Simulation of CO\textsubscript{2} Conversion into Methanol in Fixed-bed Reactors: Comparison of Isothermal and Adiabatic Configurations

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Abstract

CO\textsubscript{2} capture and utilization (CCU) has been widely considered as a potential solution to overcome global warming. Conversion of CO\textsubscript{2} into methanol is an interesting option to transform waste into value-added chemical while also reducing greenhouse gases emissions in the atmosphere. In this paper, utilization of CO\textsubscript{2} into methanol was simulated using Aspen Plus software. The reaction between CO\textsubscript{2} and H\textsubscript{2} to produce methanol and water was carried out in a simulated fixed-bed reactor with Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} commercial catalyst, following LHHW (Langmuir – Hinshelwood – Hougen – Watson) kinetic model. Isothermal and adiabatic reactor configurations were compared under similar feed conditions and the concentration profile along the reactor was observed. The result showed that isothermal configuration converted 3.23\% more CO\textsubscript{2} and provided 16.34\% higher methanol yield compared to the adiabatic reactor. Feed inlet temperature variation was applied and the effect to methanol production on both configurations was studied. The highest methanol yield for adiabatic and isothermal reactor was obtained at 200 °C and 240 °C respectively.

Keywords: Aspen Plus simulation; carbon capture and utilization; CO\textsubscript{2} hydrogenation; methanol reactor

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INTRODUCTION

The awareness of global warming issue has driven rigorous mitigation actions worldwide. Evidences suggested that CO\textsubscript{2} gives over 60\% contributions to global warming due to its huge emission which exceeds 30 Gt a year (IEA, 2012). Copenhagen Accord has requested that by 2100, the global temperature raise should be limited to 2 °C above pre-industrial level (Huang and Tan, 2014). According to IEA (2012), the 2 °C target can be achieved given that the atmospheric CO\textsubscript{2} concentration is kept at 450 ppm, which means that 43 Gt of CO\textsubscript{2} should be reduced. Mitigation strategies have been implemented to reach this goal, including energy efficiency improvement, utilization of low-carbon fuels, and replacement of fossil fuel with renewable energy sources (Leung et al., 2014). However, the majority of
the world is still predicted to depend on fossil fuels for the next couple of decades (Kenarsari et al., 2013).

Carbon capture and storage (CCS) is often considered as a potential solution for reducing CO₂ emissions while fossil fuel is still utilized as the main energy source. This technology involves capturing CO₂ from the large point emission sources and injecting it to underground and ocean storage. According to Haszeldine (2009), CCS has the potential to reduce 20% of world energy emissions in the future. However, public concern regarding the safety of the storage sites has shifted the attention to CO₂ utilization instead of storage. CO₂ capture and utilization (CCU) is increasingly becoming more popular as it also gives additional value to the captured CO₂ (Huang and Tan, 2014).

Among the various CO₂ utilization pathways, CO₂ conversion into methanol is an interesting option which produces a chemical with wide application in industries. Methanol is conventionally produced from synthesis gas (a mixture of CO, CO₂, and H₂) via catalytic conversion. Most of synthesis gas produced today comes from natural gas, making conventional methanol production another fossil fuel dependent process. According to Van-Dal and Bouallou (2013), around 29 to 33 GJ of natural gas is consumed to produce one metric ton of methanol. This number can be significantly reduced by switching to the captured CO₂ from carbon capture technology.

Methanol is characterized by its excellent combustion properties, making it a strong candidate for alternative vehicles fuel. Although the energy density is only half compared to that of gasoline, it produces less pollution compared to conventional fossil fuels (Van-Dal and Bouallou, 2013). Methanol can be used as an additive to gasoline or in its pure form, although the latter one possesses a toxicity hazard which restricts its use as vehicle fuel. Another scenario is to dehydrate methanol, producing DME (dimethyl ether) that can be used to substitute conventional diesel. Therefore, conversion of captured CO₂ into methanol will allow CO₂ recycle, reduce the amount of CO₂ released to the atmosphere, and cut down the amount of fossil fuel consumption in the future.

According to Chen et al. (2011), one of the key parts in methanol production is the methanol synthesis reactor. The reactors existing in conventional methanol production plants generally can be classified into adiabatic and isothermal reactor. This paper intends to explore the performance of CO₂ conversion into methanol in both reactor types under similar feed condition. Aspen Plus software was employed to simulate the reactors, where the captured CO₂ is reacted with hydrogen to produce methanol. The concentration profile along the reactor was observed, and the feed inlet temperature was varied to determine its effect on methanol production.

Even though commercial methanol production has been established since early 1900s, methanol generation from captured CO₂ is still relative new in the field. Several studies have discussed about CO₂ hydrogenation into methanol in catalytic reactors (Van der Ham et al., 2012; Tidona et al., 2013, Milani et al., 2015). However, none of them provided a comparison between different reactor configurations. This study provides new information by comparing adiabatic and isothermal reactor configurations in methanol production from CO₂.

### RESEARCH METHOD

The reaction between CO₂ and H₂ to produce methanol was carried out in a simulated fixed-bed reactor with Cu/ZnO/Al₂O₃ catalyst. The rate equation follows LHHW (Langmuir – Hinshelwood – Hougen – Watson) kinetic model including three independent reactions occurring in parallel:

\[
\text{CO}_2(g) + 2\text{H}_2(g) \leftrightarrow \text{CH}_3\text{OH}(l) \quad \Delta H = -128 \text{ kJ/mol (298 K)}
\]  
\[
\text{CO}_2(g) + 3\text{H}_2(g) \leftrightarrow \text{CH}_3\text{OH}(l) + \text{H}_2\text{O}(g) \quad \Delta H = -87 \text{ kJ/mol (298 K)}
\]  
\[
\text{CO}_2(g) + \text{H}_2(g) \leftrightarrow \text{CO} + \text{H}_2\text{O}(g) \quad \Delta H = +41 \text{ kJ/mol (298 K)}
\]

Reaction (1) and (2) are exothermic reactions which produce methanol, while reaction (3) is endothermic Reverse Water Gas Shift (RWGS) reaction. Aspen Plus software requires kinetic equations to be arranged in certain form. For this reason, Van Dal and Bouallou (2013) has proposed a kinetic model for reactions (1) to (3) and calculated the parameters which match Aspen Plus specifications. The kinetic rate equations are shown in equation (4) and (5), and the kinetic parameters are displayed in Table 1.

\[
T_{CH3OH} = \frac{k_5 \text{P}_{\text{CO}_2} \text{P}_{\text{H}_2} - k_4 \text{P}_{\text{H}_2\text{O}} \text{P}_{\text{CH}_3\text{OH}} \text{P}_{\text{H}_2}^{-2}}{(1 + k_2 \text{P}_{\text{H}_2\text{O}} \text{P}_{\text{H}_2}^{-1} + k_3 \text{P}_{\text{H}_2}^{0.5} + k_4 \text{P}_{\text{H}_2O}^{3})}
\]

\[
T_{RWGS} = \frac{k_5 \text{P}_{\text{CO}_2} - k_2 \text{P}_{\text{H}_2\text{O}} \text{P}_{\text{CO}} \text{P}_{\text{H}_2}^{-1}}{1 + k_2 \text{P}_{\text{H}_2\text{O}} \text{P}_{\text{H}_2}^{-1} + k_3 \text{P}_{\text{H}_2}^{2/3} + k_4 \text{P}_{\text{H}_2O}}
\]

\[
\ln k_i = A_i + \frac{b_i}{T}
\]

| Parameters | Value |
|------------|-------|
| k₁         | A₁    | -29.87 |
|            | B₁    | 4,811.2 |
| k₂         | A₂    | 8,147 |
|            | B₂    | 0 |
| k₃         | A₃    | -6,452 |
|            | B₃    | 2,068.4 |
| k₄         | A₄    | -34.95 |
|            | B₄    | 14,928.9 |
| k₅         | A₅    | 4,804 |
|            | B₅    | -11,797.5 |
| k₆         | A₆    | 17.55 |
|            | B₆    | -2,249.8 |
| k₇         | A₇    | 0.1310 |
|            | B₇    | -7,023.5 |

Table 1. Parameters of the LHHW Kinetic Model (Van Dal and Bouallou, 2013)
Table 2. Properties of the feed stream

| Properties          | Value         |
|---------------------|---------------|
| Mass flow (kg/s)    | 2.8 x 10^-5   |
| Pressure (bar)      | 50            |
| Temperature (°C)    | 220           |
| Composition (% molar) |            |
| CO                  | 4.00          |
| CO₂                 | 3.00          |
| H₂O                 | 0.00          |
| Methanol            | 0.00          |
| H₂                  | 82.00         |
| Argon               | 11.00         |

Table 3. Properties of the catalyst

| Catalyst | Density (kg/m³) | Fixed bed porosity | Mass (g) |
|----------|-----------------|--------------------|----------|
|          | 1775            | 0.5                | 34.8     |

Table 4. Reactor configuration

| Reactor Configuration | Tube diameter (m) | Length (m) |
|-----------------------|-------------------|------------|
|                       | 0.016             | 0.15       |

Properties of the feed stream, catalyst, and reactor configurations are displayed in Table 2, 3, and 4 respectively (Van Dal and Bouallou, 2013). These data was based on their adiabatic reactor simulation, which then becomes the base case simulation in this study. The results obtained from our base case simulation were compared to Van Dal and Bouallou’s result in order to ensure validity of our simulation.

The validated model was then employed to simulate isothermal reactor configuration using similar feed, catalyst, and reactor condition. The obtained result was analysed in comparison with the base case adiabatic reactor. Lastly, temperature variation was simulated on both adiabatic and isothermal configurations by changing the feed temperature entering the reactors.

RESULTS AND DISCUSSIONS

This study conducted reactor simulations by employing reaction conditions and rate equation similar to the previous work by Van Dal and Bouallou (2013). Therefore, the first thing to check was the validity of the simulation result compared to their work. Figure 1, which describes molar fractions of the species in the adiabatic reactor, shows a strong resemblance with the profile obtained by Van Dal and Bouallou. This indicates the validity of the model used this study, and confirms that it can be used for other simulations of the methanol reactor.

The molar fractions of CO₂, CO, H₂O, and methanol as the reaction progresses along the adiabatic reactor are plotted on Figure 1. The graph shows a steep increase of methanol molar fraction at the first 0.02 m of the reactor. However, the methanol molar fraction levels off at the remaining length of the reactor, indicating that the reactions no longer produce methanol at this point. To explain this drop of methanol production, it should be noted that methanol is generated via reversible exothermic reaction (1) and (2), which benefits from low temperature. High temperature shifts the equilibrium to the left, therefore promoting deformation of the methanol. A quick check at the temperature profile (Figure 2) shows a significant temperature rise at the beginning of the adiabatic reactor, caused by the heat released from the exothermic reactions. In adiabatic configuration, this released heat accumulates inside the reactor, as there is no cooling system available to take the heat out of the reactor. Consequently, the temperature increase inhibits the exothermic reactions and eventually suppresses the methanol production. As the exothermic reaction dwindles, the heat production decreases, causing the temperature to level off as illustrated on Figure 2.

In contrary to the adiabatic trends, the methanol molar fraction consistently increases through the length of the isothermal reactor (Figure 3), which is an advantage of having constant temperature along the reactor. The constant temperature can be achieved by providing a cooling system which takes out the heat produced from the exothermic reaction, keeping the temperature constant. This maintains the reaction equilibrium in favour of the methanol production, eventually leading to a higher methanol yield at the end of the isothermal reactor. The methanol concentration...
is 16.34% higher and CO₂ conversion being 3.23% more compared to those of adiabatic reactor. This result demonstrates the advantage of using isothermal configuration for CO₂ conversion to methanol. It is also worth noting that methanol production in isothermal reactor does not level off until the end of the reactor length, indicating possibility of obtaining even higher methanol yield when the length of the reactor is added.

According to Chen et al. (2011), temperature profile is a significant factor contributing to the operation of methanol synthesis reactor. Among other factors that can influence the temperature profile, inlet feed temperature is considerably easy to modify. Therefore, the effect of inlet feed temperature on methanol production was also observed in this study. Temperature variation of 200, 220, 240, and 260 °C was employed on the adiabatic and isothermal reactors, resulting in Figure 4 and Figure 5 respectively.

Figure 4 shows how feed temperature affects methanol production in the adiabatic reactor. It clearly indicates that as the feed temperature goes up, the methanol production decreases, and the reaction rate levels off at shorter reactor length. In this case, similar explanation as the previous simulation applies: high temperature inhibits the exothermic reaction. As the adiabatic configuration does not take out any heat produced in the reaction, a higher feed temperature means even higher temperature along the reactor, shifting the equilibrium even more to the left side and causing methanol production to diminish faster. This theory is confirmed by the adiabatic temperature profile as shown on Figure 5, where the reactor temperature reaches above 260 °C for all feed temperature variation.

In the isothermal reactor, as displayed on Figure 6, the effect of the temperature rise is quite the opposite: although high temperature shifts the methanol production equilibrium to the left, it is compensated by the promotion of methanol production rate. Moreover, the reaction equilibrium can be maintained along the reactor as the cooling system keeps the temperature constant. The overall result is the higher methanol molar fraction as the feed temperature is increased. This explanation applies for feed temperature of 200, 220, and 240 °C. However, when the feed temperature is increased to 260 °C, the higher reaction rate can no longer compensate the shifted equilibrium, causing the methanol production to drop.

In summary, the effect of feed inlet temperature on methanol molar fraction is presented on Figure 7. The highest methanol production was obtained using isothermal reactor at feed temperature of 240 °C. At the lowest feed temperature of 200 °C, methanol production in adiabatic reactor is higher than isothermal reactor; however it decreases as the feed
temperature is raised. On the other hand, the isothermal reactor tends to produce higher methanol concentration as the temperature increases, except for feed temperature of 260 °C where it has exceeded the optimal temperature.

CONCLUSIONS

Conversion of CO₂ to methanol inside fixed-bed catalytic reactor was studied using Aspen Plus commercial simulator. The reaction is catalysed by Cu/ZnO/Al₂O₃ and follows LHHW (Langmuir – Hinshelwood – Hougen – Watson) kinetic model. Both isothermal and adiabatic reactors were simulated and the outputs were compared. Overall result demonstrates that isothermal reactor generally produces higher methanol yield, up to 16.34% more compared to the adiabatic reactor. The higher methanol yield is a result of having constant temperature along the isothermal reactor. Temperature variation was employed on both configurations, resulting in highest methanol yield at 200 °C and 240 °C for adiabatic and isothermal reactor respectively.

Nomenclature

| Symbols | Parameters | Units |
|---------|------------|-------|
| rᵢ      | Rate of reaction related to component i | kmol kg⁻¹ cat⁻¹ s⁻¹ |
| kᵢ      | Reaction rate constant | |
| Aᵢ      | Kinetic rate constant | |
| Bᵢ      | Kinetic model constant | J/mol |
| Pᵢ      | Partial pressure of component i | kPa |
| T       | Temperature | K |

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