

Direct CO₂ Hydrogenation Under Supercritical Conditions Using Proper Solvent Simulation

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Abstract

Methanol synthesis via direct CO₂ hydrogenation has potential to contribute to the limitation of worldwide CO₂ emissions; the main obstacle of this process is thermodynamics limitation, where it shows low conversion less than 40% for single stage pass. The direct hydrogenation of CO₂ under supercritical conditions in presence and absence of proper solvents were simulated. The effect of different hydrocarbon solvents as supercritical media (n-hexane, n-heptane, n-pentane) on the CO₂ conversion and the operating conditions including the mole fraction of solvent, temperature and pressure were simulated using the Aspen Hysys V3.2 software using the Gibbs reactor model, Soave-Redlich-Kwong equation of state for non-ideal gas mixture at high pressure was considered. The conversions of CO₂/H₂ mixtures under supercritical condition approximate (8MPa total pressure) and 430-530K to methanol is assisted by the presence and absence of amounts of hydrocarbon solvents (mole fraction 0.1 - 0.6). The results showed that the addition of proper solvents such as n-hexane, n-heptane and n-pentane could improve the CO₂ conversion greatly under supercritical conditions. Where the single stage conversion can be 82.32 mol% with 0.2 mole fraction of n-heptanes solvent, n-hexane at CO₂:H₂: n-heptane 1:3:2. N-heptanes, n-hexane, n-pentane have given probably the same effect at temperature below 460K and pressure 8Mpa. However, at temperatures below 460K, the addition of n-heptane with CO₂:H₂: n-heptane ratios were 1:5:2 improves the CO₂ conversion, where the CO₂ conversion was 99.98%. The addition of mixed n-hexane with n-heptanes with mole fraction of 0.4:0.1 respectively will be favourable for the CO₂ conversion.

Keywords: CO₂ hydrogenation; methanol synthesis; supercritical conditions.

1. Introduction

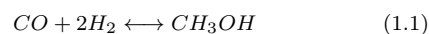
Methanol (MeOH) is a primary liquid petrochemical and it is a liquid energy-carrier, which is an excellent alternative fuel, and it can be blended with gasoline, moreover, it can be used in fuel cells [1]. It is considered as one of the most important chemical feedstocks used in industry due to the ease in its storage and transportation with world demand of approximately 50 Million Metric ton per year (MMTA), and the world demand is expected to reach 137MMTA in 2022 [2].

Methanol can be synthesized by two processes, the first process is the conventional process so called

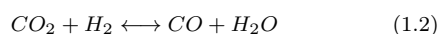
(low-pressure process), which operates at 50-100 atm and 220 - 250 °C. Almost all the methanol plants built after year 1967 operate at the low-pressure process [3].

The primary feedstock in this process is synthesis gas – a mixture of CO, CO₂ and hydrogen, in this route steam methane reforming produces a mixture of CO, CO₂ and H₂ then syngas is converted to methanol using CuO/ZnO/Al₂O₃ catalyst where three overall reactions [4].

Methanol decomposition:



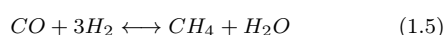
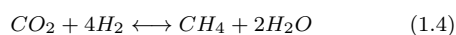
Water gas shift:



Methanol steam reforming:



Methanol synthesis from both CO_2 (Equation 1.3) and CO (Equation 1.1) is mildly exothermic reactions, the main obstacle reaction in synthesis process is Methanol steam reforming (MSR) refers to the inverse of reaction 1.3 and the inverse of reaction 1.1 which are an undesired side reaction. The slightly endothermic reverse water-gas shift (RWGS) reaction (Equation 1.2) occurs as a side reaction to methanol synthesis and MSR [4]. In addition to reactions 1.1, 1.2 and 1.3, other two reactions may occur:



Reactions 1.4 and 1.5 indicate that methane formation are also the main obstacle limiting the production of methanol [5].

According to Le Chatelier's principle, CO_2 hydrogenation to methanol is thermodynamically an exothermic process. It is favored at low temperature and high-pressure conditions. However, methanol production is in competition with CO formation via the reverse water gas shift reaction (RWGS), Thus to pick the proper operating conditions we need to know just how this equilibrium constant behaves as a function of its inputs. On the other hand, the resulting high temperature enhances the deteriorating effect of equilibrium conversion, resulting in the net methanol production decreasing [6].

The second process is the hydrogenation of CO_2 , which considered as new and as a green chemical process because it uses CO_2 as raw material which contributing to the mitigation of CO_2 , the major man made greenhouse gas causing of global warming. This process serve as an alternative carbon source to fossil fuels, if a renewable source of hydrogen is available, environmentally benign only if this process utilizes CO_2 more than that produced in H_2 manufacturing [7].

However, this process can be divided into two different process, one-step or tow step process. In one-step conversion, process the CO_2 directly converted to methanol without a preliminary reduction to CO where as in two step conversion CO_2 is first converted into CO through Reverse water gas shift reaction (RWGSR) (the opposite of Equation 1.2) then CO is converted into CO_2 . Tow step process

subjected to many studies, where concluded that it has higher yield than one-step process. However, gas feeds for industrial methanol synthesis usually contain both CO and CO_2 . Which carbon oxides serve, as the primary source for methanol formation, has been arguably the most important question pertaining to the reaction mechanism. Early work by Klier and co-workers assumed that CO was the primary source. However, Klier's model predicted a zero rate of methanol production in the absence of CO_2 [8].

In the 1980's experiments conducted by Razovskii and later by Chinchén et al. involving the use of ^{14}CO or $^{14}CO_2$ tracers in methanol synthesis from $CO_2/CO/H_2$ mixtures over commercial catalysts proved conclusively that CO_2 was the primary methanol source [9]. In addition, there are few previous works describing the reaction pathway of methanol from syngas using Cu/ZnO catalyst, where the methanol production were promoted even at low CO_2 concentration in $CO/CO_2/H_2$ mixtures. Furthermore, they found that the CO_2 hydrogenation rate was much lower than the CO hydrogenation rate, and this affected methanol production [10].

In another study to address the origin of the methanol, competitive tracer experiments were performed with CO_2/CO mixtures. Where, the rates of CO versus CO_2 hydrogenation under commercial conditions (500-550K and 50 bar total pressure) on commercial Cu/ZnO catalysts, the results showed that CO_2 is the preferred reactant [11].

However, the main obstacle to methanol synthesis from CO rich streams is thermodynamics. The a one-pass methanol yield of nearly 40% can be obtained at 525K, while pure CO_2 would only yield 18%. For this reason, many efforts now is being put on CO_2 direct conversion to methanol using useful strategy of CO_2 utilization and a practical approach to sustainable development to overcome the thermodynamic limitation through many suggestions [12].

Firstly, operating at lower temperatures, but operating at lower temperatures an option that requires catalysts that are more active or by implementing higher recycle ratios, or product extraction option that requires higher capital investment [13].

Second effort to overcome this limitation is through innovative reactor design. These design considerations involve efficient product removal without excessive recycling of feed gases. Third strategy involves using high boiling hydrocarbon oil solvents

under supercritical conditions, the methanol and water can be separated from the solvents upon cooling whereby the solvents is recycled back into the reactor [13]. Where in experimental study in china by (Jianguo et, al. 2001) that carried out on the synthesis reaction under supercritical state for CO₂ hydrogenation in two-step process. Results showed that, under supercritical conditions, the CO₂ equilibrium conversion is improved and the heat and mass transfer coefficient enhanced greatly and the single stage conversion can be greater than 90% (mol). The reaction was operated at temperature around 473-483K and pressure of 8.5MPa with n-hexane as solvent and the favored solvent fraction was 0.2-0.3 [14].

In this paper the direct hydrogenation of CO₂ (one-step process) under supercritical conditions in presence and absence of proper solvents as supercritical media were simulated, the super critical properties of reaction material listed in (Table 1.1). The effects of different solvents as supercritical media (n-hexane, n-heptane, n-pentane) on the CO₂ equilibrium conversion and the operating conditions including the mole fraction of solvent, temperature and pressure were considered and simulated. The reaction was operated at temperature around 430-530K and pressure of 8MPa.

Table 1.1: Critical temperature and pressure of reactant material

gas	T _c , K	P _c , MPa
H ₂	33.18	1.313
CO ₂	304.19	7.382
H ₂ O	647.13	22.055
CH ₃ OH	512.58	8.096

2. Methodology

The direct hydrogenation of CO₂ under supercritical conditions in presence and absence of proper solvents will be simulated where; the effect of Different hydrocarbon solvents as supercritical media (n-hexane, n-heptane, n-pentane) on the CO₂ conversion and the operating conditions including the mole fraction of solvent, temperature and pressure will be simulated using the Aspen Hysys V3.2 software. Thermodynamic analysis performed using the Gibbs reactor model (RGibbs) available in the HYSYS3.2. RGibbs models simultaneous phase and

chemical equilibrium minimizing the Gibbs free energy and does not require the specification of the reactions involved and their stoichiometric.

The Soave Redlich kwong (SRK) equation of state has extensively used in calculating phase and reaction equilibrium and it gives good agreement with experiment, so it was used to calculating the reaction equilibrium at high pressure and to correct the non-ideality of the gas mixture, Carbon dioxide equilibrium conversion (Equation 1.3) (XCO₂ %) was determined by:

$$X_{CO_2} \% = \frac{F_{(CO_2)in} - F_{(CO_2)out}}{F_{(CO_2)in}} \times 100 \quad (2.1)$$

Where, F stands for the molar flow rate at the inlet (in) or outlet (out) of the CO₂ in Gibbs reactor.

3. Results and discussion

Methanol synthesis is a volume-reduced as well as an exothermic reaction the CO₂ equilibrium conversion will decrease with the temperature and increase with pressure with the addition of a solvent there will be tow factors that affect the CO₂ conversion simultaneously which will discuss in next paragraphs: the dilution effect and solvent type effect.

3.1. Effects of supercritical Media

The effects of supercritical media on the equilibrium CO₂ conversion has been investigated, where, several hydrocarbon solvents including, n-pentane, n-hexane, and n- heptanes were added into the reactant mixtures of methanol synthesis based on CO₂ direct hydrogenation, with different ratio. As shown in Figure 3.1. CO₂:H₂: solvent ratio is 1:3:2 where used the CO₂ equilibrium conversion change with temperature in the absence and in presence of solvents at supercritical pressure 8MPa.

The CO₂ equilibrium conversions can be enhanced greatly by the addition of three types of solvents examined, and compared with the case in the absence of solvent, the addition of n-hexane, n-heptane, n-pentane has a strong effect on the CO₂ equilibrium conversions in the range of temperature examined (430 to 530K) as inlet stream temperature. Where the n-heptane has the strongest effect at a temperature 430K, however, the CO₂ conversion is a little bit lower for both of n-hexane and n-pentane. As a result, The CO₂ equilibrium conversions were increased approximately by 4 times in present of n-heptane compared with no solvent at critical pressure and temperature. However, the ratio changed

to $\text{CO}_2:\text{H}_2$: solvent as 1:5:2 where the simulation results shown in Figure 3.2. At 8MPa and 430K, all types of solvent examined were given the highest conversion about 99.24, 99.88, 99.98 for n-pentane, n-hexane, n-heptane respectively. However, as the ratio of H_2 in feed increased, the conversion enhanced greatly, but on the other hand; the unreacted components must be separated and recycled into the reactor as well as the solvents, which increase the operating cost.

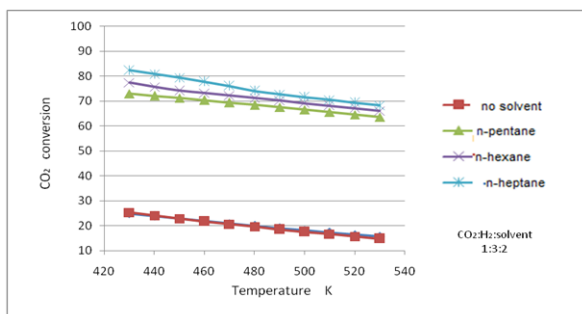


Figure 3.1: CO_2 equilibrium conversion versus temperature using different solvents at reaction pressure 8 MPa ($\text{CO}_2:\text{H}_2$: solvent 1:3:2)

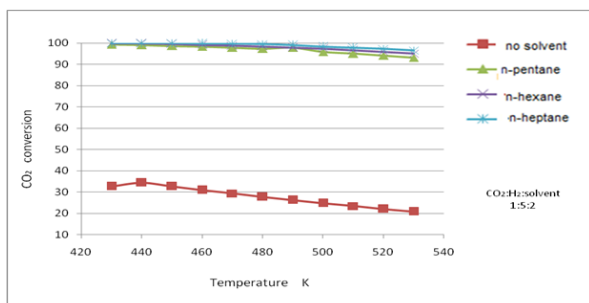


Figure 3.2: CO_2 equilibrium conversion versus temperature using different solvents at reaction pressure 8 MPa ($\text{CO}_2:\text{H}_2$: solvent 1:5:2)

3.2. Effects of solvent concentrations

To examine the effects of solvent concentration, different amounts of n-heptane with a mole fraction of 0.1, 0.2, 0.4, and 0.6 were added into reactant mixture while the H_2/CO_2 ratio was fixed at 1:3 and the pressure is set as 8MPa. As shown in Figure 3.3, at a temperature below 460K, the addition of n-heptane with a mole fraction of 0.1, 0.2, improves the CO_2 Equilibrium conversion higher than 0.4 and 0.6 mole fractions and the solvents effect dominates the reaction. At higher temperature, the

more solvent is added the more rapidly the CO_2 equilibrium conversion decreases. Therefore, it can be concluded that the addition of n-heptane with a mole fraction of 0.1-0.2 will be favorable for the CO_2 equilibrium conversion at temperature below 460K.

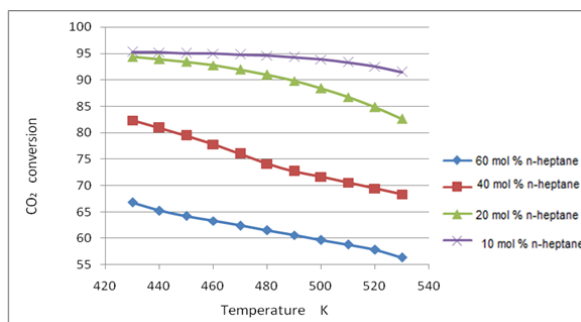


Figure 3.3: Effects of heptane concentration (mole fraction in feed) as a solvent on CO_2 equilibrium conversion at reaction pressure 8MPa.

3.3. Effects of temperature and pressure

Conversion of CO_2 decrease with temperature increase, But reaction rate will be low at low temperature. Considering these two opposite aspects, the reaction was done in a temperature near that of critical temperature. In the presence of n-heptane in the feed with mole fraction of 0.2, the CO_2 equilibrium conversion at different temperatures and pressure are shown in Figure 3.4. It can be seen that the CO_2 equilibrium conversion decreases with temperature and increasing with pressure. There is a clear result of higher equilibrium conversion at temperature Between 430 to 460K when the pressure is equal to supercritical pressure 8Mpa or higher using less mole fraction of n-heptane, which provides a suitable zone for carrying out the synthesis reaction.

3.4. Effects of the mixed solvent

The effects of mixed solvent (n-hexane and n-heptane) concentrations on the equilibrium CO_2 conversion were also investigated. As shown in Figure 3.5. The CO_2 equilibrium conversion can be enhanced by the addition of a mixed solvent of n-hexane and n-heptane. Different results were obtained by varying the mole fraction of mixed solvents that have been added. The best mole fraction in this study was 0.4 n-hexane and 0.1 n-heptane, however, when 0.1 of n-heptane and 0.1 of n-hexane was used it gives less conversion improvement and an opposite

of using pure n-heptane and for this reason, the thermodynamic studies for the mixtures is needed.

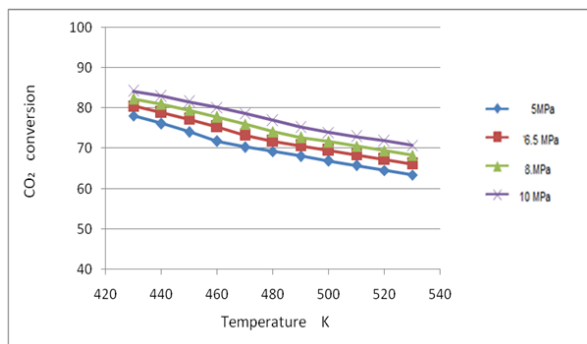


Figure 3.4: Effects of temperature on the CO₂ conversion at different pressure with n-heptane as a solvent and CO₂:H₂: n-heptane: 1:3:2

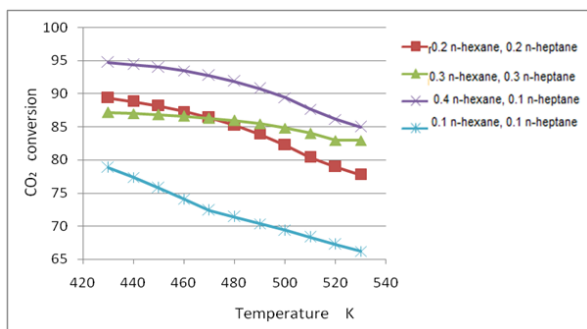


Figure 3.5: Effect of mixed solvents (n-hexane + n-heptane) mole fraction in feed on CO₂ conversion, the reaction pressure 8MPa and CO₂:H₂: solvent: 1:3:2

4. Conclusion

The system of methanol synthesis based direct CO₂ hydrogenation described by the SRK equation of state, and the CO₂ equilibrium conversions in the presence/absence of solvents at different temperatures and different pressures is simulated. The results showed that the addition of proper solvents such as n-hexane and n-heptane could improve the CO₂ conversions greatly under supercritical conditions. When using n-heptane only, the favorite solvent fraction is 0.1-0.2, the optimum temperature is in the range of 430-460K and the pressure 8MPa or above. It can be drawn from the work that the operating condition with the addition of 10-20 mole percentage n-hexane or n-heptane, at temperature be-

tween 430-460K and pressure 8MPa or above will be suitable for the methanol synthesis by direct CO₂ hydrogenation.

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