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Thermodynamic Analysis of Methanol Synthesis *via* CO₂ Hydrogenation Reaction

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Abstract

The most inspiring opportunity to reduce greenhouse gas emissions is direct hydrogenation of CO₂ into a commodity of products, which is also an appealing choice for generating renewable energy. CO₂ hydrogenation can yield methanol which has a broad range of applications. In the present study, a thermodynamic feasibility analysis of the CO₂ hydrogenation reaction is carried out using the Aspen Plus tool. CO₂ hydrogenation to methanol, reverse-water-gas-shift (RWGS), and methanol decomposition reactions were considered in this analysis. The effect of different parameters such as temperature (ranging from 50 to 500 °C), pressures (ranging from 1 bar to 50 bar), and CO₂:H₂ molar ratio (ranging from 1:3 to 1:20) on methanol yield has been investigated. The Aspen predicted data is compared with the fixed-bed reactor experimental data. High pressure and low-temperature conditions are found to be the favourable option for a higher value of methanol yield. The CO₂ conversion and CH₃OH selectivity are favourable when the H₂/CO₂ molar ratio is greater than 3. A substantial gap between the Aspen predicted equilibrium conversion of CO₂ and the experimental value of CO₂ conversion is observed in the study.

Keywords: CO₂ hydrogenation, Methanol synthesis, Aspen simulation, Equilibrium analysis.

1. Introduction

The growing trend of global warming, the declining trend of fossil fuel reserves, and the need for an alternative to fossil fuels are the most critical challenges of the twenty-first century. CO₂ levels in the atmosphere have already exceeded the pre-industrial era by about 280 ppm and now reached 410 ppm (Li et al. 2018; Chen et al. 2021). In this context, scientists and researchers concentrated on two key technologies: carbon capture and storage (CCS) (Atsonios et al. 2016) and carbon capture and utilization (CCU) (Han et al. 2021). For reducing CO₂ concentrations in the atmosphere, the CCU has begun to emerge as a more appealing alternative than CCS (Sha et al. 2020). When considering CCU, CO₂ hydrogenation pathways have become essential for producing useful chemicals such as syngas (CO₂, CO, and H₂), methane (CH₄), methanol (CH₃OH), ethanol (C₂H₅OH), dimethyl ether (CH₃OCH₃), and formic acid (CH₂O₂) (Leonzio et al. 2019; Sharma et al. 2021). Methanol synthesis from CO₂ hydrogenation receives increasing emphasis than other commodities due to its environmental friendliness, lack of toxic emissions when burned, and other uses (Din et al. 2019; Salehi et al. 2021). Methanol is used as a solvent and a raw material to produce a wide range of chemicals (Dalena et al. 2018; Cai et al. 2020; Zhong et al. 2020). The mission is to minimize the CO₂ concentration, reduce Carbon emissions, and fulfil the requirement for the chemicals listed above.

The synthesis of methanol from CO₂ using Cu, Ag, Au, and Pd-based heterogeneous catalysts has also been studied by a group of scientists and experts. Witoon et al. (2013) studied the CO₂ hydrogenation to methanol using Cu/ZnO catalyst at 180 °C and 20 bar. Their results revealed that the CH₃OH selectivity is 98%, whereas CO₂ conversion is only 5%. Rui et al. (2020) investigated the *in-situ* characterizations using time-resolved X-ray diffraction, ambient-pressure X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy using Au/In₂O₃ catalyst. Due to the gold-indium oxide strong metal-support interactions and the dispersion of gold, their investigation demonstrated that methanol selectivity reaches 100% at 225 °C temperature and 50 bar pressure, but CO₂ conversion is only 1.3%. In another study, it is observed that Ce⁺³ ions increased the oxygen-vacant sites of the PdZn/CeO₂ catalyst, resulting in 100% methanol selectivity and 7.7% CO₂ conversion at 220 °C and 30 bar (Malik et al. 2018). Many scientists have performed experimental investigations on the hydrogenation of CO₂ for methanol synthesis using different catalysts for a wide range of pressure. Surprisingly, in many articles, nearly 100% methanol selectivity has been reported, but all of them experienced poor (<15%) CO₂ conversion. Therefore, the design of highly efficient, high-stability, and low-cost catalysts are immediately required to enable the CO₂ conversion for large-scale production. The thermodynamic analysis of any reactive system can anticipate the feasibility of the maximum amount of desired products and the optimum conditions required to obtain the desired yield. Therefore, understanding the thermodynamic aspects of the methanol synthesis reactions is essential for the strategic development of the catalytic CO₂ hydrogenation process.

In the present study, the thermodynamic feasibility of CO₂ hydrogenation into CH₃OH, RWGS, and CH₃OH decomposition reactions was investigated. The effects of various parameters such as temperature, pressure, and feed composition on CO₂ conversion and methanol selectivity have been examined. Furthermore, the simulated data has been elaborated with figures and charts to understand the optimum operating conditions for a specific conversion and selectivity. Also, the Aspen predicted data is compared with the experimental data obtained from various literature.

2. Methodology

The Gibbs free energy minimization approach can precisely define the equilibrium composition of a reaction system. The overall Gibbs free energy (G) of the system is minimum at equilibrium. The equilibrium reactor model (REquil) in Aspen Plus software was used in the present work. The Peng-Robinson equation of state (PENG-ROB EOS) model was considered to introduce non-ideal behaviour in the Gibbs energy values (Miguel et al. 2015). In order to obtain a better understanding of the concept of hydrogenation of CO₂ into methanol, we focused on three possible reactions, namely methanol synthesis from CO₂ hydrogenation (Eq. 1), RWGS (Eq. 2), and CH₃OH decomposition (Eq. 3).

The following expressions (Eq. 4-7) are used to define the CO₂ conversion, methanol selectivity and yield, and CO selectivity.

$$\text{Conversion of CO}_2 (\%) = \left[1 - \frac{F_{\text{CO}_2, \text{out}}}{F_{\text{CO}_2, \text{in}}} \right] \times 100 \quad (\text{Eq. 4})$$

$$\text{Selectivity of CH}_3\text{OH} (\%) = \left[\frac{F_{\text{CH}_3\text{OH}, \text{out}}}{F_{\text{CH}_3\text{OH}, \text{out}} + F_{\text{CO}, \text{out}}} \right] \times 100 \quad (\text{Eq. 5})$$

$$\text{Yield of CH}_3\text{OH} (\%) = \left[\frac{F_{\text{CH}_3\text{OH}, \text{out}}}{F_{\text{CO}_2, \text{in}}} \right] \times 100 \quad (\text{Eq. 6})$$

$$\text{Selectivity of CO} (\%) = \left[\frac{F_{\text{CO}, \text{out}}}{F_{\text{CH}_3\text{OH}, \text{out}} + F_{\text{CO}, \text{out}}} \right] \times 100 \quad (\text{Eq. 7})$$

where $F_{i, \text{in}}$ and $F_{i, \text{out}}$ ($i = \text{CO}_2, \text{CO}, \text{CH}_3\text{OH}$) is the reactor inlet and outlet molar flowrates of species 'i', respectively. All thermodynamic simulations are carried out under isothermal conditions. The results are shown in terms of CO₂ conversion, CH₃OH yield, and selectivity of both CH₃OH and CO for specific reaction conditions.

3. Results and Discussion

3.1. Effect of temperature on enthalpy, entropy, and Gibbs free energy change:

The shift in Gibbs free energy governs the spontaneity of a chemical reaction. Fig. 1(a-c) shows the effect of temperature in enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) change of the CO₂ hydrogenation, RWGS, and CH₃OH decomposition reactions under 1 bar pressure. As observed in Fig. 1(a) and Fig. 1(b), the ΔH and ΔS values for CO₂ hydrogenation reaction are less than zero as the temperature rises from 25 °C to 500 °C. This signifies that the CO₂ hydrogenation to methanol reaction is exothermic and decreases the randomness. In contrast, the ΔH and ΔS values for both the RWGS and CH₃OH decomposition reactions are greater than zero with temperature. This implies that the RWGS and CH₃OH decomposition reactions are endothermic with increasing molecular disorder. As shown in Fig. 1(c), the ΔG for methanol synthesis reaction has greater than zero and increases with temperature, which means this reaction is favourable at lower

temperatures. The ΔG for the RWGS reaction has positive values and decreases with temperature, implying this reaction is favourable at higher temperatures.

On the other hand, the ΔG for methanol decomposition reaction has positive values with decreasing trend up to 130 °C. This suggests that the methanol decomposition starts or favourable from 130 °C. Therefore, the CO_2 hydrogenation to CH_3OH reaction is exothermic and spontaneous at lower temperatures. In contrast, the RWGS and methanol decomposition reactions are endothermic and spontaneous at higher temperatures.

Fig. 1: Effect of temperature on (a) ΔH , (b) ΔS , and (c) ΔG for CO_2 hydrogenation, RWGS, and CH_3OH decomposition reactions under 1 bar pressure.

3.2. Influence of temperature and pressure on CO_2 conversion and CH_3OH selectivity:

According to Le Chatelier's principle and thermodynamic feasibility, higher pressure and lower temperature seem to be favourable conditions for higher methanol selectivity (Eq. 1). RWGS and methanol decomposition reactions are also limited under these conditions due to their endothermic nature. Hence, high pressures and low temperatures can be the optimum operating conditions to improve methanol selectivity and, at the same time to reduce CO selectivity. The impact of temperature and pressure on CO_2 conversion, CH_3OH selectivity, and CO selectivity was examined, and the outcomes are shown in Fig. 2(a-c).

The plots show that the equilibrium conversion of CO_2 is regulated by both temperature and pressure. As the temperature rises, the methanol formation reaction becomes less favoured, and the RWGS and methanol decomposition reactions become more favoured, resulting in U-shaped curves in the CO_2 conversion patterns. Increased pressure enhances CO_2 conversion in the low-temperature zone (e.g., 50 °C to 300 °C). However, at high temperatures (between 300 °C and 500 °C), increasing pressure has almost no influence on CO_2 conversion,

and this is why the CO₂ conversion curves eventually converged at these temperatures. The methanol synthesis reaction is improved by rising pressure, whereas the RWGS and methanol decomposition reactions are mostly unchanged. This fact illustrates that, as pressure rises, both the CH₃OH and CO selectivity curves shift to extremely high temperatures. Several scientists have confirmed this phenomenon by employing various reaction schemes and the Soave-Redlich-Kwong equation of state (Stangeland et al. 2018; Ahmad and Upadhyayula 2019).

Fig. 2: Effect of pressure and temperature on (a) CO₂ conversion, (b) CH₃OH selectivity, and (c) CO selectivity, for H₂/CO₂ mole value of 3.

The effect of pressure on the optimum value of operating temperature and CO₂ conversion to achieve 99% CH₃OH and 1% CO selectivity is concluded in Fig. 3. When the pressure rises from 1 bar to 50 bars, the CO₂ conversion is noticeable, i.e., from 13% to 48%. Hence, the optimum value of operating parameters to obtain 99% methanol selectivity and 48% CO₂ conversion is about 172 °C and 50 bar for the H₂/CO₂ molar value of 3.

Fig. 3: Effect of pressure on CO₂ conversion and reactor temperature to achieve 99% CH₃OH selectivity for H₂/CO₂ molar value of 3.

3.3. Influence of feed gas composition on CO₂ conversion and CH₃OH selectivity:

To investigate the influence of feed composition on CH₃OH selectivity, the CO₂:H₂ molar ratio was varied between 1:3 to 1:20 for a fixed value of 50 bar pressure. The simulation was performed for a temperature range between 150 °C to 400 °C, and the results are shown in Fig. 4(a-c). The plot shows that the increase of H₂ partial pressure promotes both CO₂ conversion and CH₃OH selectivity. The methanol formation from CO₂ decreased as the temperature increased, and consequently, the CO₂ consumption diminishes. As a result, the observed increase in CO₂ conversion at higher temperatures suggests that extra H₂ promotes the RWGS reaction. As the CO₂:H₂ ratio was increased from 1:3 to 1:12, the most significant change in CO₂ conversion occurs. Further increase of CO₂:H₂ ratio from 1:13 to 1:17, there seems to be a lower improvement of CO₂ conversions. From 1:18 to 1:20, almost similar conversions were obtained.

Fig. 5 depicts the influence of feed gas composition on CO₂ conversion and optimum temperature to obtain 99% CH₃OH and 1% CO selectivity under 50 bar reactor pressure. The simulation shows the CO₂ conversion improved from 48% to 87% when the CO₂:H₂ molar ratio increased from 1:3 to 1:20. About 87% CO₂ conversion and 99% methanol selectivity can be achievable at 187 °C under 50 bar pressure and a CO₂:H₂ ratio of 1:20. Though the boosting of H₂ partial pressure in the feed promotes the conversion of CO₂, it has a detrimental impact on the process economics.

Fig. 4: Effect of $\text{CO}_2\text{:H}_2$ molar ratio on (a) CO_2 conversion, (b) CH_3OH selectivity, and (c) CO selectivity at 50 bar reactor pressure.

Fig. 5: Effect of $\text{CO}_2\text{:H}_2$ molar ratio on CO_2 conversion and desired temperature to achieve 99% CH_3OH selectivity under 50 bar reactor pressure.

4. Comparison of CO₂ conversion and CH₃OH selectivity between simulation predicted and experimental results

For a similar range of reactor temperature, pressure, and feed gas composition conditions, the simulation predicted and experimental results for CO₂ conversion are shown in Fig. 6. The experimental findings are reported in the presence of Au/In₂O₃ (Rui et al. 2020) and Cu/ZnO/Al₂O₃ (Gaikwad et al. 2016) catalysts. The simulation results obtained from the present investigation are comparable and match well with the simulation data reported by Stangeland et al. (2018). However, a substantial gap between the theoretical and experimental values of CO₂ conversion is noted. The equilibrium CO₂ conversion and experimental CO₂ conversions (over Au/In₂O₃ and Cu/ZnO/Al₂O₃ catalysts) show more deviation at lower temperatures. However, the gap reduces gradually with the increase of reactor temperature. The lower value of CO₂ conversion in the presence of catalysts can be related to the weak activity of the catalysts.

We further compared the equilibrium CH₃OH selectivity data with experimental CH₃OH selectivity results, as shown in Fig.7. The Cu/ZnO/Al₂O₃ catalyst shows a significant deviation from the equilibrium CH₃OH selectivity, whereas the gap is much less for the Au/In₂O₃ catalyst. The methanol selectivity of the Au/In₂O₃ catalyst is greater than the equilibrium CH₃OH selectivity and which may be due to the presence of Au^{δ+}-In₂O_{3-x} interfacial sites in the Au/In₂O₃ catalyst. A summary of literature data on CO₂ conversion, CH₃OH selectivity is shown in Table 1, along with the present simulation results.

Fig. 6: Comparison of theoretical and experimental CO₂ conversion for CO₂: H₂ molar ratio of 1:3.

Fig. 7: Comparison of theoretical and experimental CH₃OH selectivity for CO₂: H₂ molar ratio of 1:3.

Table 1: A comparison between the simulation and experimental findings on CO₂ conversion and CH₃OH selectivity for the methanol synthesis via CO₂ hydrogenation.

Catalyst	CO ₂ :H ₂ ratio	T _R (°C)	P _R (bar)	X _{CO2} (%)	S _{MeOH} (%)	Reference
PdZn/CeO ₂	1:3	220	30	7.7	100	(Malik et al. 2018)
Au/In ₂ O ₃	1:3	225	50	1.3	100	(Rui et al. 2020)
Pd-Zn/CNTs	1:3	250	30	6.3	99	(Liang et al. 2009)
Cu/ZnO	1:3	180	20	5	98	(Witoon et al. 2013)
Cu/ZnO/Al ₂ O ₃	1:3	240	46	20	40	(Gaikwad et al. 2016)
Cu/ZnO/Al ₂ O ₃	1:3	170	50	25	73	(Liu et al. 2007)
-	1:3	200	50	39	98	Stangeland et al. (2018)
-	1:3	250	50	28	68	Stangeland et al. (2018)
-	1:3	172	50	48	99	Present work
-	1:3	250	50	28	72	Present work
-	1:10	184	50	77	99	Present work
-	1:10	250	50	51	80	Present work
-	1:20	187	50	87	99	Present work

where, T_R = Reaction temperature; P_R = Reaction pressure; X_{CO2} = CO₂ conversion, S_{MeOH} = Methanol selectivity.

5. Conclusions

A comprehensive and detailed thermodynamic investigation of CO₂ conversion to methanol is presented in this study. Based on the thermodynamic feasibility findings, the methanol decomposition reaction has a higher endothermicity than the RWGS reaction, while methanol production from CO₂ is an exothermic reaction. The methanol decomposition reaction has a greater entropy change with temperature than the methanol and RWGS

reactions. Due to more negative changes in Gibbs free energy, the methanol decomposition reaction is more spontaneous at higher temperatures. In the methanol synthesis, the effect of various critical parameters such as pressure, temperature, feed gas composition on CO₂ conversion, and methanol selectivity is investigated. Low temperature, high pressure, and a high CO₂:H₂ feed ratio are found to be favourable conditions to facilitate methanol production from CO₂ and H₂. The CO₂ conversion is prominent at a 1:3 CO₂:H₂ feed gas molar ratio if the pressure builds up from 1 bar to 50 bar, i.e., from 13% to 48%. At 50 bar pressure, the CO₂ conversion improved from 48% to 87% with the increase of CO₂:H₂ mole ratio from 1:3 to 1:20. However, methanol synthesis at higher (> H₂:CO₂ mole ratio of 5) H₂ partial pressure may not be economically viable. The gap in CO₂ conversion between the simulation predicted and experimental data may be due to the insufficient activity of the catalyst. Therefore, to enhance the CO₂ conversion and CH₃OH selectivity, developing a highly efficient, thermally and chemically stable, and low-cost catalyst is essential.

Declarations:

Ethics approval and consent to participate: ‘Not applicable’

Consent for publication: ‘Not applicable’

Availability of data and materials: very few data have been extracted from published articles for comparison purpose, and same has been mentioned in the manuscript with proper reference.

Conflict of interest statement: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Authors' contributions: SK: Conceptualization, Investigation, Data generation, Writing-original draft; SAS: Conceptualization, Methodology, Result validation; SPD: Resources, Data validation; CC: Project administration; SR: Project administration, data validation; SD: Conceptualization, Supervision, result validation, Writing- review and editing; ‘All authors read and approved the final manuscript.’

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