Simulation of CO_2 Conversion into Methanol in Fixed-bed Reactors: Comparison of Isothermal and Adiabatic Configurations

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Abstract

CO_2 capture and utilization (CCU) has been widely considered as a potential solution to overcome global warming. Conversion of CO_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_2 into methanol was simulated using Aspen Plus software. The reaction between CO_2 and H_2 to produce methanol and water was carried out in a simulated fixed-bed reactor with $Cu/ZnO/Al_2O_3$ 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_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.

INTRODUCTION

The awareness of global warming issue has driven rigorous mitigation actions worldwide. Evidences suggested that CO_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_2 concentration is kept at 450 ppm, which means that 43 Gt of CO_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 CO_2 emissions while fossil fuel is still utilized as the main energy source. This technology involves capturing CO_2 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 CO_2 utilization instead of storage. CO_2 capture and utilization (CCU) is increasingly becoming more popular as it also gives additional value to the captured CO_2 (Huang and Tan, 2014).

Among the various CO_2 utilization pathways, CO_2 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, CO_2, and H_2) 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 CO_2 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 CO_2 into methanol will allow CO_2 recycle, reduce the amount of CO_2 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 CO_2 conversion into methanol in both reactor types under similar feed condition. Aspen Plus software was employed to simulate the reactors, where the captured CO_2 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 CO_2 is still relative new in the field. Several studies have discussed about CO_2 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 CO_2.

RESEARCH METHOD

The reaction between CO_2 and H_2 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:

$$CO_{(g)} + 2H_{2(g)} \leftrightarrow CH_3OH_{(l)}$$
$$\Delta H = -128 \text{ kJ/mol (298 K)} \qquad (1)$$

$$CO_{2(g)} + 3H_{2(g)} \leftrightarrow CH_3OH_{(l)} + H_2O_{(g)}$$
$$\Delta H = -87 \text{ kJ/mol (298 K)} \qquad (2)$$

$$CO_{2(g)} + H_{2(g)} \leftrightarrow CO_{(g)} + H_2O_{(g)}$$
$$\Delta H = +41 \text{ kJ/mol (298 K)} \qquad (3)$$
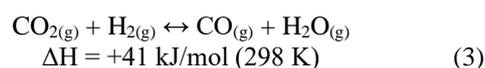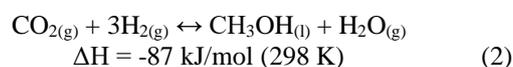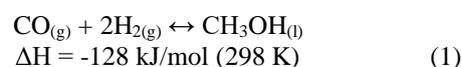
Reaction (1) and (2) are exothermic reactions which produce methanol, while reaction (3) is endothermic Reverse Water Gas Shift (RWGS) reaction. Aspen Plus software requires kinetic equations to be arranged in certain form. For this reason, Van Dal and Bouallou (2013) has proposed a kinetic model for 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.

$$r_{CH3OH} = \frac{k_1 P_{CO2} P_{H2} - k_6 P_{H2O} P_{CH3OH} P_{H2}^{-2}}{(1 + k_2 P_{H2O} P_{H2}^{-1} + k_3 P_{H2}^{0.5} + k_4 P_{H2O})^3} \qquad (4)$$

$$r_{RWGS} = \frac{k_5 P_{CO2} - k_7 P_{H2O} P_{CO} P_{H2}^{-1}}{1 + k_2 P_{H2O} P_{H2}^{-1} + k_3 P_{H2}^{0.5} + k_4 P_{H2O}} \qquad (5)$$

$$\ln k_i = A_i + \frac{B_i}{T} \qquad (6)$$

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

Parameters		Value
k_1	A_1	-29.87
	B_1	4,811.2
k_2	A_2	8.147
	B_2	0
k_3	A_3	-6.452
	B_3	2,068.4
k_4	A_4	-34.95
	B_4	14,928.9
k_5	A_5	4.804
	B_5	-11,797.5
k_6	A_6	17.55
	B_6	-2,249.8
k_7	A_7	0.1310
	B_7	-7,023.5

Table 2. Properties of the feed stream

Properties	Value
Mass flow (kg/s)	2.8×10^{-5}
Pressure (bar)	50
Temperature (°C)	220
Composition (% molar)	
CO	4.00
CO_2	3.00
H_2O	0.00
Methanol	0.00
H_2	82.00
Argon	11.00

Table 3. Properties of the catalyst

Catalyst	
Density (kg/m^3)	1775
Fixed bed porosity	0.5
Mass (g)	34.8

Table 4. Reactor configuration

Reactor Configuration	
Tube diameter (m)	0.016
Length (m)	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 CO_2, CO, H_2O, 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
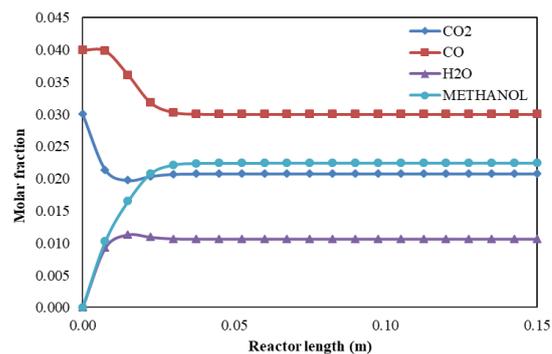
Figure 1. Molar Fraction of Reactants and Products along Adiabatic Reactor

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
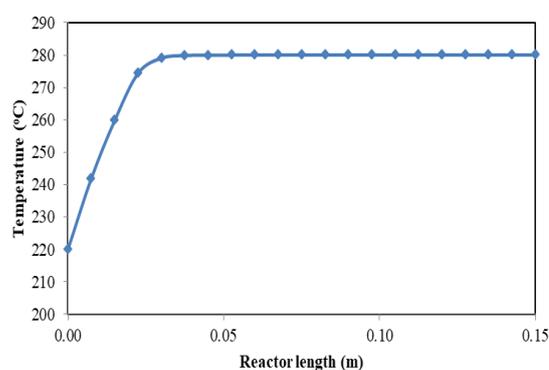
Figure 2. Temperature Profile along Adiabatic Reactor
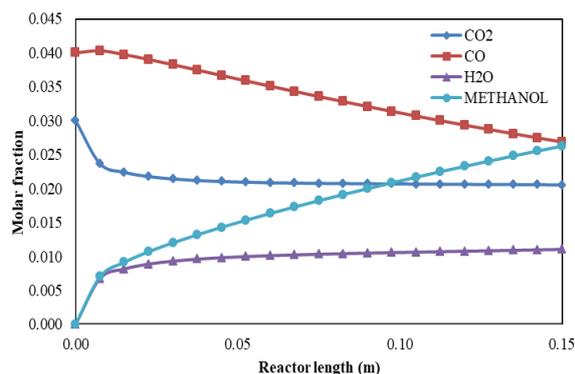
Figure 3. Molar Fraction of Reactants and Products along Isothermal Reactor

is 16.34% higher and CO_2 conversion being 3.23% more compared to those of adiabatic reactor. This result demonstrates the advantage of using isothermal configuration for CO_2 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 ℃ 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,
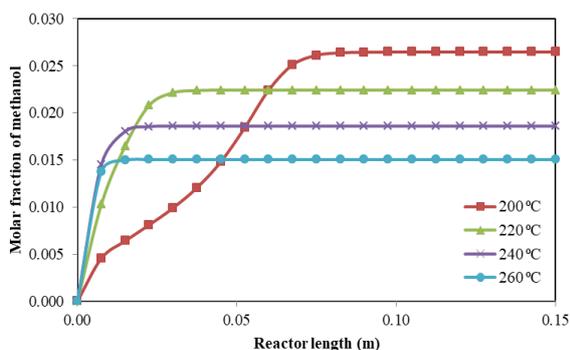
' Figure 4. Feed Temperature Effect on Methanol Production in Adiabatic Reactor
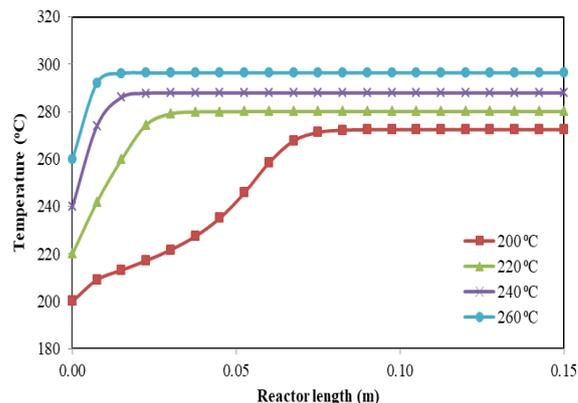
Figure 5. Feed Temperature Effect on Temperature Profile in Adiabatic Reactor

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 ℃ 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 ℃. However, when the feed temperature is increased to 260 ℃, 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 ℃. At the lowest feed temperature of 200 ℃, methanol production in adiabatic reactor is higher than isothermal reactor; however it decreases as the feed
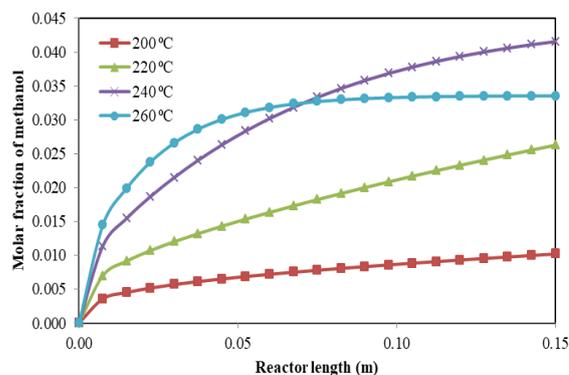
Figure 6. Feed Temperature Effect on Methanol Production in Isothermal Reactor
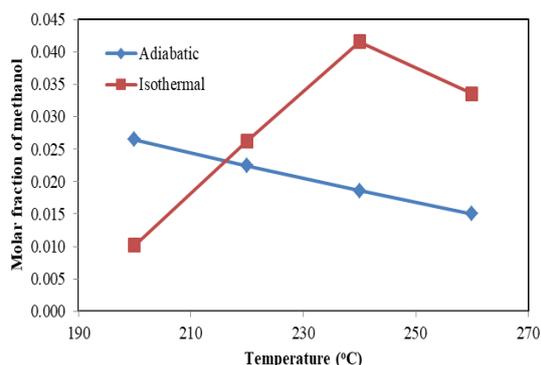
Figure 7. Feed Temperature Effect on Methanol Production in Adiabatic and Isothermal Reactor

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 CO_2 to methanol inside fixed-bed catalytic reactor was studied using Aspen Plus commercial simulator. The reaction is catalysed by $Cu/ZnO/Al_2O_3$ 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
r_i	Rate of reaction related to component i	$kmol\ kg_{cat}^{-1}\ s^{-1}$
k_i	Reaction rate constant	
A_i	Kinetic model constant	
B_i	Kinetic model constant	J/mol
P_i	Partial pressure of component i	kPa
T	Temperature	K

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