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Design and simulation of methanol production process from CO_2 and CO hydrogenation with reverse water-gas shift reaction

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Abstract

Over the past century, due to the excessive utilization of fossil fuels and increasing population around the globe, the anthropogenic emissions of CO_2 have increased drastically. The captured CO_2 can be utilized as to turn into a profitable business in addition to its positive impact of controlling the CO_2 concentration in the atmosphere. A production process of high purity methanol from CO_2 captured has been discussed in detail in this paper. The process is designed and simulated with Pro/II V.10.2. A comparison is made of the overall methanol yield resulting from consideration of only CO_2 hydrogenation and the reverse water gas shift reaction with the addition of CO hydrogenation reaction in the reactor. The reaction set was chosen accordingly. The balance on CO_2 in the process showed that it is possible to abate 2.12 tonnes of CO_2 per tonne of methanol produced. The CO_2 and H_2 were used in the ratio 1:3 and the methanol so obtained was 4139 kg/h (overall yield of 0.47) with 99 % purity. This shows that the reaction kinetics and the process flow proposed in this paper can be employed.

Keywords: RWGS; Hydrogenation; Methanol, Pro/II; Simulation; Yield

1. Introduction

Technological advancements and rapid population growth have been causes for increase in the global energy demand and its consumption. Fossil fuels, renewable energy and nuclear energy are the sources of energy and amongst which fossil fuels are the primary and major source. This primary dependence on fossil fuels has led to increasing carbon dioxide emission into the atmosphere which has raised the alarming issue of global warming.

The large growth in global CO_2 emissions has had a significant impact on its concentrations in Earth's atmosphere with fossil fuels being one of its major contributors. Carbon dioxide has made up 76 percent of all global greenhouse gas emissions, followed by methane at 16 percent and nitrous oxide at 6 percent [1]. A change in climate with potential ecological and physical impacts with extreme weather events such as droughts, floods, rise in sea level, alteration on crop growth and water system disruptions can be attributed to global warming. A total increment in global temperature amounts to 1.2 °C since the pre-industrial times [2].

Developed countries and major emerging economy nations possess a great share in total carbon dioxide emissions while some developing countries are increasing in the growth rate of carbon dioxide emissions. China, Russia, USA, India and Japan stand as top 5 countries contributing for global carbon dioxide emission from fuel combustion [2].

A critical universal challenge has originated from shifting the global energy with a balanced use of oil, gas and coal while still protecting the environment. Extraction of maximum energy from fossil fuels with as much minimization as possible of the harm to the environment is a clear technical and socio-economic goal of the scientific community until the implementation of a new, totally renewable or sustainable energy source that supplants oil, coal and natural gas. A recent paper on emissions pathways by Rogeli et al. [3] showed that the scale of the CO_2 emissions problem is not being addressed quickly enough. The atmospheric CO_2 emission has increased drastically after the industrial revolution with a concentration of 411.29 parts per million (ppm) until Sept. 2020 considered its highest level in the last three million years. To begin to stabilize, or even reduce atmospheric CO_2 concentrations, our emissions need to not only stabilize but also decrease significantly [4-6].

Greenhouse gases have helped in maintaining earth's temperature by preventing heat from escaping; however, excessive use of these gases including CO_2 have increased earth's average temperature and caused global warming [7]. If the concentration of CO_2 continues to increase at the current rate, there will be a rise in temperature by nearly 1.95 °C over the next century [8].

Carbon dioxide has direct use in wide applications such as food processing, preservation, coffee decaffeination, fire suppression, beverage carbonation and production of coolants. In beverage industries, carbonation is done in order to provide sparkling appearance and refreshing bubbles in the drinks [9]. Another approach of CO_2 utilization is converting CO_2 to fuels and chemicals through various catalytic processes for synthesis of methanol, salicylic acid, and urea [10]. The conversion of CO_2 to fuels can be an effective method for reduction in global net emission of CO_2. By converting CO_2 into methanol, issues like depletion of fossil fuels and greenhouse gas can be solved to some extent, thus making methanol production a promising process for fuel production and carbon reduction.

The industrial significance of methanol is huge. Globally, there are over 90 methanol plants with combined capacity of 110 million metric tons [11]. Major applications of methanol include the production of formaldehyde and tert-butyl methyl ether (common form of MTBE) which is used as a fuel or blended with gasoline. Along with this, the use of methanol in plastic industries and as a direct fuel or blended with petrol is gaining attention. Ease in stor-

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*Corresponding author. Email: sijandevkota2054@gmail.com age and high energy density makes it a convenient energy storage candidate. It holds excellent promise as an alternative source of energy since it offers several advantages like clean burning properties, low emissions, high octane rating, high volatility, high energy density, easy transport and the ability to be incorporated in the existing engines without major modifications in the infrastructure. It has also been used in cell research application as an energy carrier [12].

2. Reaction Mechanism

In the early 1913, carbon monoxide was reacted with hydrogen using an iron-based catalyst by German chemists named A. Mittasch and M. Pier during ammonia synthesis developmental work at BASF. Later development of a large-scale methanol production method using ZnO on Cr_2O_3-based catalyst was done by M. Pier at high pressures (25-35 MPa) and 320 °C - 450 °C [13].

Later, in 1966, copper-based catalysts were introduced for methanol synthesis. This catalytic process was operated at 50-100 bar pressure and 200-300 °C temperature [14]. Due to the high purity of synthesis gas which was free from sulfur and carbonyl contaminants responsible for catalyst contamination, the catalytic process was successful and a majority of the world's methanol production is based on this technology. Firstly, methane, a major component of natural gas, is reacted with water to produce a mixture of CO and H_2 called syngas [15].

$CH_4 + H_2O \rightarrow CO + 3H_2$ ΔH (298K, 5MPa) = +206.3 kJ/mol

This mixture of syngas is then used for synthesis of methanol. An addition of a small amount of CO_2 to the syngas mixture was also found to increase the catalytic activity and methanol yield. Thus, in order to increase the yield by about 30 %, nowadays CO_2 is added in syngas mixture [16].

Methanol synthesis via CO_2 hydrogenation is an excellent approach since it helps with CO_2 mitigation as well as for renewable energy development.

Conventionally, there are three basic steps for production of methanol:

- Production of synthesis gas,
- Conversion of synthesis gas to methanol, and
- Distillation of the reactor effluent.

The synthesis gas (H_2, CO_2 and CO) is mainly produced by natural gas reforming. It can also be produced by partial oxidation of carbon-based materials like petroleum, coal, petroleum coke, heavy oil, asphalt or biogas. A crucial part of the overall process for methanol production is syngas manufacturing and purification. It usually represents more than half of the total investment when the feedstock is natural gas and up to 70–80 % when the raw material is coal. The composition of the syngas is usually characterized by the stoichiometric number M which is defined as:

$$M = \frac{y_{H_2} - y_{CO_2}}{y_{CO_2} + y_{CO}}$$

The value of the parameter M for a stoichiometric $CO/CO_2/H_2$ mixture is 2. A value larger than 2 indicates a mixture rich in H_2, and reciprocally. Therefore, a syngas composition with a stoichiometric number M slightly above 2 is the optimum for methanol synthesis [17]. Currently, methanol is produced via synthesis processes operating at pressures of 50–100 atm and temperatures of 200–300 °C. The actual processes mostly operate using copper-based catalysts and in gas phase. The main differences among them are related to the reactor design and catalyst arrangements.

The syngas is pressurized with a compressor and heated. In the methanol converter, heating could also take place. The mixed gases, having a H_2/CO ratio from 3:1 to 5:1, are fed to the reactor.

Methanol synthesis occurs by following reactions [18]:

Hydrogenation of Carbon monoxide

$CO + 2H_2 \leftrightarrow CH_3OH$ Reaction (1)
(ΔH = -91 kJ/mol; ΔG = -25.34 kJ/mol)

Hydrogenation of Carbon dioxide

$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ Reaction (2)
(ΔH = -49.5 kJ/mol; ΔG = 3.30 kJ/mol)

Water gas shift reaction

$CO + H_2O \leftrightarrow CO_2 + H_2$ Reaction (3)
(ΔH = -41.2 kJ/mol; ΔG = -28.60 kJ/mol)

CO and H_2 were considered as main reactants in methanol synthesis and the contribution of CO_2 was neglected in the kinetic studies by Natta et al. and Leonov et al. [19, 20]. Liu et al. showed that methanol production rate increases with increasing CO_2 pressure. Later they proposed that, in the absence of water, hydrogenation of CO_2 was the primary reaction in producing methanol at low temperature with low conversion but with water presence at high temperature, CO hydrogenation was the primary reaction for methanol synthesis with high conversion [21]. Takagawa and Ohsugi determined the empirical rate equations considering all three methanol synthesis reactions. In their results, they showed that methanol production rate increased at the start of reaction with an increase in the ratio of CO_2/CO but decreased as the ratio increased and water started to form [22]. McNeil et al. found that that two-molar percentage of CO_2 in the feed yielded optimum methanol production rate and the contribution of CO_2 to methanol formation was greater at a lower temperature in their experimental study. In their rate law, they included the effect of CO_2 as a methanol producer and as a rate inhibitor [23]. Methanol synthesis and water gas shift reaction was studied by Sun et al. using IR technique and they found that CO_2 hydrogenation was the principle pathway in methanol production for both CO_2 and CO_2/CO hydrogenation reactions. Formate species hydrogenation was the rate determining step and addition of CO lowered the activation energy of the production process, in addition to affecting the reaction path [24].

2.1. Thermodynamics

Thermodynamic aspects of a chemical reaction, for understanding and predicting the stability of the desired chemical species, yield, conversion and selectivity of the products, are very important. It even provides information about reaction mixture phases, impact of temperature, pressure and feed ratio. Carbon dioxide is a doubly bonded linear molecule having high stability ($\Delta G°$ = -394.4 kJ mol^{-1}) and requiring substantial energy input, highly active and stable catalysts and its reaction conditions require optimization.

CO_2 and H_2 can react together to form methanol and water as in reaction 2. The formed water consumes one third the hydrogen that is charged for reaction, requiring more hydrogen than in the methanol formation reaction from syngas (reaction 1). Both of the methanol formation reactions are exothermic and take place with a loss in reaction volume. A possibility exists for the reverse water gas shift reaction to take place on the catalyst surface with CO_2 as feed, as shown in reaction 3. The produced CO from this reaction undergoes hydrogenation to yield methanol as per reaction 1. The CO_2 and CO hydrogenation to methanol are exothermic reactions and bring a loss of volume; high pressure and low temperature hence should help to achieve a higher conversion as predicted by Le Chatelier's principle.

Graaf et al. performed a thermodynamic study on methanol synthesis by the reactions of CO, CO_2 and H_2 and also calculated chemical equilibria for methanol synthesis using equilibrium constants. Fugacity coefficients in the equilibrium constants were calculated using Soave-Redlich-Kwong (SRK) equation of state (EOS) by taking non-ideal behavior of the gas mixture into account [25].

Further, Solbraa performed a study to model the solubility of carbon dioxide in water with SRK EOS with Huron-Vidal (HV) mixing rules. The model showed a capability of predicting highly accurate water-gas solubility. This mixing rule with SRK also allowed accurate modelling of solubilities of gases in liquid and vice versa. Despite the reported inapplicability at low pressures due to differences of Gibbs energy near atmospheric pressure from that at infinite pressures, this model with its high accuracy can be applied to model high pressure mixtures [26].

In our design research, methanol formation was compared between two cases: one case with reactions 2 and 3 as in Vanden Bussche and Froment [27] and the other with all of the three 1, 2 and 3 reactions in Graff et al.

2.2. Catalyst

Recently, several catalysts for hydrogenation of CO_2 to produce methanol have been reported. According to Lim et al., [18] Cu, Zn, Cr, and Pd are commonly used to minimize by-product formation (i.e. hydrocarbons) and maximize methanol yield and selectivity. The key to increasing the one-pass conversion is to develop the optimum catalyst active for low-temperature synthesis with high surface area.

The most commonly used catalysts are copper, palladium, zinc and chromium. Among these, $CuO/ZnO/Al_2O_3$ catalyst is well-known for its high activity and selectivity for the methanol synthesis reaction and is highly adopted in industry. To improve the catalytic performance of methanol synthesis from H_2/CO_2 feeding gas, CuO/ZnO catalysts have been widely modified by adding various activators or other metals (Zr, Si, La, Ti, Cr, Ga, Ce, Fe, Nb, Pd, etc.) A support such as Al_2O_3 can further increase the activity and selectivity. Furthermore, the copper dispersion as well as the catalytic activity of methanol synthesis catalysts have also been known to be promoted by Zr. CuO ranges between 20 to 80 percent, ZnO ranges between 15 to 50 percent and Al_2O_3 ranges from 4 to 30 percent. The investigation on enhancing the catalytic activity by the addition of supports and promoters are increasing. Lachowska and Skrzypek found that $CuO/ZnO/ZrO_2$ had a catalytic activity higher than $CuO/ZnO/Al_2O_3$ [28]. Nowadays, methanol is produced industrially from synthesis gas mixtures ($CO/CO_2/H_2$) over $Cu/ZnO/Al_2O_3$ catalysts at 50 to 100 bar total pressure and at a temperature between 200 and 300 °C [29].

Many Cu-based catalysts like CuO/ZrO_2, $CuO/ZnO/ZrO_2$, $CuO/ZnO/Ga_2O_3$, modified $CuO/ZnO/Al_2O_3$ and multi-component catalysts have been extensively studied. Furthermore, several copper-based catalysts with boron, vanadium and gallium as promoters have also been investigated. To investigate the potential of catalysts containing Cu and Zr in methanol synthesis, Raudaskoski et al. reviewed recent works done by various researchers [30].

In our present research, the catalyst used for methanol synthesis reaction is $Cu/ZnO/Al_2O_3$ (CuZA). A ZrO_2 promoted Cu/ZnO catalyst (CuZZ) can also be used. But the apparent density of CuZZ is three times that of CuZA and has to be diluted with SiC in order to meet the same catalytic bed volume.

3. Kinetic Modeling

The work of Grabow and Mavrikakis [31] which is not mentioned in Table 1 describes a microkinetic model, with 49 elementary steps, and considers the different intermediates involved in the methanol synthesis. It deals with the density functional theory calculations and provides an interesting result that the two-third of the methanol is produced from CO_2 hydrogenation. Still there is a contradiction that whether the methanol synthesis and RWGS (Reverse Water-Gas Shift) reaction are parallel pathways, shares a common intermediate, or methanol formation proceeds by sequential RWGS and CO hydrogenation.

Table 1: Several studies on methanol carbon source.

Authors	Carbon Source
Leonov et al., 1970-1973 [20]	CO
Rozovskii et al., 1975-1977 [32, 33]	CO_2
Schermuly and Luft., 1977 [34]	CO
Denise and Sneeden., 1982 [35]	$CO + CO_2$
Klier et al., 1982 [36]	$CO + CO_2$
Monnier et al., 1984 [37]	CO
Bardet et al., 1984 [38]	$CO + CO_2$
Chincen et al., 1984 [39]	CO_2
Villa et al., 1985 [40]	CO
Liu et al., 1985 [21]	$CO + CO_2$
Seyfert and Luft., 1985 [41]	CO
Dybkjaer., 1985 [42]	CO_2
Takagawa and Ohsugi., [22]	CO
Chincen et al., 1987 [43]	$CO + CO_2$
Graaf et al., 1988 [44]	$CO + CO_2$
Shack et al., 1989 [45]	$CO + CO_2$
McNeil et al., 1989 [23]	$CO + CO_2$
Skrzypek et al., 1991 [46]	CO_2
Askgaard et al., 1995 [47]	CO_2
Vanden Bussche and Froment et al., 1996 [27]	CO_2
Kubota et al., 2001 [48]	CO_2

Van den Bussche and Froment [27] have established a kinetic model taking into account only the water gas-shift reaction and the carbon dioxide hydrogenation for the catalyst of $CuO/ZnO/Al_2O_3$ at 180 to 280 °C and pressure of 15 to 51 bar. The reactor taken was an isothermal plug flow reactor and the effects of the operating conditions and the CO fractions were studied.

Struis et al. [49] performed experiments for the single pass methanol production with CO_2 and H_2 as a feed on the membrane reactor at 200 °C and 40 bar and GHSV of 5000 h^{-1}. The catalyst used was CuO/ZnO and the kinetic parameters (kinetic constants and adsorption constants) were also determined through the experiments.

Skrzypek et al. investigated kinetics of low-pressure methanol synthesis over $CuO/ZnO/Al_2O_3$ commercial catalyst [46] The ranges of parameters were applied, especially concerning inlet concentrations of reactants. It has been reported that methanol synthesis favors through CO_2 route than through CO. Langmuir-Hinshelwood type kinetic equations were also determined based on the feed taken.

A kinetic model for the synthesis of methanol over commercial catalysts based on CO and CO_2 adsorption onto various active sites of copper was developed by Park et al. [50] while by fitting 118 experimental sets of data obtained under varying conditions, the kinetic parameters were estimated. Besides, dual site adsorption additional adsorption sites for CO_2 was taken into account for determining the rate expressions and the kinetic parameters. The reaction conditions were in the range of 220 to 340 °C and 50 and 90 bar.

The kinetics of low-pressure methanol synthesis with CO, CO_2, and H_2 as starting materials were studied over a commercial $CuO/ZnO/Al_2O_3$ catalyst by Graaf et al. [44] at 15-50 bar and 210-245 °C. Methanol can be produced from both CO_2 and CO with water gas shift reaction as shown by the results. Based on these three reactions and the assumption of dual-site adsorption mechanism, 48 kinetic rate models are derived. Hydrogen is believed to be adsorbed dissociatively. Experimental data supported their assump-

Table 2: Parameter values of the kinetic model (B is given in J/mol).

Parameters		Values
k_1	A_1	1.07
	B_1	40,000
k_2	A_2	3453.38
	B_2	-
k_3	A_3	0.499
	B_3	17,197
k_4	A_4	6.62×10^{-11}
	B_4	124,119
k_5	A_5	1.22×10^{10}
	B_5	-98,084

tions.

Other different kinetic models are available based on the reactants available and the rate determining steps. This kinetics was studied for decades and the improvement in the yield and the selectivity over CO are the major factors considered. Based on the reaction kinetics the optimization processes and also the catalyst activity is studied. Presently, different metal-based catalysts are available and used for the production with so much more yet to come. Beside the availability of different catalysts, $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/ZrO_2$ are used commercially because of their high selectivity and operating performance [51].

On the basis of the analysis of literature data, both CO and CO_2 are involved in the synthesis of methanol. It could be interesting to compare the behavior of the different proposed kinetic models in their application to real-reactor modeling. In fact, the Graaf et al. and Van den Bussche and Froment rate equations are the only ones extensively used in reactor modeling [27, 44].

3.1. Kinetic expressions and constant factors

3.1.1. For Two Reaction consideration

Reactions [27] (parameter values shown in Table 2):

$CO_2 + 3H_2 \leftrightarrow CH_3OH$

$CO_2 + H_2 \leftrightarrow CO + H_2O$

$$r_{CH_3\mathrm{OH}} = \frac{k_1\ P_{CO_2}\ P_{H_2}\left(1-\ \frac{1}{K_{\mathrm{eq},1}}\ \frac{P_{H_2O}\ \ P_{CH_3\mathrm{OH}}}{P_{H_2}^3\ P_{CO_2}}\right)}{\left(1+\ k_2\ \frac{P_{H_2O}}{P_{H_2}}+\ k_3P_{H_2}^{0.5}+\ k_4P_{H_2O}\right)^3}\ \left[\frac{\mathrm{mol}}{\mathrm{Kg_{cat}}\,s}\right]$$

$$r_{\mathrm{RWGS}} = \frac{k_5\ P_{CO_2}\left(1-\ K_{\mathrm{eq},2}\ \frac{P_{H_2O}\ P_{\mathrm{CO}}}{P_{CO_2}\ P_{H_2}}\right)}{\left(1+k_2\ \frac{P_{H_2O}}{P_{H_2}}+k_3\ P_{H_2}^{0.5}+k_4\ P_{H_2O}\right)}\ \left[\frac{\mathrm{mol}}{\mathrm{Kg_{cat}}\,s}\right]$$

$$k_i = A_i\exp\left(\frac{B_i}{\mathrm{RT}}\right)$$

$$\log_{10}K_{\mathrm{eq},1} = \frac{3066}{T} - 10.592$$

$$\log_{10}K_{\mathrm{eq},2} = -\frac{2073}{T} + 2.029$$

3.1.2. For three reaction consideration

Reactions [52] (parameter values shown in Table 3):

$CO + 2H_2 \leftrightarrow CH_3OH$

$CO_2 + 3H_2 \leftrightarrow CH_3OH$

$CO_2 + H_2 \leftrightarrow CO + H_2O$

$$r_{\mathrm{CO}} = \frac{k_1\ K_{\mathrm{CO}}\left(P_{\mathrm{CO}}\ P_{H_2}^{1.5} - \frac{P_{CH_3\mathrm{OH}}}{P_{H_2}^{0.5}K_{P,A}}\right)}{\left(1+K_{\mathrm{CO}}\ P_{\mathrm{CO}}+K_{CO_2}\ P_{CO_2}\right)\left[\ P_{H_2}^{1.5}+\ \frac{K_{H_2O}}{K_{H_2}^{0.5}}\ P_{H_2O}\right]}$$

$$r_{CO_2} = \frac{k_2\ K_{CO_2}\left(P_{CO_2}\ P_{H_2}^{1.5} - \frac{P_{CH_3\mathrm{OH}}\ P_{H_2O}}{P_{H_2}^{1.5}\ K_{P,B}}\right)}{\left(1+K_{\mathrm{CO}}\ P_{\mathrm{CO}}+\ K_{CO_2}P_{CO_2}\right)\left[P_{H_2}^{1.5}+\frac{K_{H_2O}}{K_{H_2}^{0.5}}\ P_{H_2O}\right]}$$

$$r_{\mathrm{RWGS}} = \frac{k_3\ K_{CO_2}\left(P_{CO_2}P_{H_2}-\frac{P_{H_2O}\ P_{\mathrm{CO}}}{K_{P,B}}\right)}{\left(1+K_{\mathrm{CO}}\ P_{\mathrm{CO}}+K_{CO_2}\ P_{CO_2}\right)\left[\ P_{H_2}^{1.5}+\ \frac{K_{H_2O}}{K_{H_2}^{0.5}}\ P_{H_2O}\right]}$$

$$k_i = A_i\exp\left(\frac{B_i}{\mathrm{RT}}\right)$$

Table 3: Parameter values for the kinetic model (B is given in J/mol).

Parameters	A	B
k_1 (kmol s^{-1} kg^{-1} Pa)	4.0638×10^{-6}	-11,695
k_2 (kmol s^{-1} kg^{-1} Pa)	1.5188×10^{-33}	-266,010
k_3 (kmol s^{-1} kg^{-1} $Pa^{0.5}$)	9.0421×10^{8}	-112,860
$K_{P,A}$ (atm^{-2})	2.3717×10^{-13}	98,438
$K_{P,B}$ (atm^{-2})	6.6688×10^{-11}	54,499
$K_{P,C}$	2.8118×10^{2}	-43,939
K_{CO} (Pa^{-1})	8.3965×10^{-11}	118,270
K_{CO2} (Pa^{-1})	1.7214×10^{-10}	81,287
$\frac{K_{H_2O}}{K_{H_2}^{0.5}}$ ($Pa^{-1/2}$)	4.3676×10^{-12}	115,080

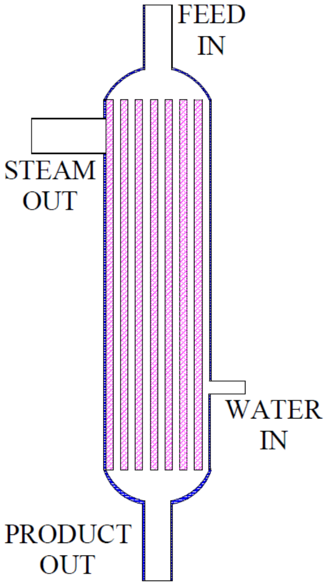

Figure 1: Linde isothermal reactor.

3.2. Reactors

The design of a reactor should consider the control of reactor temperature since the overall methanol synthesis reaction is exothermic. The generated heat has to be recovered efficiently and optimized for the economics of the process and similarly high conversion is required to minimize the cost involved in further separation processes [53]. The reactor technologies that are available fall under two categories: namely gas phase technologies and liquid phase technologies. This research is limited to the discussion of some of the gas phase technologies.

These reactors can be either adiabatic or isothermal. ICI low pressure quench converter is among the most commonly applied adiabatic reactors in the industry [54]. The operating conditions are generally 50-100 bar and 270 °C. In a single bed, there exists a $Cu/ZnO/Al_2O_3$ catalyst support and distributors to inject cooling gas into the bed at multiple locations. The fresh and recycled syngas helps for reaction temperature mitigation which is a factor in optimizing the reactor design. Kellogg, Brown and Root reactor, is another adiabatic fixed bed reactors' series. It has a cost lowering advantage because the wall thickness could be reduced to half due to the spherical shape. [55]. The Toyo Engineering Corporation (TEC) reactor, called MRF-Z® reactor allows maximum allowable reaction temperature which is maintained with optimal conversion per pass [51].

Linde isothermal reactor is suitable for both endothermic and exothermic catalytic reactions and for gas/gas, gas/liquid or liquid/liquid systems Maximum reaction rate is possible and opti-

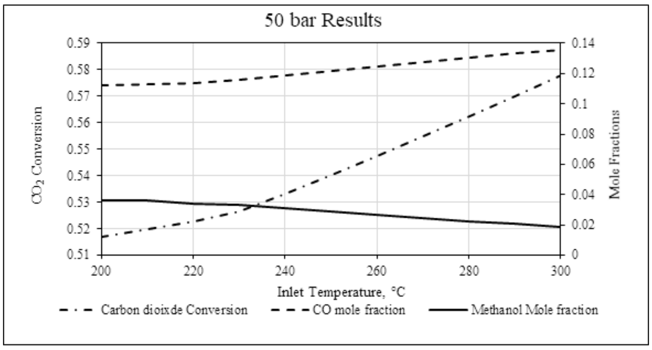

Figure 2: Comparison of CO_2 Conversion, CO and CH_3OH mole fraction involving 2 reactions versus temperature at 50 bar.

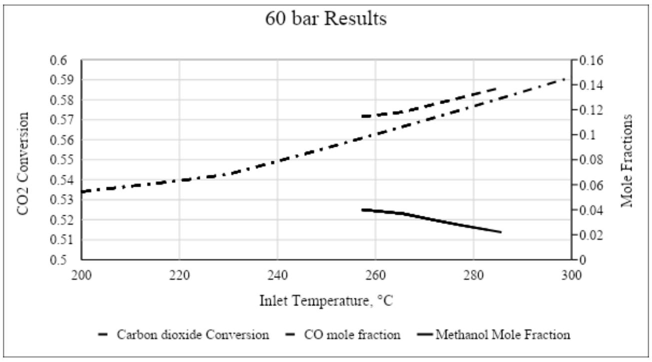

Figure 3: Comparison of CO_2 Conversion, CO and CH_3OH mole fraction involving 2 reactions versus temperature at 60 bar.

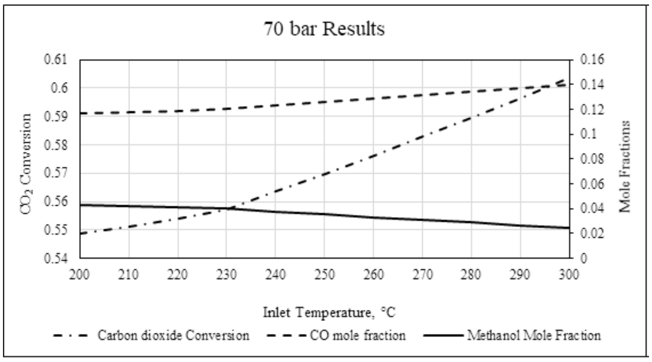

Figure 4: Comparison of CO_2 Conversion, CO and CH_3OH mole fraction involving 2 reactions versus temperature at 70 bar.

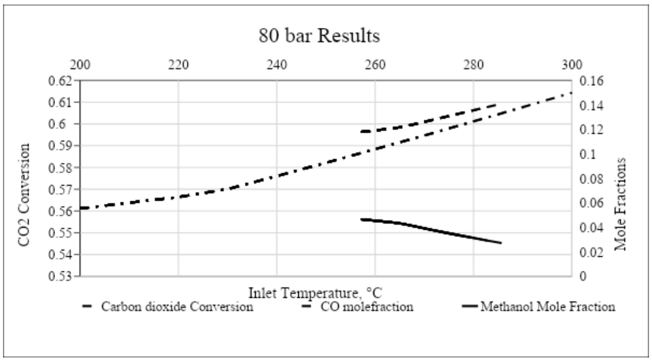

Figure 5: Comparison of CO_2 Conversion, CO and CH_3OH mole fraction involving 2 reactions versus temperature at 80 bar.

mum temperature profile can be insured by heating or cooling tubes resulting in higher productivity, along with increased catalyst life, fewer by-products, efficient reaction heat recovery and lower operating costs [51] as shown in Fig. 1. The Air Liquid converter is among the most preferred reactors for methanol production in large-scale plants and has an advantage of ensuring a tight control of the temperature profile and to help in producing high-pressure steam [56-58].

4. Results and Discussion

4.1. Equilibrium conversion results for both two and three reactions

To see the influence of varying temperature and pressure on resultant CO_2 conversion, and CO and CH_3OH mole fractions, several simulations are performed by reacting CO_2 with H_2 in an adiabatic equilibrium reactor. The feed is CO_2 and H_2 with 22:3 mass ratio. Fig. 2 to 5 are plots of CO_2 conversion along with the resulting CO and CH_3OH vapor mole fractions from an adiabatic equilibrium reactor simulated with Pro/II for varying inlet pressures and temperatures. The inlet pressure ranges from 50 bar to 80 bar with 10-bar increment and the inlet temperature from 200 °C to 300 °C with 10 °C increment.

From the comparison of the graphs of Fig. 6 through Fig. 9, it can be deduced that with the increasing temperature CO_2 conversion increased while the mole fraction of CH_3OH decreased and that of CO increased, which means that most of the CO_2 is being converted to CO rather than CH_3OH. The possible explanation for this phenomenon is that by increasing temperature the RWGS reaction producing CO is endothermic reaction and favored but the exothermic methanol formation is suppressed. It can also be seen, with comparison among the graphs, the CO_2 conversion increased with increasing pressure. Even though there is an increase in individual mole fractions of both CO and CH_3OH with the increasing pressure, the results show that the rate of CO formation is higher and dominant than methanol formation and results are unsatisfactory to be employed for the methanol production process design.

Similarly, by taking the CO to CH_3OH formation reaction into consideration, the adiabatic equilibrium simulation is performed once more and several results of CO_2 conversion, CO and CH_3OH vapor mole fractions are shown against varying temperature and pressure, with the inlet temperature from 200 °C to 300 °C with 10 °C increment and the inlet pressure ranges from 50 bar to 80 bar with 10-bar increment.

From the comparison of graphs of Fig. 6 through Fig. 9, we see that CO_2 conversion increases almost linearly with increasing temperature and pressure similarly as in previous consideration of only two reactions. It can also be seen that methanol mole fraction is higher than CO mole fraction. This is different from the previous simulation result with two reactions that CO mole fraction is

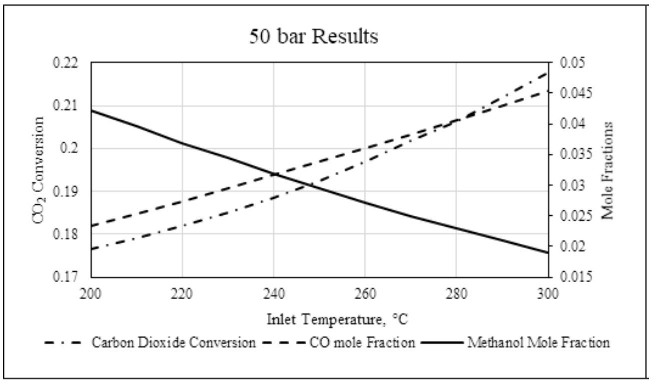

Figure 6: Comparison of CO_2 Conversion, CO and CH_3OH mole fraction involving 3 reactions versus temperature at 50 bar.

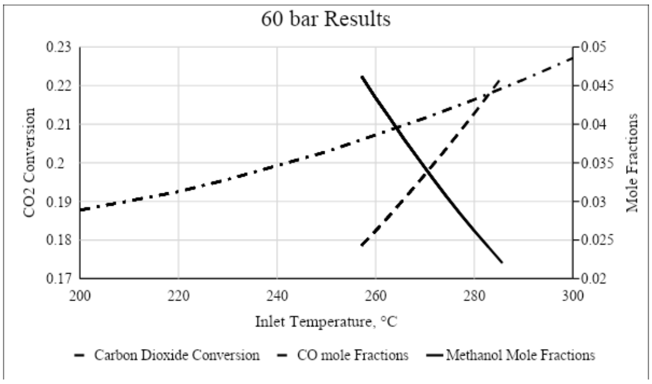

Figure 7: Comparison of CO_2 Conversion, CO and CH_3OH mole fraction involving 3 reactions versus temperature at 60 bar.

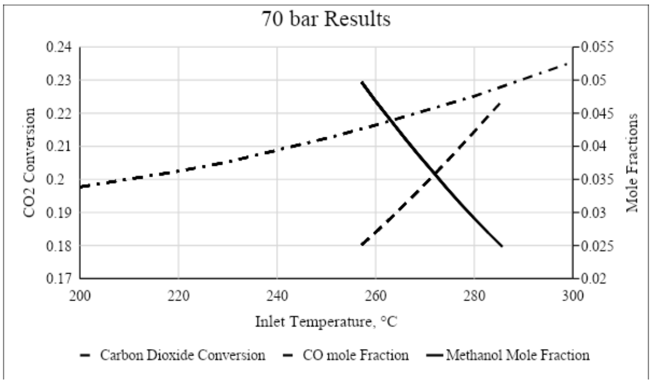

Figure 8: Comparison of CO_2 Conversion, CO and CH_3OH mole fraction involving 3 reactions versus temperature at 70 bar.

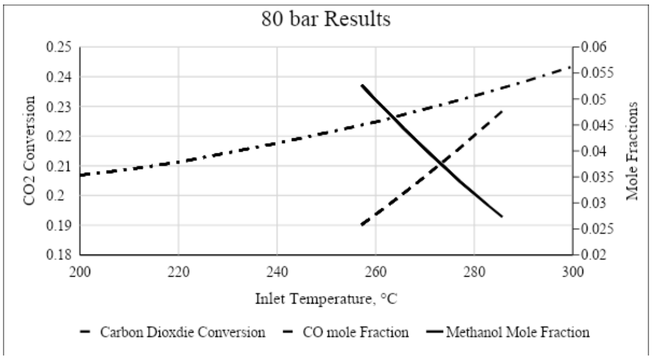

Figure 9: Comparison of CO_2 Conversion, CO and CH_3OH mole fraction involving 3 reactions versus temperature at 80 bar.

higher than that of methanol and the differences in mole fractions started to decrease with increasing temperature, decreasing the CH_3OH formation rate and increasing CO formation rate. A point is reached in each of the graphs, where CO and CH_3OH mole fractions are equal. This point shifts to the right or higher temperature as the pressure is increased. An increase in pressure increased slightly all of CO_2 conversion, CO and CH_3OH mole fractions.

Thus, the comparison between two reactions and three reactions tells that the methanol production process design is favored more by considering three reactions, yielding more methanol. Since increasing pressure had little effect on CO_2 conversion and resulting CH_3OH mole fraction, pressure may not be an important factor in the design as far as reaction equilibrium is concerned. However, there was a great influence of increasing temperature on increasing the resulting methanol mole fraction and reaction temperature was seriously taken into consideration in designing the process.

5. Process design and simulation

5.1. Flowsheet description

Streams with pure CO_2 is fed at 8800 kg/hr and at 1 bar alongside pure hydrogen at 1200 kg/hr at 30 bar, both being at 25°C (Fig. 10). Some further assumptions made for the subsequent steps include:

- Neglected pressure drop throughout the process,
- Maximum efficiency of 100 percent for all compressors, valves and flash tanks, and
- SRK with modified Huron-Vidal mixing rules (RKSMHV2) model used for estimating thermodynamic properties since the operating pressures are above 10 bar.

CO_2 is compressed to 50 bar in a series of compressors with intercooling and H_2 is compressed to 50 bar in a single stage compressor. The multi-stage compression of CO_2 is employed to minimize the power requirements. The two streams of gases are mixed in a mixer M-101 and then the mixture of the gases is heated to 513.15 K in a heat exchanger, E-104. Finally, this mixture of gases is mixed with the recycle stream inside a mixer M-102. This stream which is the mixture of original pure feed streams and the recycle stream is then injected into the fixed bed isothermal reactor R-101 where the reactions take place. For maintaining the temperature inside the reactor constant, the cooling water is used and steam is generated as a byproduct which can further be used in the heat exchanger.

A gaseous mixture of methanol, water and unreacted reactants is formed. The mixture is then cooled in a heat exchanger, E-106. The stream is then sent to a vapor liquid separator, TK-101 where the liquefied methanol and water are removed from the bottom and the uncondensed gases are passed through the top to a splitter where about 1% of the gases is removed as a purge to minimize the accumulation and the remaining gases are passed through a heat exchanger to the reactor as a recycle stream. Further a small amount of unreacted gases is still left in the liquid products drawn from the separator. A flash tank, TK-102 is used to remove the unreacted gases in the product. Before the stream enters the flash tank, two valves BV-101 and BV-102 are used to reduce the pressure to 1 bar. The residual amount of gases is removed from the top of the flash tank. Now the bottom product of the flash tank contains only methanol and water and trace amount of gases. The product is then passed to the distillation column for the separation of methanol and water. Finally, a methanol stream at 4139 kg/h with about 98.9% purity is obtained as a distillate from the distillation column.

5.2. Compressors

As the reaction takes place at 50 bar, the gases stream should also be available at 50 bar. Since CO_2 is available at 1 bar, a series of compressors with inter-stage cooling is used for the compression of CO_2 to 50 bar. The multi-stage compression was chosen to minimize total power requirements. By comparison, Hydrogen is available at a relatively higher pressure of 30 bar, and a single stage compressor is enough to compress it.

5.3. Heat Exchangers

Three heat exchangers E-101, E-102 and E-103 are used for the cooling purpose as the compression leads to the increase in temperature. Water at 25 °C is used as coolant. The reaction takes place at 240 °C. Hence, the heat exchangers E-104 and E-105 are used to heat the mixture of gases to the reaction temperature. In order to condense the mixture and separate the vapor from the liquid the mixture is cooled to around 35 °C in a heat exchanger, E-106. The boiling point of methanol is around 65 °C. So, the mixture of methanol and water from the flash tank is heated to around the boiling point of methanol which in our case it was actually heated up to 80 °C in heat exchanger E-107.

5.4. Reactor

The reactor used is a fixed bed isothermal reactor. As the pressure inside the reactor is 50 bar, the thermodynamic model used is the Redlich-Kwong-Soave equation of state with modified Huron-Vidal mixing rules (RKSMHV2). First of all, we used the model proposed by Vanden Bussche. Because this model does not account for the CO hydrogenation. We found that the yield of methanol was calculated to be extremely low, implying that CO hydrogenation is not negligible. Next, we used the model developed by Xin et al. [52] that accounts for all the three reactions (CO hydrogenation, CO_2 hydrogenation and RWGS). The kinetic expressions used are given by Lim et. al [18]. Both the kinetic and the rate expressions were discussed in the above sections. In the conventional methanol synthesis process, the catalyst used is the $Cu/ZnO/Al_2O_3$. In our case we used the catalyst developed for CO_2 hydrogenation by Xin et al., which is a fibrous Cu/Zn/Al/Zr. The pressure drop in the reactor was neglected. Cooling water is used in the reactor in order to maintain the temperature of the reactor.

5.5. Vapor Liquid Separator

The outlet stream of the reactor contains methanol, water and the unreacted gases. This stream is condensed to 35 °C in the heat exchanger E-106 and passed to a vapor liquid separator TK-101. Most of the gases are separated from the mixture of methanol and water. The gases are then passed to a splitter where about 1% of the gases are removed as a purge in order to minimize the accumulation in the reactor and the remaining gases are sent to the reactor as the recycle.

5.6. Flash Tank

Some of the residual gases still exist in the liquid stream exiting vapor liquid separator. The pressure is reduced to 1 bar using the two valves BV-102 and BV-103. Due to the depressurization, the residual gases are separated from the mixture of methanol and water in the flash tank TK-102. The operating temperature of the flash tank is 35 °C.

5.7. Distillation

A distillation column is used to purify methanol. The column was simulated using a rigorous distillation model, RADFRAC in Pro/II V.10.2. The boiling point of methanol is about 65 °C. The mixture of methanol and water is heated to 80 °C which is above the boiling point of methanol in the heat exchanger E-107 and passed to the distillation column T-101. The optimum reflux ratio and the number of plates were found to be 1.5 and 57 respectively. The column was set to have 44 rectification plates and 13 stripping plates. These optimum values were set in order to meet the desired purity. Similar work done by Van dal and Bouallau considered only CO_2 hydrogenation with RWGS reaction got a slightly higher yield of 0.67 [59]. As noted in the preceding section, there will be the simultaneous production of CO that cannot be neglected. Hence, we have considered in our simulation both CO and CO_2 hydrogenation with RWGS reaction, have got a yield of 0.47 which is slightly lower but more realistic than previous work. The obtained methanol as a distillate was about 4139 kg/h with around 98.9 % pure.

5.8. Challenges and recommendations

From the design it can be noted that as the overall methanol production yield is quite low, the process may not be cost-effective. Furthermore, large heat duties have been incurred from the heat exchanger attributing to the inclusion of recycle stream making it less economic. However, cutting of operating costs can be achieved by utilizing the steam generated as a hot byproduct from the reactor in the reboiler of the distillation column T-101 and as a hot fluid in the heat exchanger E-107. Similarly, we have assumed pure feed for the process and trace amount of gases such as H_2S, SO_2, SO_3, NOx may be present in the feed gas which may cause the deactivation of catalysts as well as corrosion to the equipment. This problem can be overcome with highly pure feed gas and other alternate catalysts.

6. Conclusion

Considering the two reactions (CO_2 hydrogenation and RWGS reaction), methanol was obtained in lesser amounts with some amount of CO that cannot be neglected than when the three reactions (CO and CO_2 hydrogenation and RWGS), was considered. The optimum temperature and pressure were found to be 240 °C and 50 bar respectively, with a series of simulations done in Pro/II V.10.2. Hence, the kinetic model involving the three sets of reactions favored the yield of methanol which was used in our simulation. The processing units were optimized in order to obtain around 99 % pure methanol. The process was run with and without the recycle and we found the yield to be higher with the inclusion of recycle. The recycle stream was used with the purge of about 1% to minimize the accumulation in the reaction loop. The processing units were optimized and the methanol so obtained was 4139 kg/h (overall yield of 0.47) with 99 % purity.

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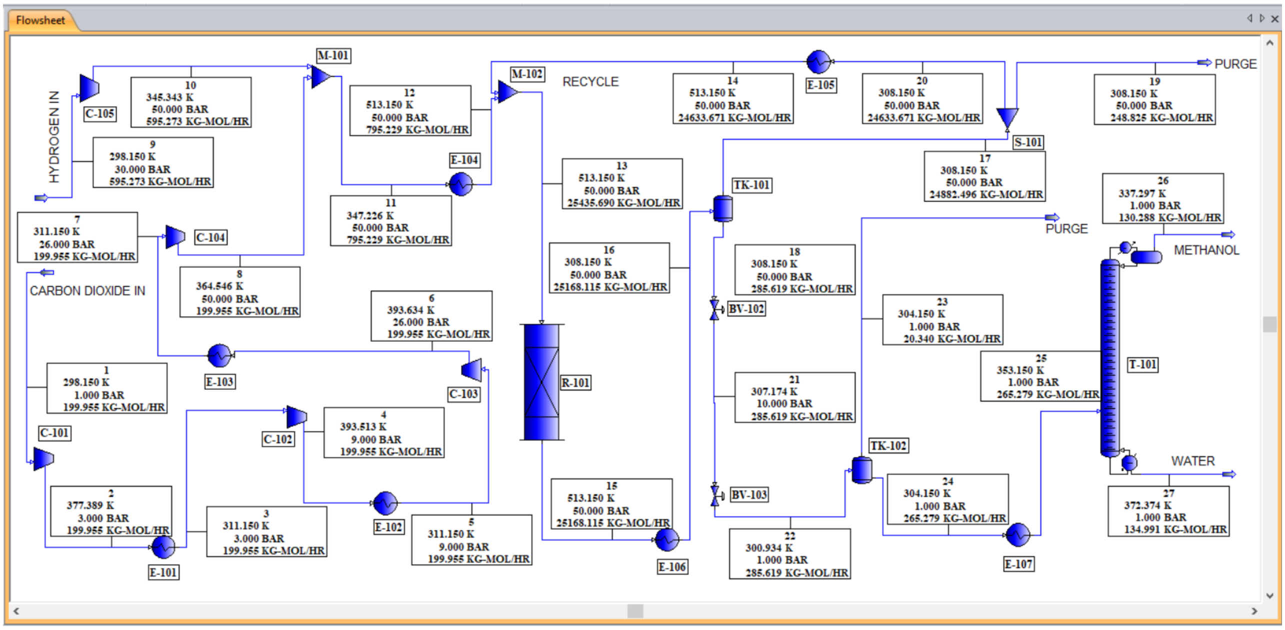

Figure 10: Process Flow Diagram for methanol production by carbon dioxide and carbon monoxide hydrogenation.

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