and often high temperatures are required for methanation. At higher temperature, both CO_2 conversion and methane yield drops. In-situ removal of methane becomes a suitable strategy for achieving high conversion and high methane yield with adequate rate of formation. Figure 6.22-6.23 depicts the change in conversion and methane yield with fraction of methane removed. It can be seen that nearly complete removal of methane results in an increase of only 5 % in methane yield. Another important aspect to be noted is that hardly any increment in yield and conversion occur till removal fraction of 0.6.

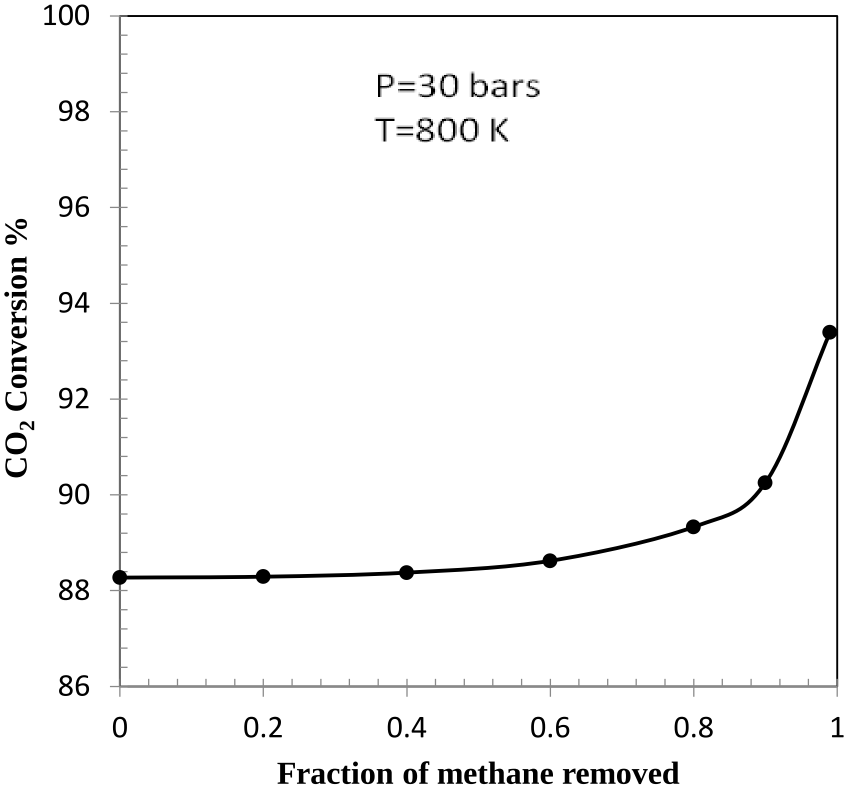

Figure 6.22 Effect of in-situ removal of methane on CO_2 conversion

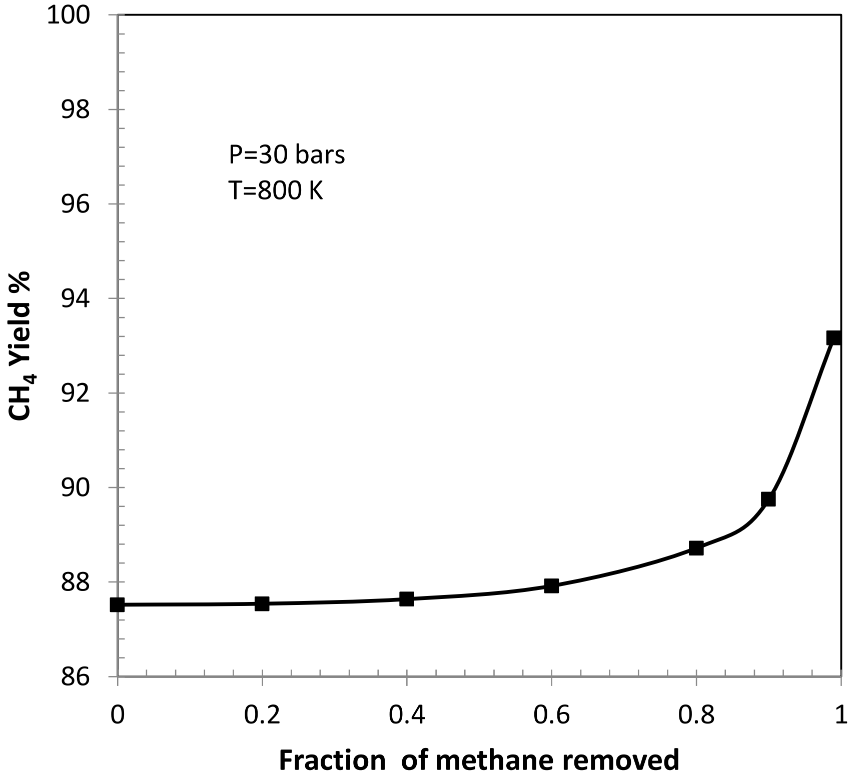

Figure 6.23 Effect of in-situ removal of methane on methane yield

6.3 Dry Reforming

6.3.1 Effects of temperature and pressure

Figure 6.24-6.28 shows the effect of pressure and temperature on conversion, yield, H_2/CO ratio and coke deposition. It can be observed from figure 6.24 that the conversion of CO_2 first decreases and then increases with increase in temperature. Reaction C1 and C2 are endothermic reactions having very low equilibrium constants at lower temperatures, thus they do not contribute to consumption of CO_2 (see figure 5.3). Conversion of CO_2 at temperature lower than 850 K is largely due to reaction C5 and C7. Predominance of reaction C5 and C7 at lower temperature is also supported by formation of water along with coke. The initial decline up to the temperature of 800-850 K is due to the exothermic nature of reaction C5 and C7. Beyond these temperatures, reactions C1 and C2 start to dominate over coking reactions. The subsequent increase in conversion of CO_2 is due to the endothermic nature of reactions C6 and C7. Pressure shows both positive and negative effects depending on the temperature. High pressure has a positive effect on CO_2 conversion at low temperature while low pressure has a positive effect on CO_2 conversion at high temperature. Both reaction C1 and reaction C2 are moles increasing reactions, thus it is expected CO_2 conversion will be favored by low pressure. The expected effect is observed at temperatures above 850 K but not at lower temperature. This happens because at lower temperatures reaction C5 and C7, which are favored 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 C6 and C7 are endothermic and mole increasing.

It can be seen from Figure 6.26 that the H_2/CO ratio varies widely over the studied temperature range. Ideally the reforming should result in H_2/CO ratio of 1 as evident from reaction C1 but reaction C3 and C5 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 1250 K, the H_2/CO ratio drops below unity as reaction C2 starts to dominate over reaction C1, effectively increasing the CO content and reducing the H_2 content. Pressure does not have any significant effect on H_2/CO ratio. Reaction C5 and C7 are largely responsible for formation of coke in the systems. Figure 6.28 illustrates that the coke formation increases with increase in pressure and decreases with an increase in temperature. This is because both reaction C5 and C7 are volume reducing and exothermic.

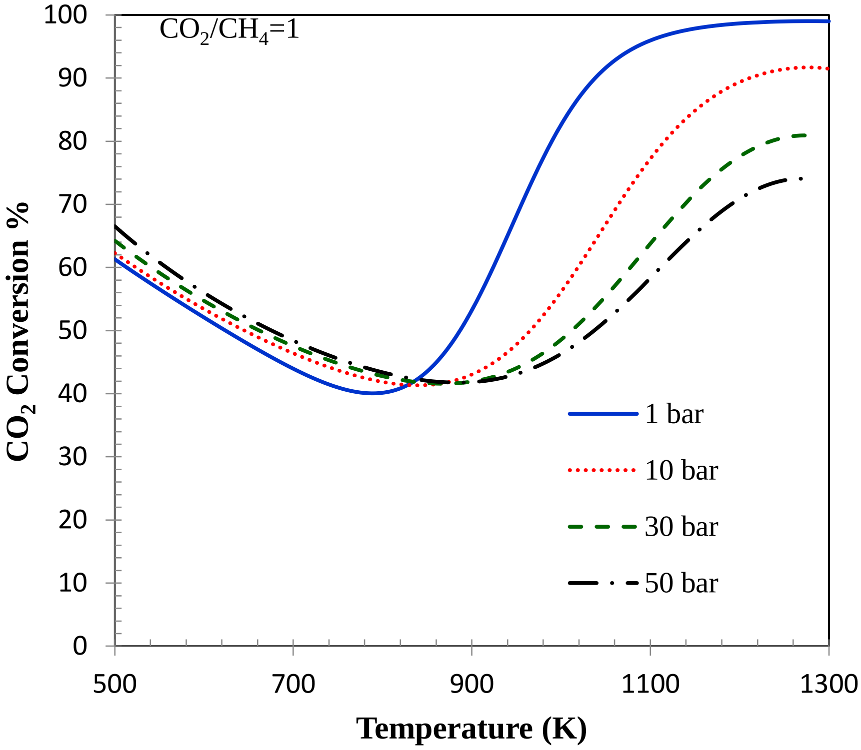

Figure 6.24 Influence of Temperature and Pressure on CO_2 conversion

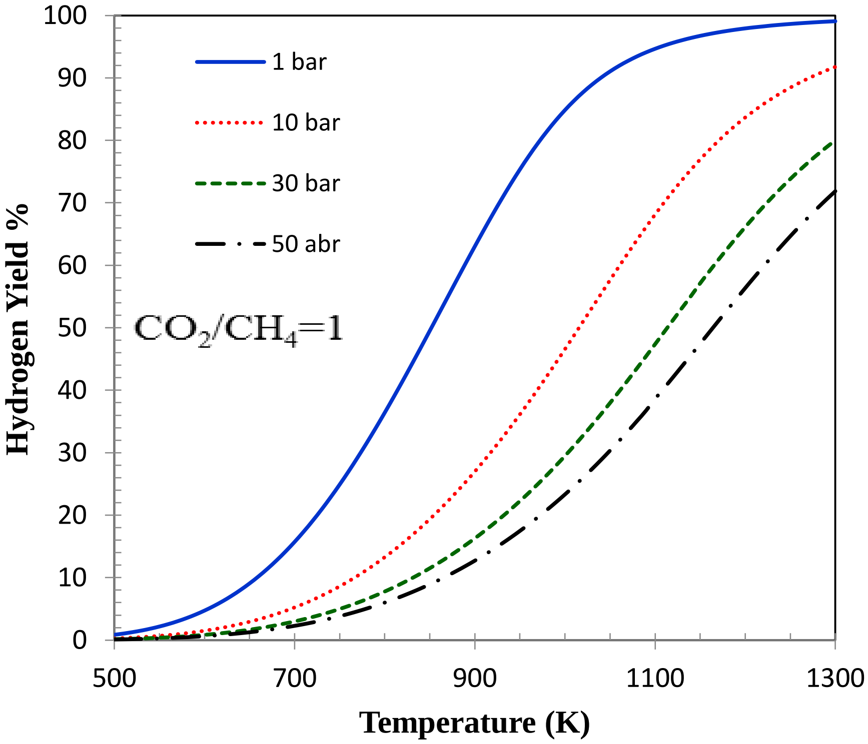

Figure 6.25 Influence of Temperature and Pressure on hydrogen yield

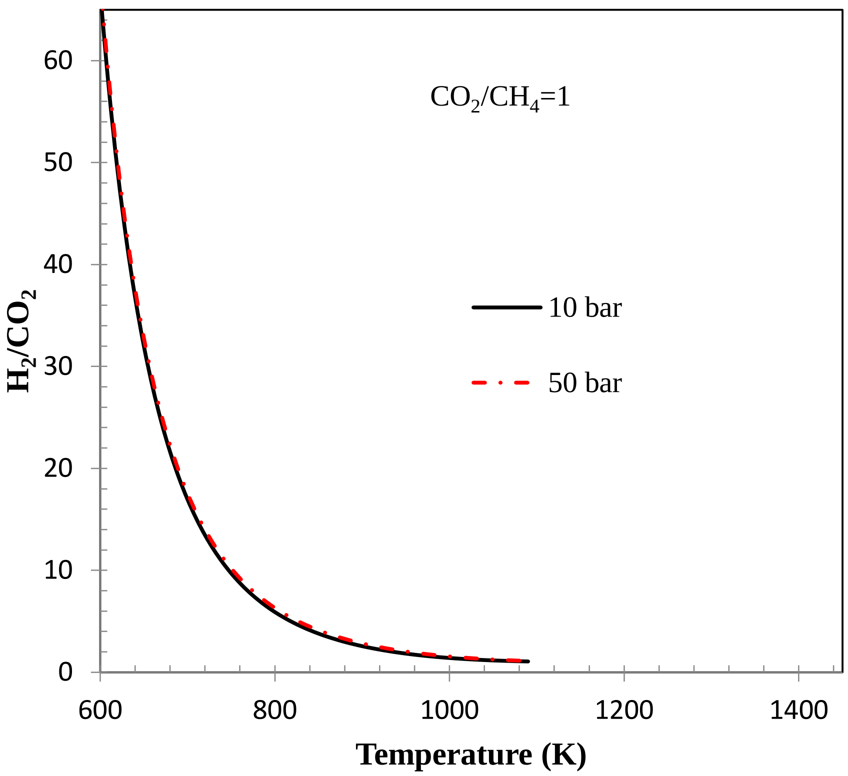

Figure 6.26 Influence of Temperature and Pressure on H_2/CO ratio

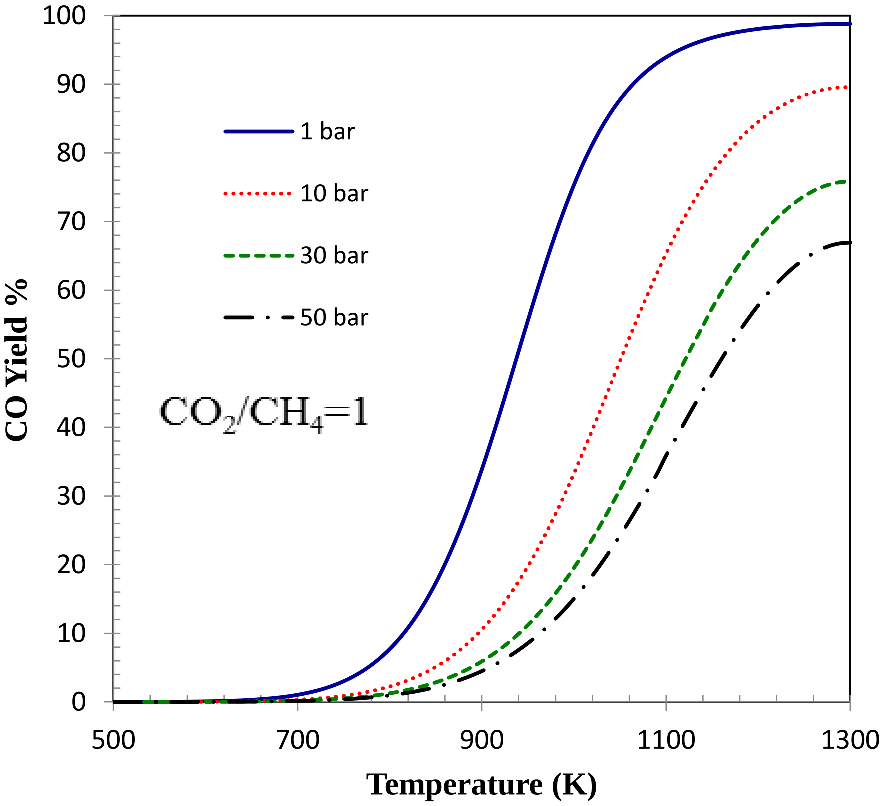

Figure 6.27 Influence of Temperature and Pressure on CO yield

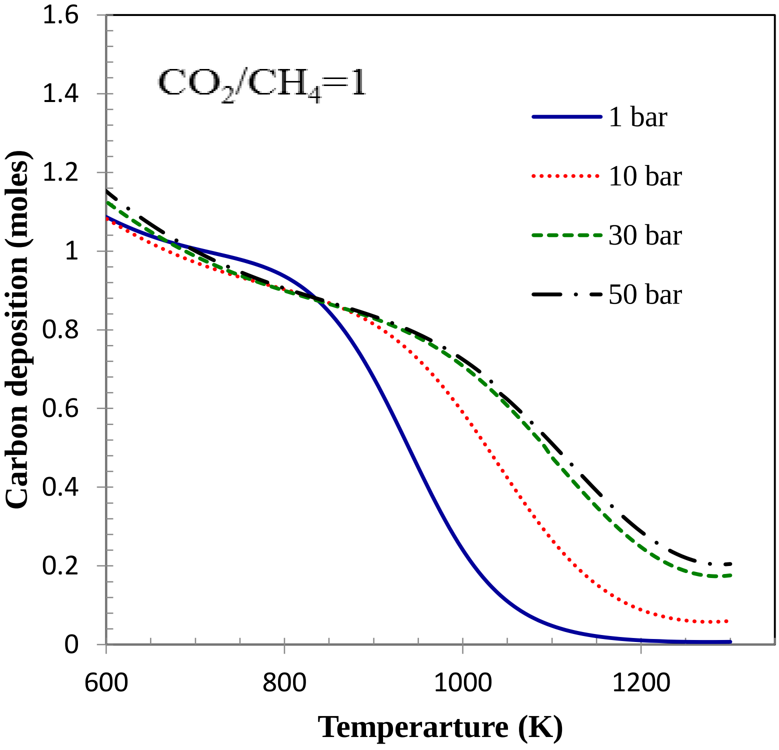

Figure 6.28 Influence of Temperature and Pressure on coke deposition

6.3.2 Effect of CO_2/CH_4 ratios

Figure 6.29-6.32 illustrates the effect CO_2/CH_4 ratios on CO_2 conversion, CO yield, coke formation and H_2/CO ratios at 30 bar. Figure 6.29 depicts that the CO_2 conversion is favored by low CO_2/CH_4 ratios. For CO_2/CH_4 ratios less than 1, CO_2 is the limiting reagent. As a result it is consumed to maximum extent. For CO_2/CH_4 ratios greater than 1, CH_4 becomes the limiting reagent; thereby, limiting the conversion of CO_2. The profile of CO_2 conversion over the studied temperature range remains same irrespective of CO_2/CH_4 ratio.

CO_2/CH_4 ratios show both positive and negative impact of CO yield depending upon whether CO_2/CH_4 ratio is less than or greater than 1 as show in figure 6.30. For CO_2/CH_4 ratios less than 1, CO yield increases with an increase in CO_2/CH_4 ratio as CO_2 is the limiting reagent. Any incremental addition of CO_2 at CO_2/CH_4 ratios less than 1 is largely consumed resulting in higher CO 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. Thus any addition of CO_2 does not increase the moles of CO formed, instead it effectively reduces the yield of the CO.

It can be seen from figure 6.31 that low CO_2/CH_4 ratios results in higher H_2/CO ratios. Reaction C2 consumes H_2 and produces CO. With increase of CO_2/CH_4 ratio, more CO_2 becomes available for reaction C2. 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 favored by low CO_2/CH_4 ratio (see figure 6.32). Coke formation for CO_2/CH_4 ratio greater than 1 drops to zero at higher temperature as the primary coke forming reactions (C5, C7, and C3) are exothermic. Methane cracking (reaction C4), 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, 2011 and Sun et al., 2011.

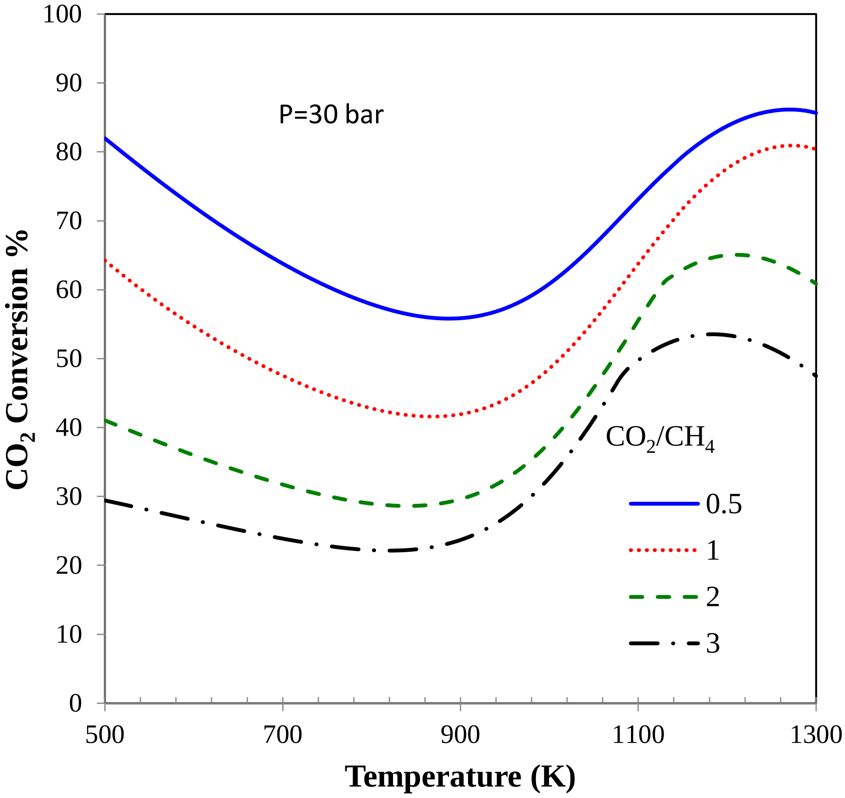

Figure 6.29 Influence of CO_2/CH_4 ratios on CO_2 conversion

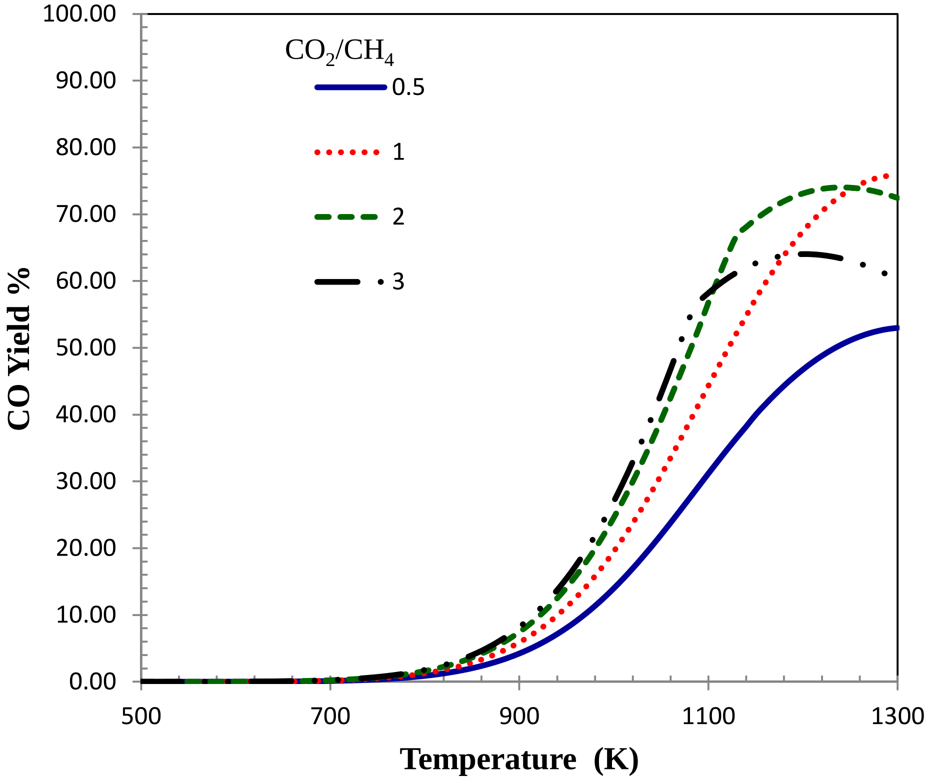

Figure 6.30 Influence of CO_2/CH_4 ratios on CO yield

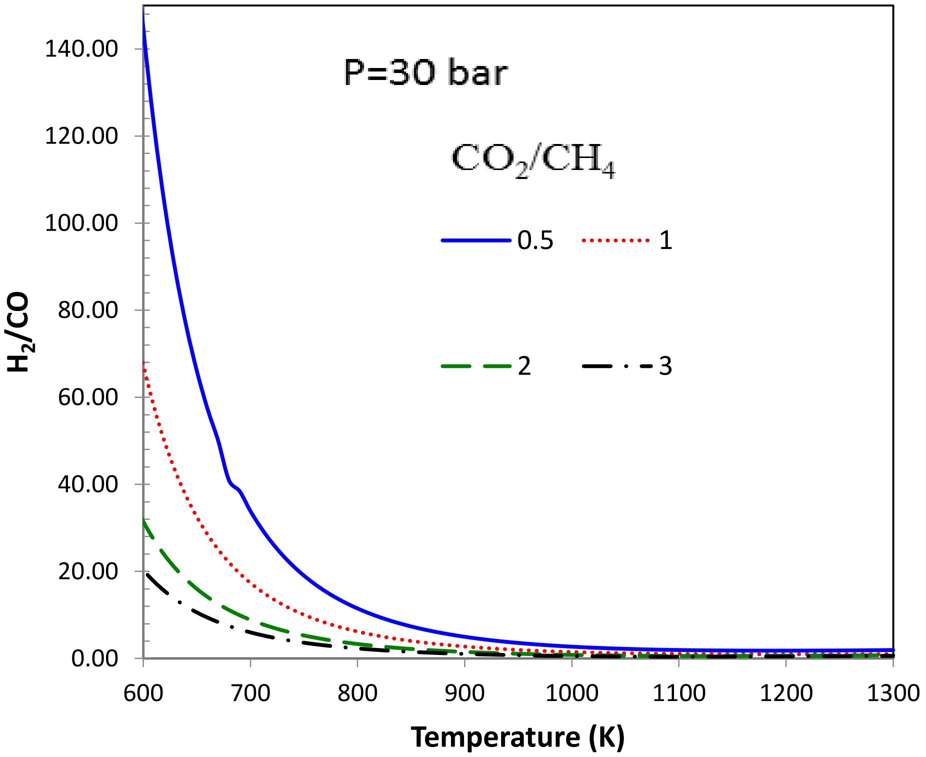

Figure 6.31 Influence of CO_2/CH_4 ratio on H_2/CO ratios

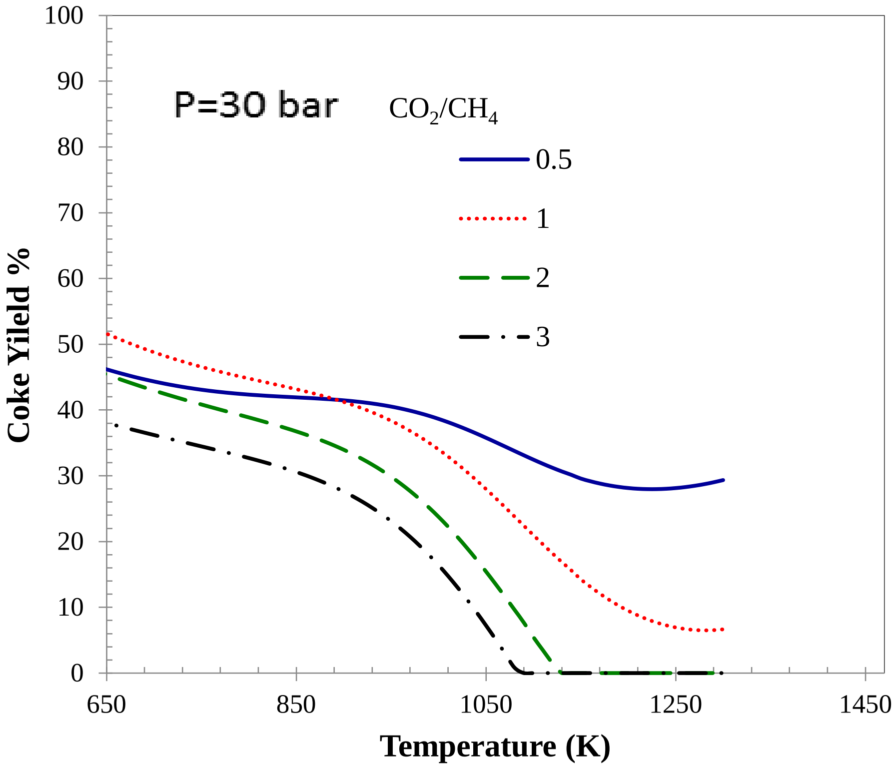

Figure 6.32 Influence of CO_2/CH_4 ratio on coke yield

6.3.3 Effect of presence of CO in feed

Figure 6.33 depicts the effect of CO on CO_2 conversion. Presence of CO, which is the main product, reduces CO_2 conversion. CO does not have any significant effect on Hydrogen and CO yields.

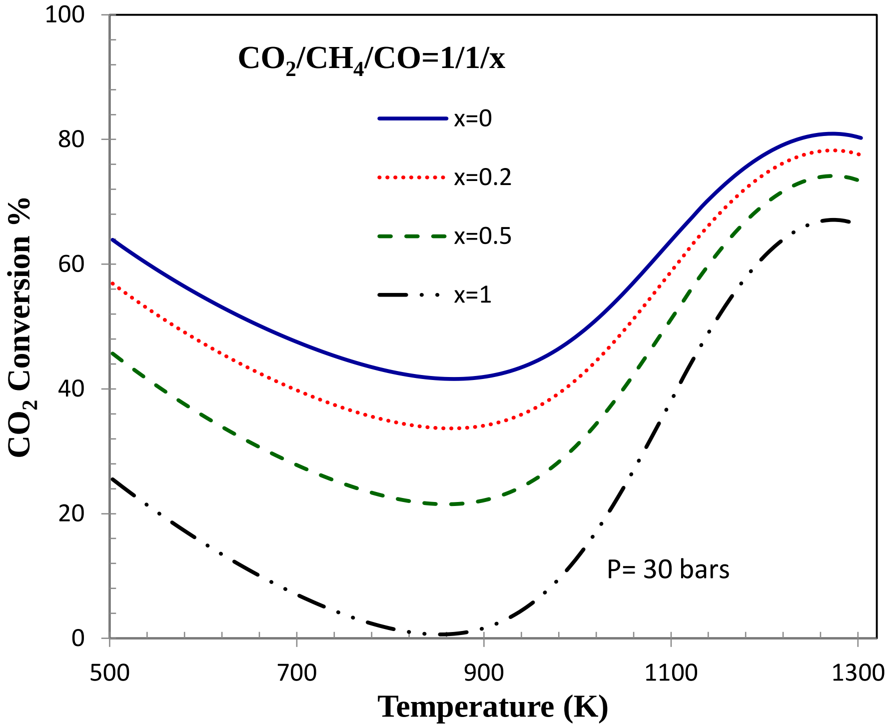

Figure 6.33 Effect of presence of CO on CO_2 conversion

6.3.4 Effect of in-situ removal of CO

Utility of synthesis gas is largely decided by the H_2/CO ratio. The in-situ removal of either CO or H_2 can be used for enhancing the yield and adjusting the H_2/CO ratio. Figure show the effect of in-situ removal of CO on CO_2 conversion and CO yield respectively. It can be seen from figure that at lower temperature a CO removal results in 20-50 % increase in CO_2 conversion. In-situ removal of CO also reduces the coke formation to large extent. In-situ removal of CO makes it possible to achieve higher yield at low temperatures. As expected, in-situ removal of CO enhances the CO yield. (see figure 6.35)

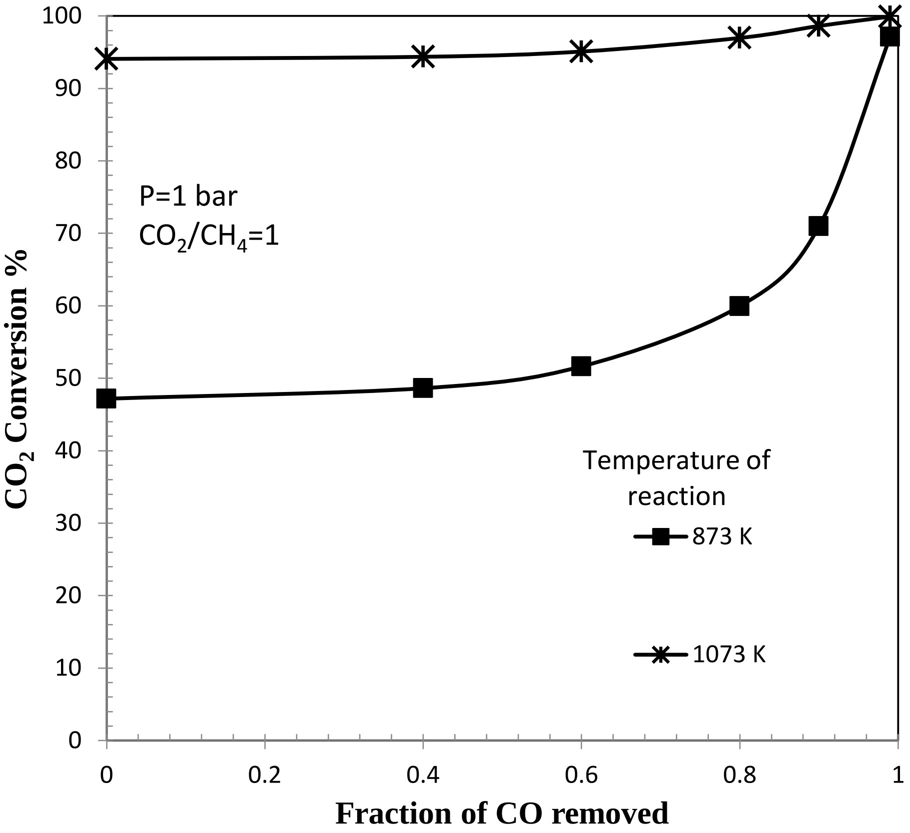

Figure 6.34 Effect of in-situ removal of CO on CO_2 conversion

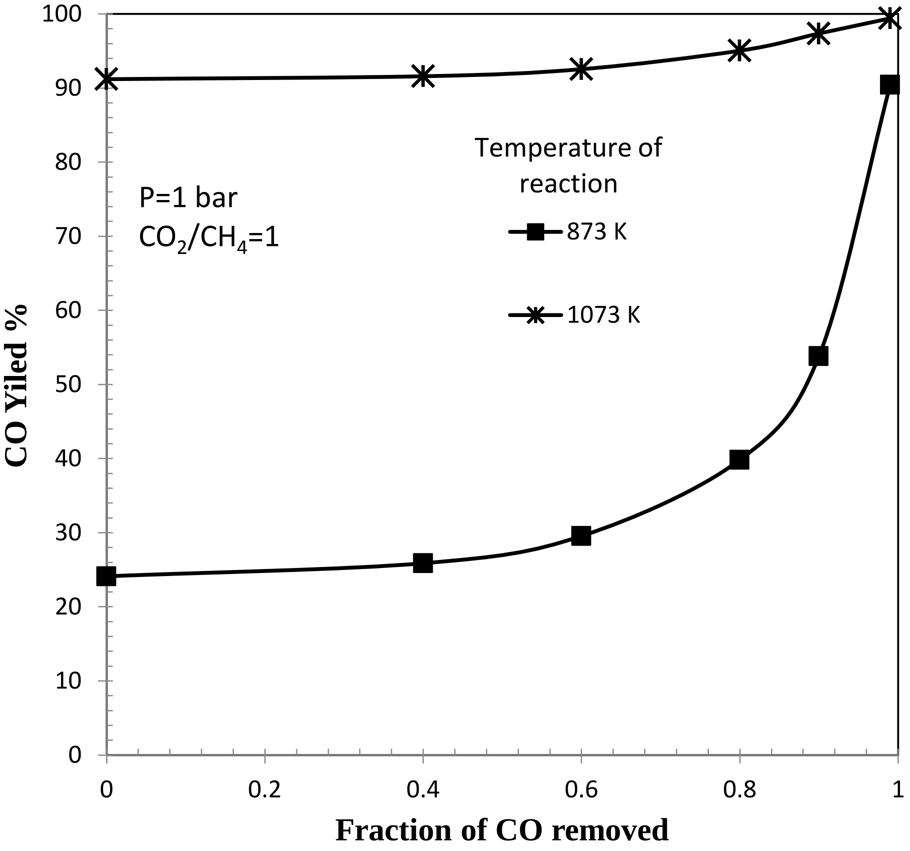

Figure 6.35 Effect of in-situ removal of CO on CO yield

6.4 DME synthesis from dry reforming product

6.4.1 Effect of temperature and pressure.

The analysis of dry reforming coupled with DME synthesis is done in two steps. The output from analysis of dry reforming is taken as the feed to DME synthesis. Water and coke formed in dry reforming are not taken in feed for DME. Figure 6.39 and 6.67 show the effect temperature on CO_2 conversion and DME yield. They also depict the effect of dry reforming temperature on CO_2 conversion and DME yield. Pressures for dry reforming and DME synthesis are taken as 1 bar and 30 bar respectively. Feed with CO_2/CH_4 ratio of 1 is taken for calculations. Figure 6.36 depicts the effect of temperature on CO_2 conversion. For temperatures below 550 K, low temperature feeds from dry reforming have higher CO_2 conversions but opposite trend is observed beyond 550 K. Low temperature feed contain only unreacted CO_2 with trace amount of CO and H_2 (see Table 6.1). As a result, hardly any 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 6.37 that DME yield decrease with increasing temperature. This happens because synthesis of DME from CO is exothermic in nature. High dry reforming temperature also favors DME yield because higher dry reforming temperature leads to increased availability of CO and hydrogen. Dry reforming is favored by low pressure. As a result, low pressure feeds have better CO_2 conversion and DME yield (see figure 6.38 and 6.39).

Table 6.1 Dry reforming Product composition (P= 1 bar)

Temperature	CO_2	H_2	CH_4	CO	H_2O	C (solid)	H_2/CO
800	0.598	0.728	0.311	0.154	0.649	0.936	4.727273
900	0.468	1.261	0.176	0.678	0.387	0.678	1.859882
1000	0.174	1.697	0.079	1.507	0.146	0.241	1.126078
1100	0.040	1.893	0.033	1.879	0.041	0.048	1.007451
1200	0.013	1.958	0.015	1.961	0.012	0.011	0.99847

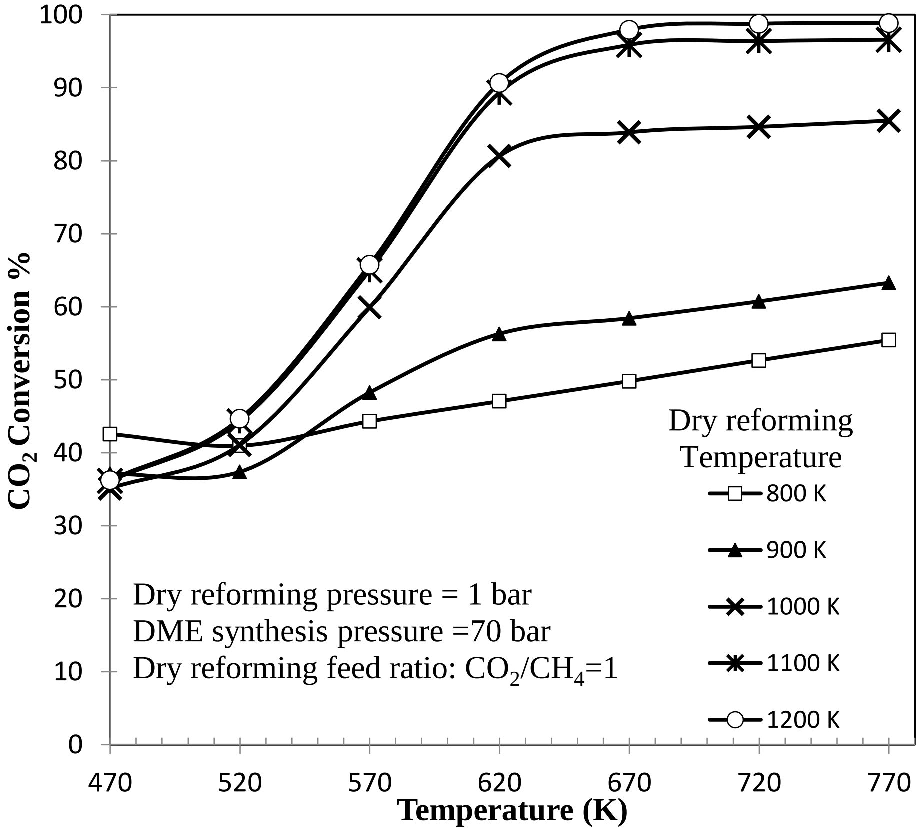

Figure 6.36 Effect of temperature on CO_2 conversion

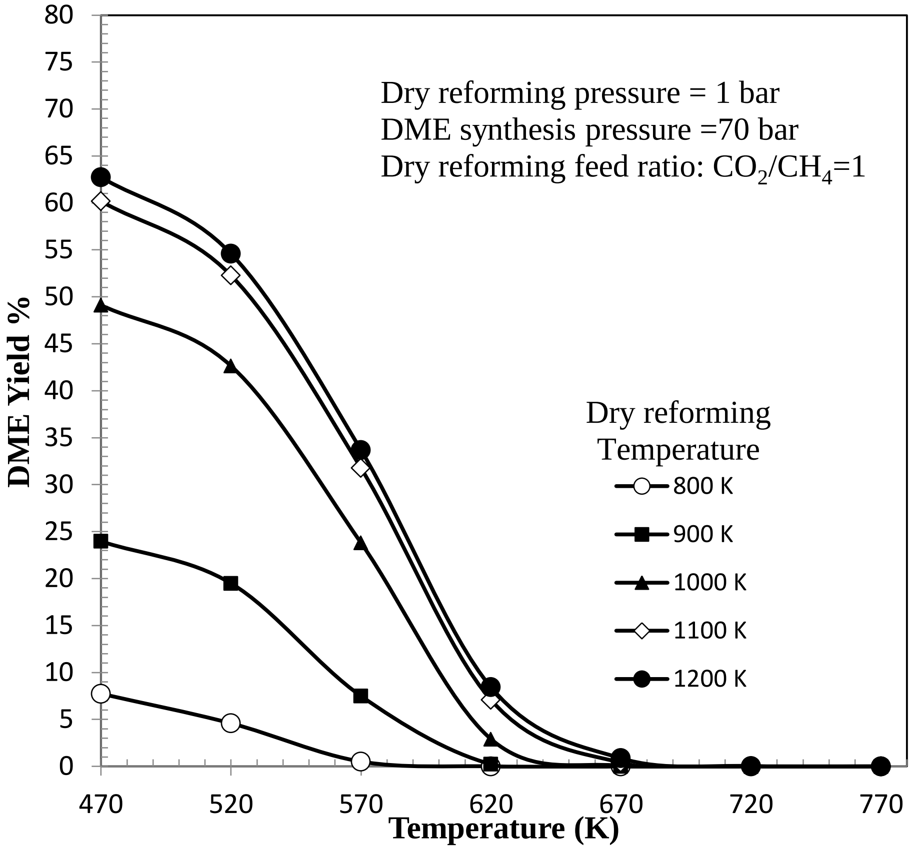

Figure 6.37 Effect of temperature on DME yield

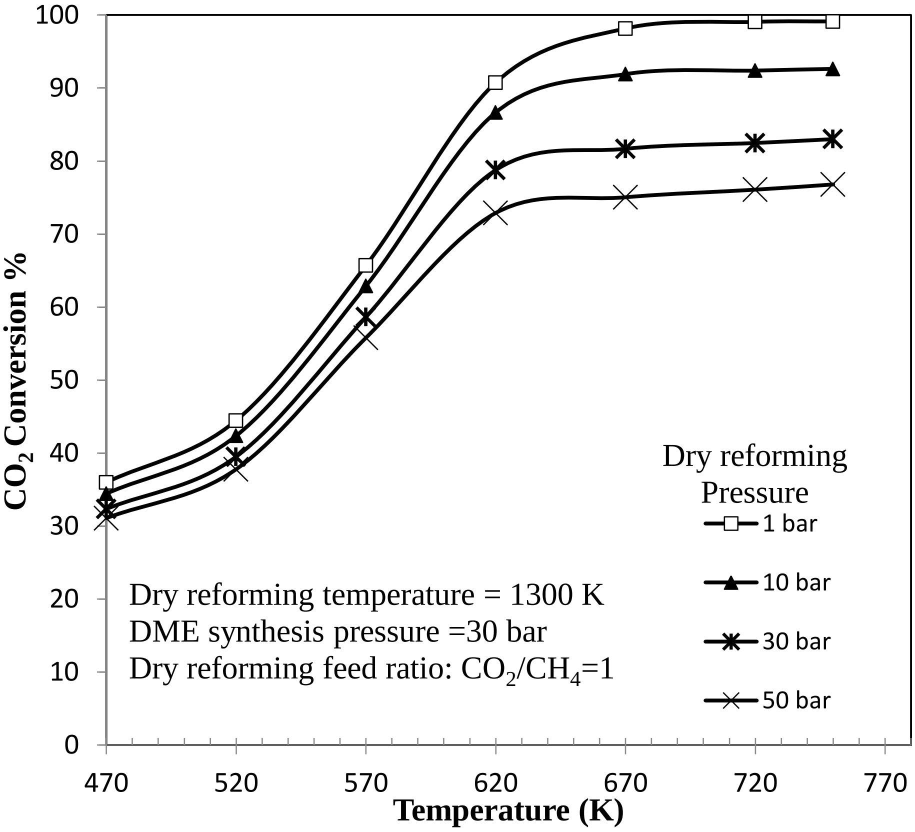

Figure 6.38 Effect of pressure on CO_2 conversion

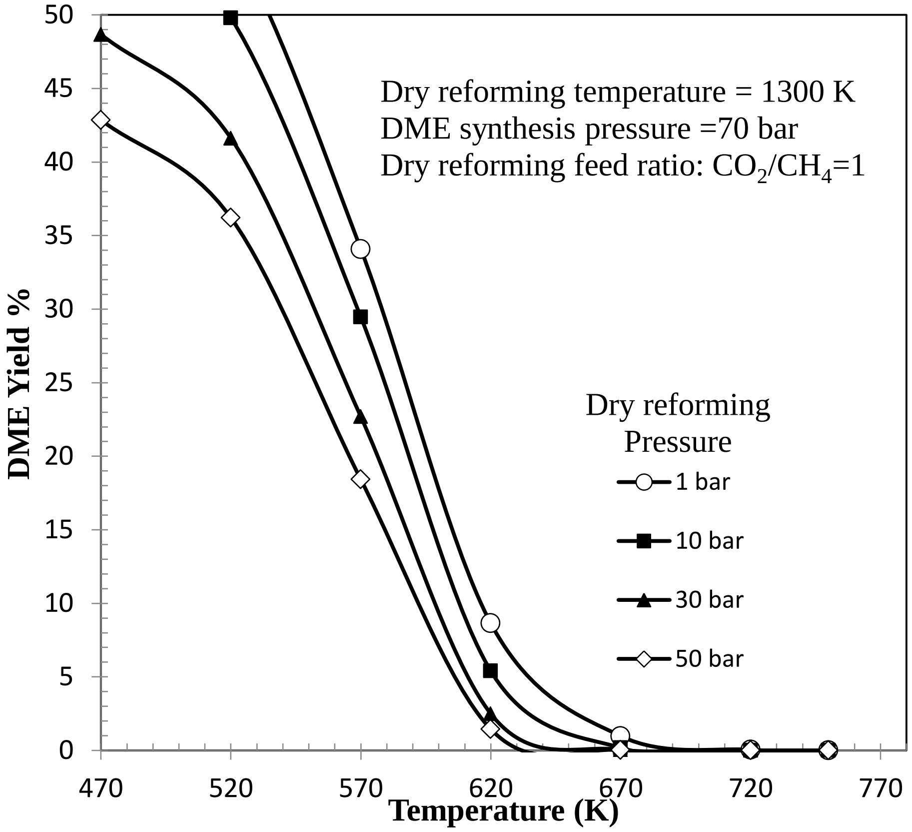

Figure 6.39 Effect of pressure on DME Yield

6.4.2 Effect of feed composition.

DME synthesis via CO hydrogenation is favored 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 temperatures but they are accompanied by low CO yield and coke formation (see Table 6.1). As a result, overall DME yield from high H_2/CO (low temperature DME 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 6.31 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 DME yield

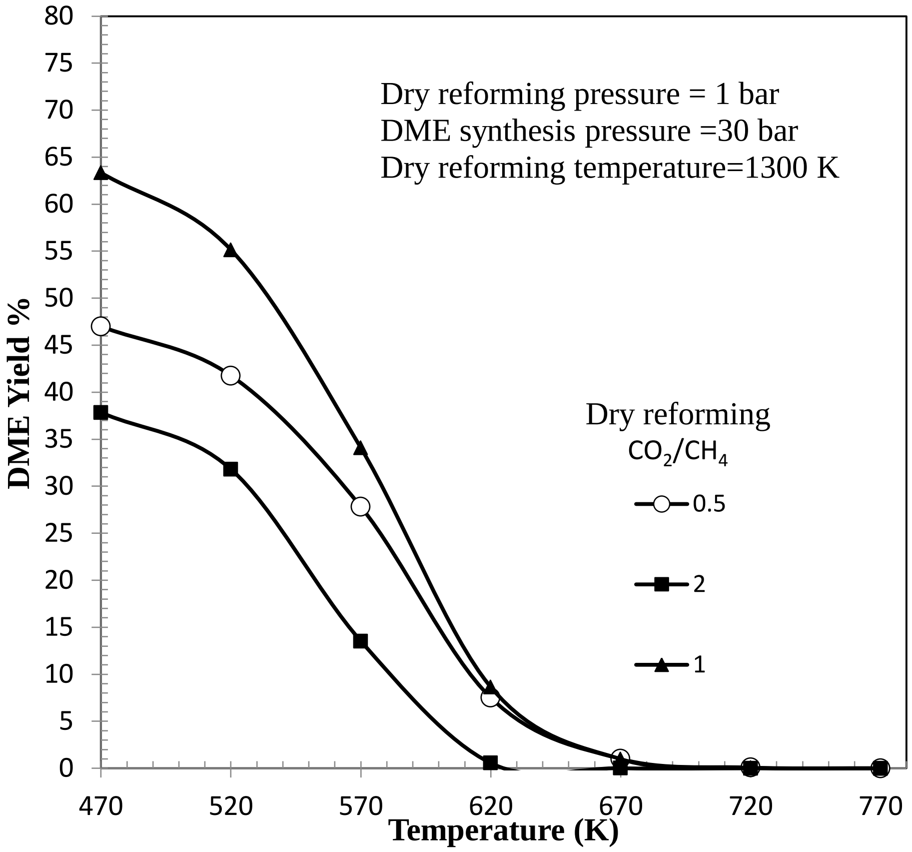

Figure 6.40 Effect of feed composition on DME yield.

6.5 Model Validation

For model validation, we compared thermodynamic calculations with experimental results, which were adopted from literature. Figure 6.41 depicts the comparison of our calculations for DME synthesis with experimental results from An's work (An et al., 2008) on CuO-ZnO-Al_2O_3-ZrO_2/HZSM-5 bi-functional catalyst. It can be seen that CO_2 conversions observed in experimental study is lower than CO_2 conversions obtained from thermodynamic study but the difference is small. For CO_2 methanation, experimental results of Tada (Tada et al., 2012) work on CO_2 methanation using Ni/CeO_2 catalyst. It can be seen in figure 6.42 that thermodynamic calculations and experimental results are almost identical beyond 580 K but a large difference is observed at lower temperatures. Similar trends are also reported by Ocampo (Ocampo et al., 2009) and Buels (Beuls et al., 2012) in their work. This happens because methanation of CO_2, which involves reduction of fully oxidized carbon, has kinetic limitations (Park and McFarland, 2009) . Figure 6.43 depicts the comparison of our calculations for dry reforming with experimental results reported by Zhang (Zhang et al., 2013) in their study of Mg-SBA-15-Supported Nickel Catalyst for CO_2 reforming of methane.

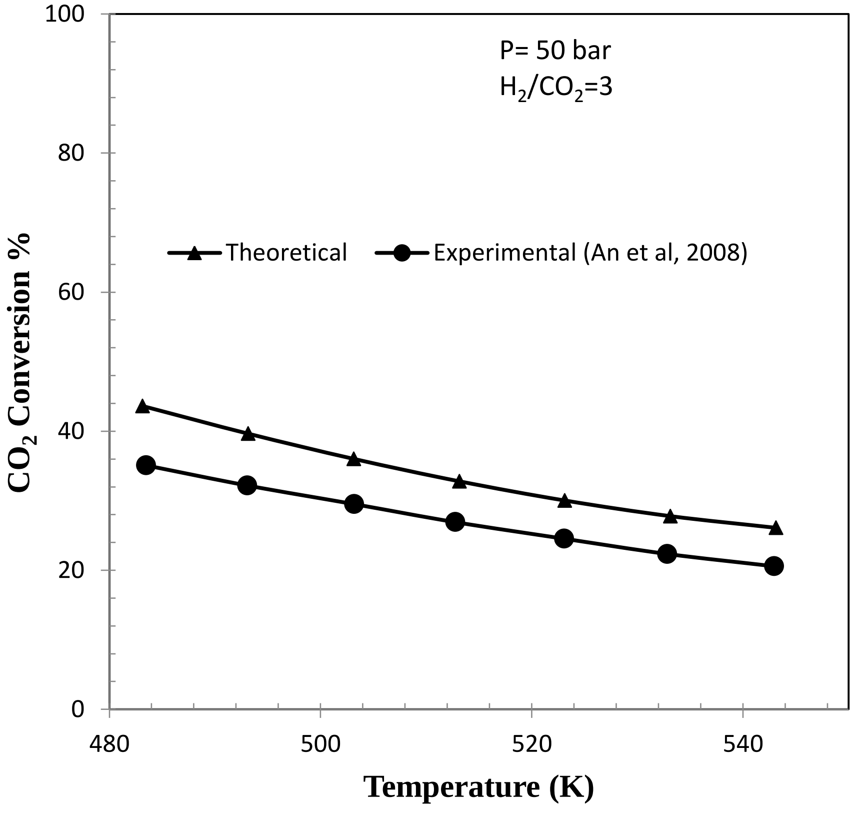

Figure 6.41 Model Validation- DME (CO_2 conversion)

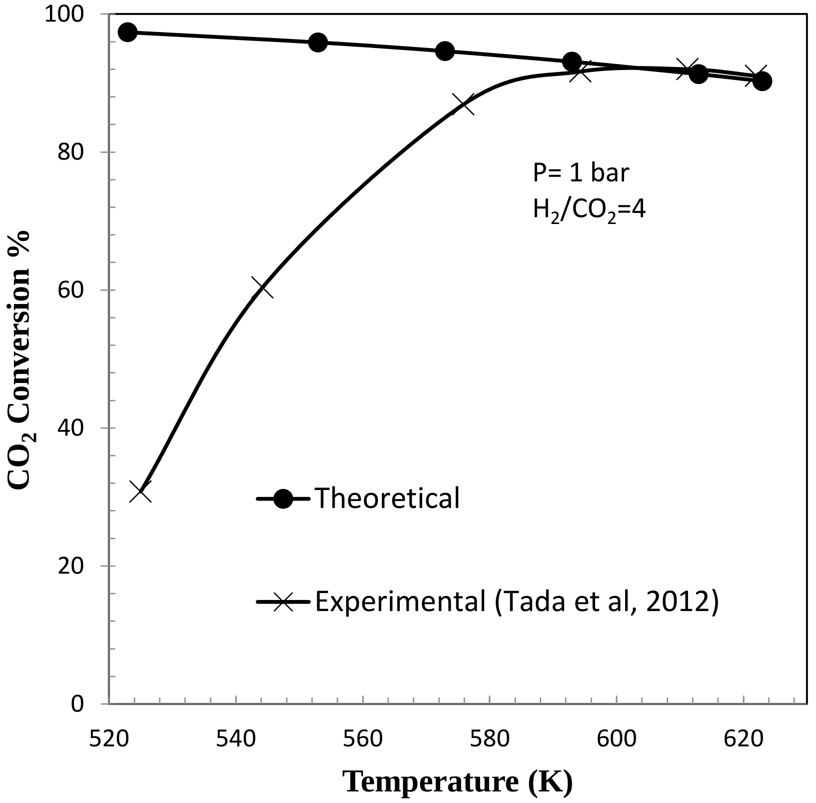

Figure 6.42 Model Validation- Methanation (CO_2 conversion)

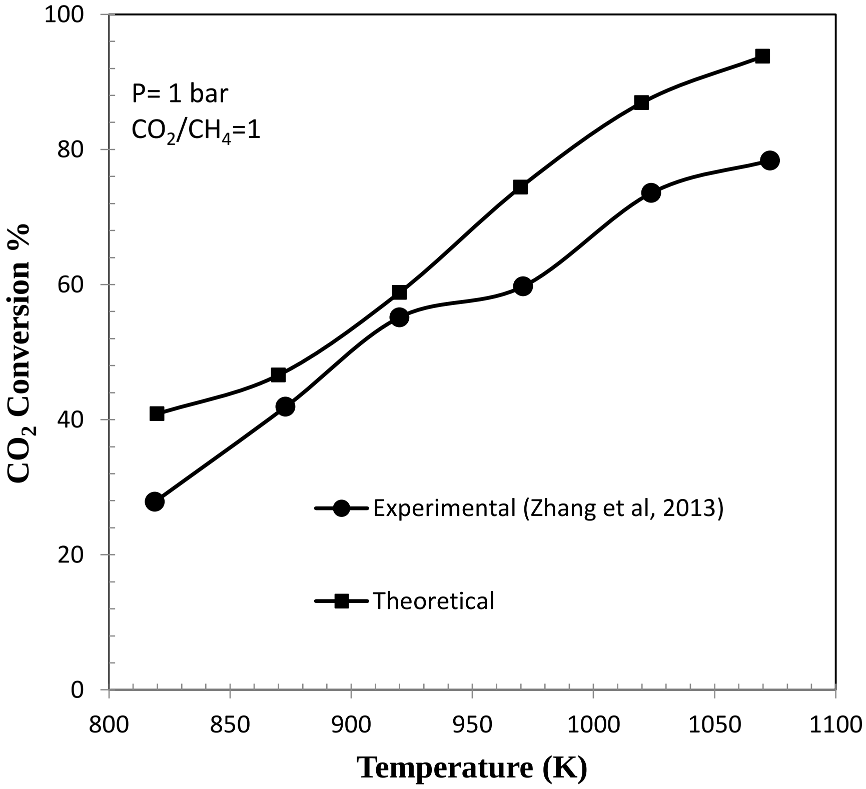

Figure 6.43 Model Validation- Dry reforming (CO_2 conversion)

6.6 Comparison among the 4 processes

Comparison between the any two similar processes can be carried in two ways. One way is to compare the processes for same feed composition and operating condition. The other way is to compare the conversions and yield of the processes for their respective favorable conditions pressure. Both types of comparisons have been used in the present study. The two most important aspects for any process being considered for CO_2 utilization are CO_2 conversion and yield of the desired product.

Figure 6.44-6.46 depicts comparison among the 4 process on the basis of conversion and yield for various pressure, temperature and feed composition. A feed with CO_2 concentration of 0.2 is taken as the basis for the comparison in figure 6.44 and 6.45. Methanation has highest conversion till the temperature of 700 K, after which DME from dry reforming product has the highest conversion. DME synthesis using dry reforming product shows nearly complete conversion beyond 700 K. The difference between conversion values of the other processes at higher temperature becomes small. This happens largely due to predominance of reverse water gas shift reaction at higher temperature. DME synthesis via CO_2 hydrogenation has the lowest yield throughout the temperature range. Methanation shows very high yield at lower temperature while dry reforming shows at higher temperatures. The yield of DME becomes zero after 650 K. Also the maximum possible yield for both DME synthesis processes are very low compared to maximum possible yields in methanation and dry reforming. Figure 6.46 illustrates that conversion is favored by low CO_2 concentration in feed for all processes except for dry reforming coupled with DME. An important take away from figure 6.46 is that methanation provide better conversion than dry reforming for CO_2 concentration below 0.3 while dry reforming provides better conversion for CO_2 concentration above 0.3. Irrespective of CO_2 concentration, DME has the lowest CO_2 conversion among the 3 processes. DME synthesis using dry reforming product shows the best CO_2 conversion at higher CO_2 concentration.

Figure 6.47-6.48 compare the CO_2 conversion and product yield of 4 processes in their respective optimum condition based on the results in section 6.1-6.4. Methanation show 100 % conversion till about 900 K. Dry reforming also show 100 % conversion beyond 1200 K. Dry reforming coupled with DME show 100 % conversion after 700 K. DME process gives the lowest average conversion over the range of study. It can be seen for figure 6.48 that both dry reforming and methanation give nearly 100 % yields. Maximum yield from both DME synthesis processes is about 70 %. DME synthesis using dry reforming product from dry reforming feed gives better DME yield than DME synthesis via CO_2 hydrogenation.

Table 6.2 Favorable condition for the processes

Process	Pressure	Feed composition
DME via CO_2 hydrogenation	70 bar	$H_2/CO_2=6$
Methanation	70 bar	$H_2/CO_2=8$
Dry reforming	1 bar	$CO_2/CH_4=1$
DME from dry reforming feed	1 bar, 70 bar	$CO_2/CH_4=1$

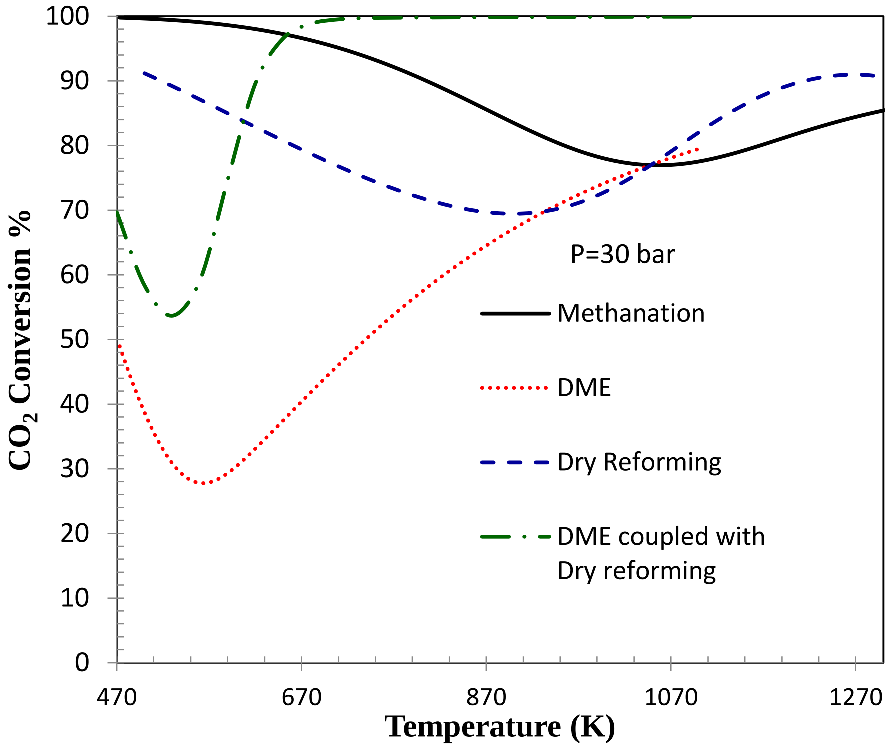

Figure 6.44 CO_2 conversions at CO_2 concentration of 0.2 and pressure of 30 bars

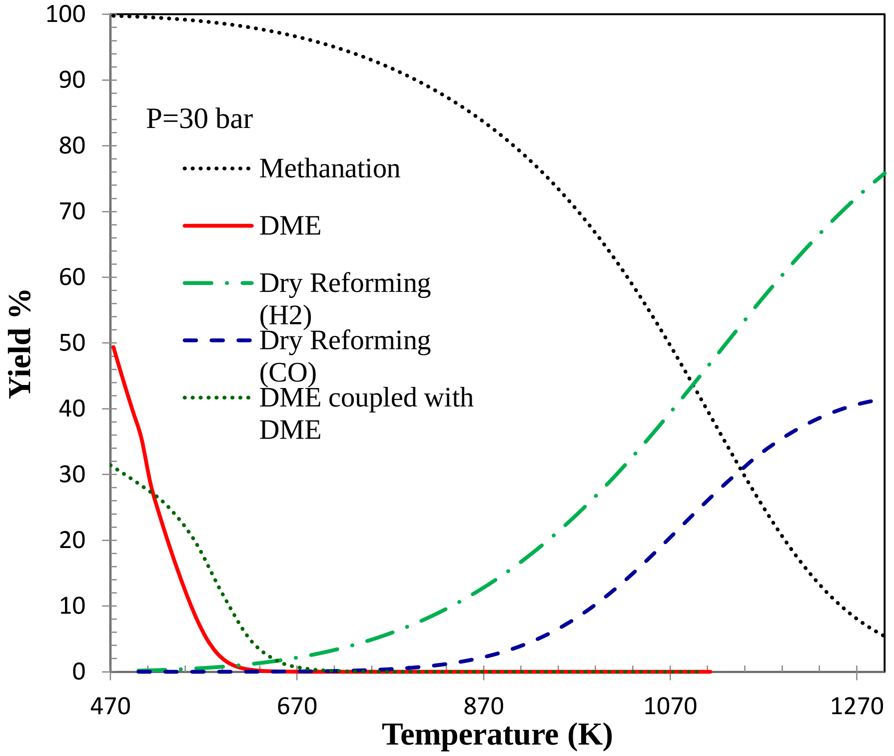

Figure 6.45 Yield at CO_2 concentration of 0.2 and pressure of 30 bars

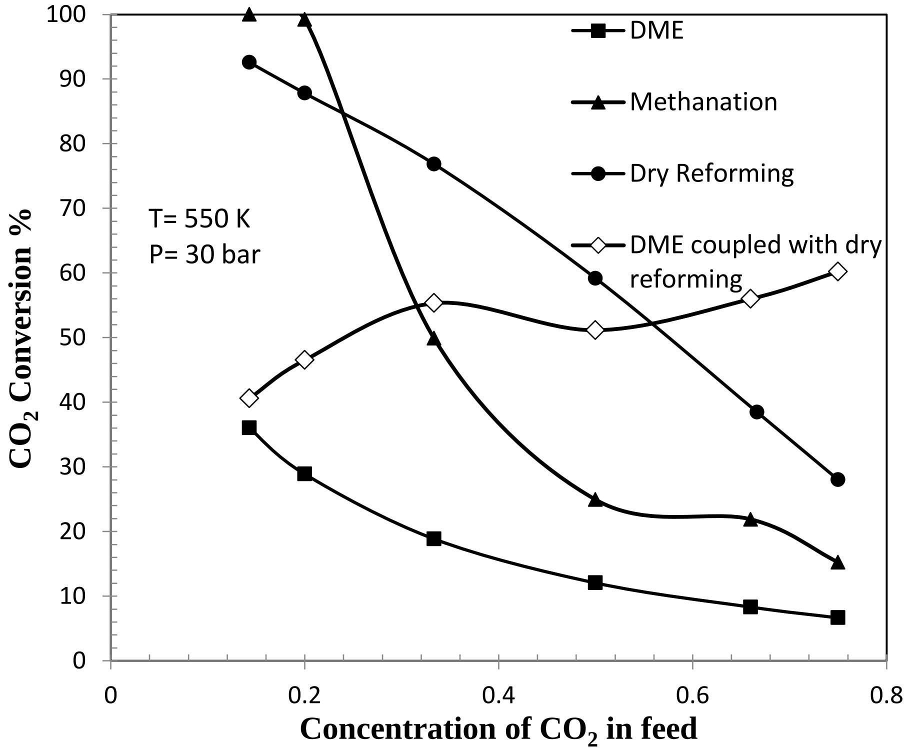

Figure 6.46 Effect of CO_2 concentration in feed on CO_2 conversion at temperature of 550 K and pressure of 30 bar

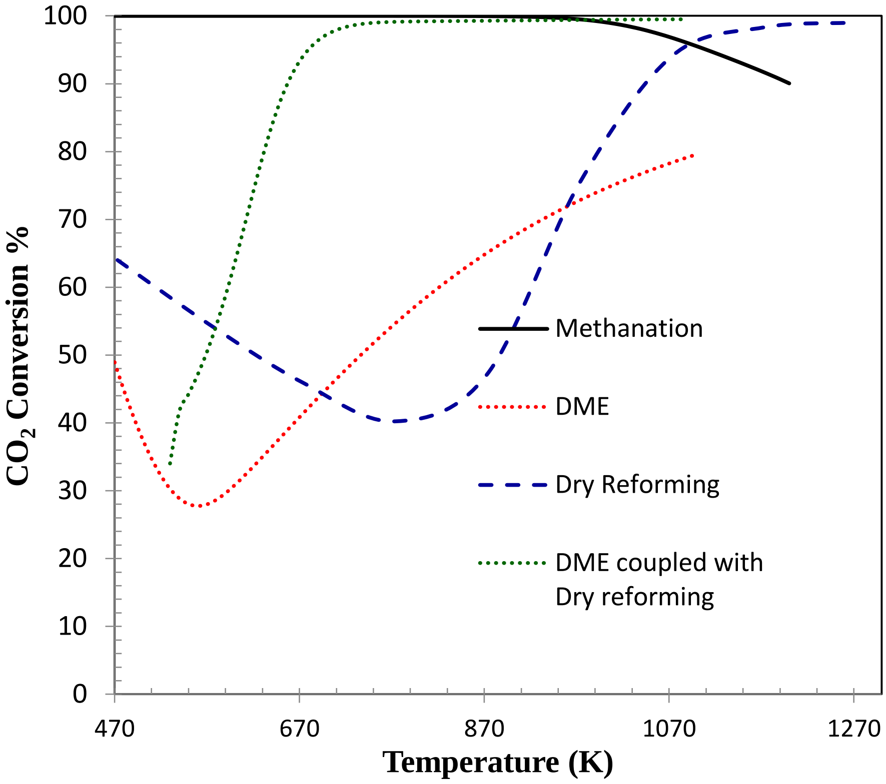

Figure 6.47 Comparison of CO_2 conversions of 4 processes at their respective optimum condition

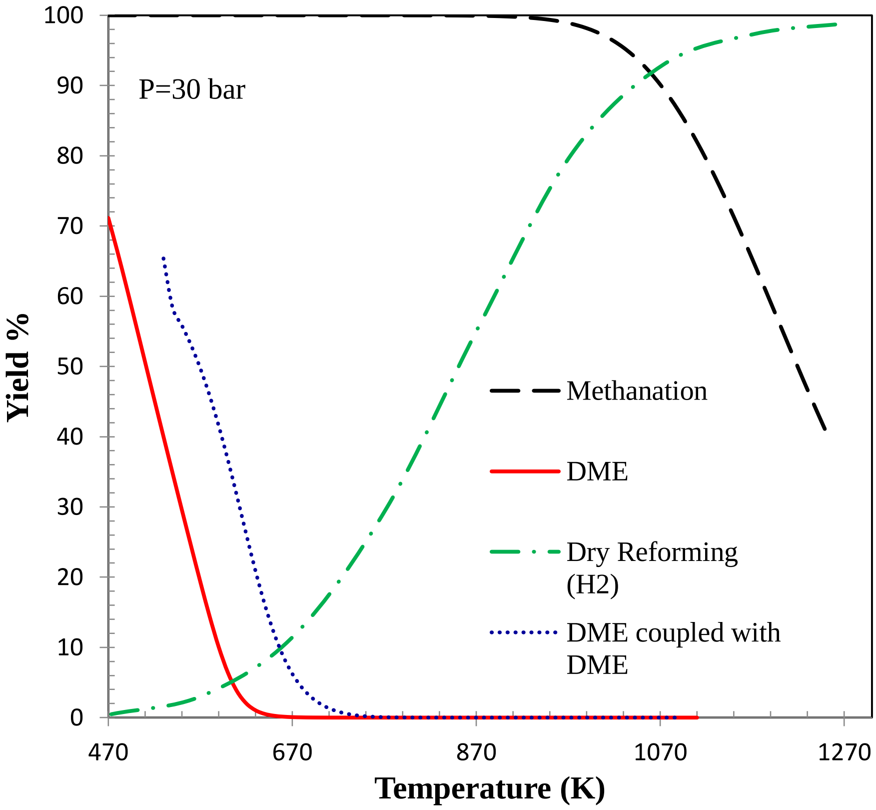

Figure 6.48 Comparison of product yield of 4 processes at their respective optimum condition

Chapter 7 Conclusion

Detailed thermodynamic study of four systems: synthesis of DME from CO_2, synthesis of methane by CO_2 hydrogenation, dry reforming of methane and DME synthesis using dry reforming product was performed in the present study. Influence of temperature, pressure, feed compositions and addition of CO to feed were investiagetd in terms of their impact on conversion, yield and selectivity. It was found that DME synthesis via CO_2 hydroehenation is favored by low temperature, high pressure and high H_2/CO_2 ratio. For CO_2 methanation, high H_2/CO_2 ratios, low temperature provide the best CO_2 conversion and methane yield. On the other hand for dry reforming, high temperature and low pressure are more favorable. DME synthesis using dry reforming product is favored by high dry reforming temperature, low dry reforming pressure, high DME process pressure and low DME process temperature.

DME synthesis from dry reforming product shows better DME yield than synthesis of DME from CO_2 hydrogenation but the CO_2 conversion is better for synthesis of DME from CO_2 hydrogenation. Synthesis of DME from CO_2 hydrogenation has the lowest yield as compared to other three processes. Both methanation and dry reforming provide high yield and conversion but at opposite range of temperatures.

Ideal process from point of view of CO_2 utilization is the one that produces a high-value product with high yield and CO_2 conversion. On the basis of comparison of the three processes, it can be said that CO_2 methanation is most suited for CO_2 mitigation because it provides very high yield and CO_2 conversion at low temperature. Despite being favored by high pressure, methanation gives very high conversion at low pressure also. Low temperature and low pressure operations make its industrial application easy. Moreover, coke deposition, a major catalyst deactivator, is largely absent in CO_2 methanation process. Thermodynamic analysis presents only one aspect of chemical process. Final application of any process at practical level will also be based other factor such as kinetics and economics.

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_i^o	Fugacity of pure species i in standard state
G	Total Gibbs free energy of the system
G_i^o	Gibbs free energy of species i in standard state
$\Delta G^o_{298,i}$	Gibbs free energy change of reaction at standard conditions
ΔH^o_{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
$\hat{\phi}_i$	Fugacity coefficient of species i in reaction mixture

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