Simulation and experiment study of dimethyl ether synthesis from syngas in a fluidized-bed reactor

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Abstract

As syngas to dimethyl ether (DME) reaction is highly exothermic and the catalyst temperature window is very narrow, fluidized-bed reactor is an ideal candidate as it is highly effective both in heat and mass transfer. In this paper, a new mechanism and kinetics model for DME synthesis are established and a laboratory fluidized-bed reactor is set up. Experiments are carried out to assess the performance of DME synthesis in this reactor. The experimental results show that CO conversion and DME productivity are higher than those of fixed bed or slurry reactor. Two two-phase models are used to simulate DME synthesis in the lab fluidized-bed reactor with the bubble phase assumed to be in plug flow, and the dense phase in plug flow (P–P model) and in fully back-mixed flow (P–M model). Comparison between calculated and experimental results shows P–M is more valid than P–P model, and then influences of different parameters on reactor performance are investigated based on P–M model.

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1. Introduction

Dimethyl ether (DME), as a multi-source, multi-purpose product, has received growing attention considering global environment pollution and energy supply problem today. DME can be produced from syngas, which is from natural gas, coal or biomass. DME has wide applications, such as LPG substitute, transportation fuel, propellant, chemical feedstock and fuel cell fuel (Ng et al., 1999).

Been identified as a potential diesel and cooking fuel, DME has many excellent characteristics. It has an oxygen concentration of 34.78% and can be burned without soot emission, while for traditional diesel fuels, one cannot expect simultaneous NOx and soot emission control target. It has a boiling point of −25 °C, which is 20 °C higher than LPG and can be liquidized at 0.54 MPa (20°C). Therefore, based on the matured technology of LPG application, there does not exist any problem for the storage, transportation and usage of DME.

At present, DME is commercially prepared by dehydration of methanol using acidic porous catalysts such as zeolites, silica–alumina, alumina, etc. It has been reported that using syngas as a starting material, DME can be prepared in a one-step process, which is more thermodynamically and economically favorable than the two-step process of syngas to methanol and further to DME.

Three reactions take place in the syngas-to-DME process, namely,

Methanol synthesis reaction

$$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$$

$$\Delta H = -56.33 \text{kJ/mol}$$ (1)

Methanol dehydration reaction

$$2\text{CH}_3\text{OH} \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$$

$$\Delta H = -21.255 \text{kJ/mol}$$ (2)
Water gas shift reaction
\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2 \]
\[\Delta H = -40.9 \text{ kJ/mol}\] (3)

Overall reaction
\[3\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{CO}_2\]
\[\Delta H = -256.615 \text{ kJ/mol}\] (4)

Reactions (1) and (3) are catalyzed by a methanol synthesis catalyst (Cu/ZnO/Al\textsubscript{2}O\textsubscript{3}) and Reaction (2) by an acidic catalyst (e.g. HZSM-5). These three reactions form a synergistic system yielding higher syngas conversion or greater productivity when compared to the syngas-to-methanol process. The synergy works in the following manner: methanol, which would otherwise be near its equilibrium value, is consumed by Reaction (2), and water formed by Reactions (2) and (1) is consumed by Reaction (3), while Reaction (3) generates hydrogen which improves Reaction (1).

All the three reactions are reversible and exothermic. Moreover, the catalyst for Reactions (1) and (3) is subject to severe deactivation when overheated to above 270°C. To avoid thermodynamic limitations and excessive catalyst deactivation, conventional gas-phase reactors must be operated at a low per-pass conversion to maintain reactor temperature below 270°C, implementing a high-syngas recycle rate, and resulting in large capital investments and operating costs. In addition, in order to avoid serious pressure drop, the diameter of catalyst particles in fixed-bed reactor is usually over 4 mm, which brings a certain inner mass-transfer resistance.

Manufacture of DME in one step in slurry reactor was proposed by Air Product and Chemicals, Inc. (Brown et al., 1991). This kind of reactor can provide not only an efficient heat management, but also a very high mass-transfer resistance, as an extra liquid phase is added. This is demonstrated by the experimental results reported by Du et al. (1993) and Guo et al. (2000), where the apparent activity energies of methanol synthesis by CO hydrogenation and methanol dehydration reactions have been determined as 102.4 and 99.8 kJ/mol in a gas-phase fixed-bed reactor, and as 14.1 and 23.5 kJ/mol in a slurry reactor, respectively, thus implying a considerable inter-phase mass-transfer resistance.

The fluidized-bed reactor is proposed as an ideal reactor for the DME synthesis (Xiao and Lu, 2002). Compared with the slurry reactor and fixed-bed reactor, the gas–solid mass-transfer resistance in a fluidized-bed reactor is so small that it can be neglected, and excellent temperature control is also achievable due to the vigorous mixing of catalyst particles in the bed. Simulation of fluidized-bed reactor for DME synthesis has been performed by Lu et al. (2003) using P–P model, which shows the great advantage of fluidized-bed over fixed-bed or slurry reactor.

In this paper, a laboratory fluidized-bed reactor, 0.026 m in diameter and 2 m high, is established. Experiments are carried out to assess the performance of DME synthesis in the fluidized-bed reactor, and results show that CO conversion and DME productivity are better compared with those in a fixed bed or slurry reactor. Then a two-phase model is used to simulate DME synthesis in a fluidized-bed reactor, and simulation results are compared with those from experiments. Finally, the influences of different factors, such as pressure, temperature, H\textsubscript{2}/CO ratio in feed gas and space velocity are simulated and analyzed.

2. Catalyst and kinetics

The selected catalyst is Cu–ZnO–Al\textsubscript{2}O\textsubscript{3}/HZSM-5, manufactured by co-precipitation deposition method with the component for methanol synthesis, Cu–ZnO–Al\textsubscript{2}O\textsubscript{3}, and that for methanol dehydration, HZSM-5. Fig. 1 shows the activity of Cu–ZnO–Al\textsubscript{2}O\textsubscript{3}/HZSM-5 at different temperatures in a lab fixed-bed reactor. The optimum ratio of the two components is about 5.0 for Cu–ZnO–Al\textsubscript{2}O\textsubscript{3}/HZSM-5 catalyst.

According to the recent analytical results by XPS and XAES method (Li, 2004), the main active center for methanol synthesis on this catalyst is Cu(0), which was proposed to be Cu clusters (Nakatsuji and Hu, 2000), but not Cu atom. The key intermediate of the methanol synthesis, which is formed from the CO\textsubscript{2} and Cu–Cu clusters, is supposed to be the ring-type ester. This kind of ester also has the structure of two C–O bonds observed by others (Neophytides et al., 1992), and can be hydrogenated more easily than formate species, although formate is usually assumed to be the key intermediate (Bussche and Froment, 1996). Water gas shift reaction also takes place on Cu clusters and it proceeds through two steps: H\textsubscript{2}O dehydrogenation to provide adsorbed O and CO\textsubscript{2} formed by the quick reaction of CO with adsorbed O (Sun et al., 1998). Thus the reaction mechanisms for CO\textsubscript{2} hydrogenation to methanol and water gas shift reaction are as
follows:

\[ 2\text{Cu}_2 + \text{H}_2 \rightleftharpoons 2\text{Cu}_2\text{H}, \]  
(a)

\[ \text{CO}_2 + \text{Cu}_2 \rightleftharpoons \text{Cu}_2\text{O} + \text{Cu}_2, \]  
(b)

\[ \text{CH}_3\text{O} + \text{Cu}_2\text{H} \rightleftharpoons \text{Cu}_2\text{CH}_2\text{O} + \text{Cu}_2 + \text{H}_2, \]  
(c)

\[ \text{Cu}_2\text{CH}_2\text{O} + \text{Cu}_2 \rightleftharpoons \text{Cu}_2\text{CH}_3\text{O} + \text{Cu}_2, \]  
(d)

\[ \text{Cu}_2\text{CH}_3\text{O} + \text{Cu}_2 \rightleftharpoons \text{Cu}_2\text{CH}_2\text{OH} + \text{Cu}_2, \]  
(e)

\[ \text{Cu}_2\text{CH}_3\text{OH} \rightleftharpoons \text{Cu}_2 + \text{CH}_3\text{OH}(a), \]  
(f)

\[ \text{Cu}_2\text{O} + 2\text{Cu}_2\text{H} \rightleftharpoons 2\text{Cu}_2 + 2\text{Cu}_2\text{H}_2\text{O}, \]  
(g)

\[ \text{H}_2\text{O}(a) + \text{Cu}_2 \rightleftharpoons \text{Cu}_2\text{O} + \text{H}_2, \]  
(h)

\[ \text{CO} + \text{Cu}_2\text{O} \rightleftharpoons \text{Cu}_2 + \text{CO}_2. \]  
(j)

Reaction (c) and (i) are assumed to be the rate determining steps individually, and thus expressions of the rate of methanol synthesis and water gas shift reaction are obtained as follows:

\[ r_1 = K_1 \frac{P_{\text{CO}_2} P_{\text{H}_2}(1 - P_w P_M/K_{P,1} P_{\text{CO}_2} P_{\text{H}_2}^3)}{(1 + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{CO}} P_{\text{CO}} + K_{\text{MeO}} P_M + K_W P_w + \sqrt{K_{\text{H}_2_P} P_{\text{H}_2}^3})}, \]

\[ r_3 = K_3 \frac{P_{\text{CO}} P_{\text{H}_2}/K_{P,3} P_{\text{CO}}}{1 + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{CO}} P_{\text{CO}} + K_P P_M + K_W P_w + \sqrt{K_{\text{H}_2_P} P_{\text{H}_2}}} \]

Methanol formed by CO2 hydrogenation is transferred to acidic site on HZSM-5 where it obtains a proton. According to organic chemistry theory, it forms a leaving radical. DME is then formed by a nucleophilic-displacement reaction caused by another adsorbed methanol molecule on the carbon cation. This reaction mechanism is as follows:

\[ \text{CH}_3\text{OH}(a) + \text{HX} \rightleftharpoons \text{HXCH}_3\text{OH}, \]  
(k)

\[ \text{HXCH}_3\text{OH} \rightleftharpoons \text{CH}_3^+ \text{X}^- + \text{H}_2\text{O}(a), \]  
(l)

\[ \text{CH}_3^+ \text{X}^- + \text{HXCH}_3\text{OH} \rightleftharpoons \text{HXCH}_3\text{O} + \text{H}^+ + \text{X}^-, \]  
(m)

\[ \text{HXCH}_3\text{O} \rightleftharpoons \text{CH}_3^+ \text{O} + \text{H}^+, \]  
(n)

\[ \text{CH}_3^+ \text{O} \rightleftharpoons \text{CH}_3 + \text{H}^+, \]  
(o)

\[ \text{HXCH}_3 - \text{O} - \text{CH}_3 \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{HX}, \]  
(p)

\[ \text{H}^+ + \text{X}^- \rightleftharpoons \text{HX}. \]  
(q)

Assuming reaction (m) to be the rate-determining step, the expression of rate of methanol dehydration reaction is as follows:

\[ r_2 = K_2 \frac{(P_M^2 / P_W) - (P_D/K_{P,2})}{(1 + K_M P_M + K_{\text{H}_2\text{O}} P_W)^2}. \]

The experimental results showed that, both methanol and water had very little concentration in the outlet mixture. and the syngas to DME reaction proceeds through the overall reaction: 3CO + 3H2 = DME + CO2. Thus the terms of methanol and water adsorption can be neglected and the above-kinetics equations can be simplified as follows:

\[ r_1 = K_1 \frac{P_{\text{CO}_2} P_{\text{H}_2}(1 - P_w P_M/K_{P,1} P_{\text{CO}_2} P_{\text{H}_2}^3)}{(1 + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{CO}} P_{\text{CO}} + \sqrt{K_{\text{H}_2_P} P_{\text{H}_2}^3})}, \]

\[ r_2 = K_2 \left( \frac{P_M^2}{P_W} - \frac{P_D}{K_{P,2}} \right), \]

\[ r_3 = K_3 \frac{P_{\text{CO}} P_{\text{H}_2}/K_{P,3} P_{\text{CO}}}{1 + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{CO}} P_{\text{CO}} + \sqrt{K_{\text{H}_2_P} P_{\text{H}_2}}}. \]

Finally, the kinetic parameters in the above expressions are obtained by regression of the experimental data, which are as follows:

\[ K_1 = 35.45 \exp(-1.7069 \times 10^4/R/T), \]

\[ K_2 = 8.2894 \times 10^4 \exp(-5.2940 \times 10^4/R/T), \]

\[ K_3 = 7.3976 \exp(-2.0436 \times 10^4/R/T), \]

where the adsorption constants, K_{H_2}, K_{CO_2}, and K_{CO} are given by Bussche and Froment (1996) and Herman and Klier (1979), shown in the following:

\[ K_{H_2} = 0.249 \exp(3.4394 \times 10^4/R/T), \]

\[ K_{CO_2} = 1.02 \times 10^{-7} \exp(6.7400 \times 10^4/R/T), \]

\[ K_{CO} = 7.99 \times 10^{-7} \exp(5.8100 \times 10^4/R/T) \]

and the equilibrium constants for the three reactions are given by Zhang et al. (2001) and Herman et al. (1979), shown as

\[ \ln K_{P,1} = -4213/T - 5.752 \ln T - 1.707 \times 10^{-3} T + 2.682 \times 10^{-6} T^2 - 7.232 \times 10^{-10} T^3 + 17.6. \]
4. Model development

The two-phase model, representing the bubble phase and the surrounding dense phase, has proved to be the most suitable model for the fluidized-bed reactor modeling (Werther, 1980), and the details of this model can be found in Kunii et al. (1991) with the hydrodynamic and transport property correlations listed in Table 1. It postulates that the gas in excess of that necessary for the catalyst particles to fluidize passes through the bed in the form of bubbles.

The assumption of plug flow in the bubble phase is usually valid, but it becomes very doubtful whether the dense phase should be modeled as being fully back-mixed (P–M model) or in plug flow (P–P model). Wagialla et al. (1991) adopted P–M model for the simulation of methanol synthesis, but Fernandes and Lona (2001) adopted P–P model for the simulation of polyethylene production.

Kunii and Levenspiel (1969, 1991) conclude that the increase of the ratio of bed height-to-diameter \((L_f/d_t)\), especially over 10, leads to plug flow in dense phase, and that there is also a general principle to judge the flow type in dense phase: if \(u_0/u_{mf} > 3–11\), the reverse flow of gas in dense phase may happen, because the increase of gas velocity leads to more back-mixing of solid particles in dense phase. In this paper, \(u_0/u_{mf}\) is between 2 and 8 under typical conditions, and the ratio of bed height to diameter \((L_f/d_t)\) equals to about 40. Thus it seems that the assumption of flow type in dense phase should be determined by the comparison of simulation with experimental results.

4.1. Assumptions

The model employs the following assumptions:

(i) The bubble phase does not contain solids and is in plug flow. The extent of reaction in the bubble-cloud phase is negligible.

(ii) The dense phase is assumed to be in plug flow or be fully back-mixed, and the temperature in dense phase keeps constant.

(iii) The ideal gas law applies to the gas-phase in both phases.

(iv) The mass and heat-transfer resistances between the particles and the dense-phase gas are negligible.

4.2. Mass balance on bubble and dense phases

Having assumed uniform temperature in dense phase, we only have to consider the material balance equations for component \(i\) in both phases and energy balance in bubble phase, which are as follows:

The steady state mass balance for the \(i\)th component in the bubble phase is given by

\[
\frac{dN_{ib}}{dz} = (K_{bd})_{ib} \left( \frac{N_{id}}{Q_d} - \frac{N_{ib}}{Q_b} \right) A \delta. \quad (20)
\]
The mass balance for the ith component in the dense phase is given by

Dense phase (plug flow):

\[ \frac{dN_{id}}{dz} = -(K_{bd})_{ib} \left( \frac{N_{id}}{Q_d} - \frac{N_{ib}}{Q_b} \right) A\delta + \rho_p (1 - \varepsilon_{mf})(1 - \delta) \]

\times \sum_{j=1}^{3} \alpha_{ij} r_j, \quad (21)

Dense phase (fully back-mixed flow):

\[ N_{id} = (N_{id})_{in} - \int_0^H (K_{bd})_{ib} \left( \frac{N_{id}}{Q_d} - \frac{N_{ib}}{Q_b} \right) A\delta \, dz \]

\[ + AH (1 - \varepsilon_{mf})(1 - \delta) \rho_p \sum_{j=1}^{3} \alpha_{ij} r_j, \quad (22) \]

where \( \alpha_{ij} \) refers to stoichiometric coefficient of component \( i \) in reaction \( j \) (negative for reactants, positive for products and zero for components not appearing in reaction), and \( r_j \) refers to kinetic rate of reaction \( j \).

Rearranging Eq. (7) and integrating (noting that \( N_{ib} = (N_{ib})_{in} \) at \( z = 0 \) we obtain:

\[ \left( \frac{N_{id}}{Q_d} - \frac{N_{ib}}{Q_b} \right) = \left( \frac{(N_{ib})_{in}}{Q_b} - \frac{N_{id}}{Q_d} \right) e^{-\alpha z}, \quad (23) \]

where

\[ \alpha = \frac{(K_{bd})_{ib}}{u_b}, \quad (24) \]

since

\[ \frac{(N_{ib})_{in}}{Q_b} = \frac{(N_{i})_{in}}{u_{in} A} \quad (25) \]

then

\[ \left( \frac{N_{id}}{Q_d} - \frac{N_{ib}}{Q_b} \right) = \left( \frac{(N_{i})_{in}}{u_{in} A} - \frac{N_{id}}{Q_d} \right) e^{-\alpha z}. \quad (26) \]
5. Results and discussions

5.1. Comparison of different reactors

The industrial implementation of the syngas-to-DME process for fuel production requires a large-scale, and is generally based on the coal-gasified syngas, so-called the CO-rich synthesis gas. The syngas-to-DME process is highly exothermic, as can be seen from Eq. (4). Thus, the critical factor for DME reactor design is the management of the heat released by reactions. It can be estimated that the heat released by DME production can produce 2.4 tons steam per ton of DME, equivalent to an adiabatic temperature rise of about 1000 °C at a complete conversion of syngas with a 1:1 ratio of H₂:CO. This problem is especially significant as the catalyst of methanol synthesis may be deactivated rapidly when the temperature is over 270 °C and the active temperature window is from 230 to 270 °C.

In this section, three kinds of reactors have been considered for comparing the performance of the syngas-to-DME process: a fixed-bed, a fluidized bed, and a slurry reactor. The fixed bed reactor is the type of wall-cooled shell-and-tubes, and the steam is co-produced in the shell side, which means the heat removal rate is defined by the inside of the tube. According to Lu et al. (2002), for a CO-rich syngas with a H₂/CO ratio of 1, the space velocity of a fixed-bed reactor should be greater than 15,000 ml/gcat/h to maintain the reactor temperature below 270 °C at 4 MPa, the upper limit of the operating temperature range of the methanol synthesis catalyst. This situation produces a very limited syngas conversion, about 10%, and requires a high-syngas recycling ratio (up to 10), inevitably resulting in a high energy consumption and a low productivity. A conclusion drawn by Lu et al. (2002) is that the fixed-bed reactor is more suitable for the H₂-rich synthesis gas.

The slurry reactor, such as that used in LPDME process developed by Air Products and Chemicals, Inc. (Brown et al., 1991), can provide an excellent heat management, since the slurry phase (liquid medium + fine catalyst particles) possesses a heat capacity 1000 times larger than the gas phase, with an adiabatic temperature rise of the reacting flow less than 20 °C, and it can be operated adiabatically with an outside recyle flow for heat removal. Nevertheless, the added liquid medium, generally consisting of paraffin wax, adds two mass-transfer resistances through the gas–liquid and the liquid–solid interfaces, which cause a constraint to the productivity. Wang et al. (2001) published the experimental results obtained in a laboratory slurry reactor. It was reported that the CO conversion was about 17%, the selectivity of DME was 70% (30% of methanol), and the DME productivity resulted to be 0.2 g/gcat/h, at the conditions: \( T = 260 ^\circ C, P = 4.0 \text{ MPa}, \text{H}_2/\text{CO} = 1.0, \) and gas space velocity of 3000 ml/gcat/h.

Under the same conditions as the slurry reactor as reported by Wang et al. (2001), however, the experimental results in this work show that CO conversion and DME selectivity can
Table 3
Comparison of different reactor performance for DME synthesis

<table>
<thead>
<tr>
<th></th>
<th>Fluidized bed</th>
<th>Slurry reactor (Wang et al., 2001)</th>
<th>Fixed bed (Lu et al., 2002)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO conversion (X_{CO})</td>
<td>48.5%</td>
<td>17%</td>
<td>10.7%</td>
</tr>
<tr>
<td>DME selectivity (S_{DME})</td>
<td>97%</td>
<td>70%</td>
<td>91.9%</td>
</tr>
<tr>
<td>DME productivity (P_{DME})</td>
<td>0.49 g/g/h</td>
<td>0.2 g/g/h</td>
<td>0.5 g/g/h</td>
</tr>
<tr>
<td>Space velocity (SV)</td>
<td>3000 ml/g/h</td>
<td>3000 ml/g/h</td>
<td>15,000 ml/g/h</td>
</tr>
</tbody>
</table>

be as high as up to 48.5% and 97.0%, respectively, with the DME productivity of 0.49 g/gcat/h, which is 2.45 times of experiment result from slurry reactor. In a fixed-bed reactor, the corresponding levels are 10.7% and 91.9% (Lu et al., 2002). Obviously, the fluidized-bed reactor demonstrates a considerable DME productivity improvement over both the fixed bed and the slurry reactor. Therefore, one can conclude that the fluidized bed is the most promising candidate reactor for conducting the DME synthesis from syngas.

5.2. Model comparison

Figs. 3–5 show the comparison of simulation results from P–P and P–M model with experimental results. Under different conditions, such as the variation of feed gas composition, pressure, and temperature, P–M model results can be in better accordance with experimental results. Moreover, from these figures, it can also be seen that at low feed gas conversion, both models can simulate practical reactor very well, but at higher conversion, the difference of simulation results adopting P–P or P–M model becomes remarkable, because at low conversion, more feed gas passes through the reactor in bubble phase, and the effect of feed gas in dense phase is not significant, but at higher conversion, the function of feed gas in dense phase becomes important, thus different assumption of gas flow type in dense phase will result in different simulation results.

5.3. Effect of feed composition (H_2/CO)

Based on P–M model, Fig. 6 shows the effect of feed composition (H_2/CO) on the reactor performance, which demonstrates that the optimum H_2/CO ratio is about 1.4, in accordance with the simulation results of Peng et al. (1999) who attributes it to a trade-off between the optimum syngas composition for methanol synthesis and that for the synergy (i.e., methanol dehydration). Methanol synthesis is favored by a H_2-rich environment with the maximum rate at H_2:CO of 2:1. The dehydration reaction, on the other hand, is fastest.
Fig. 6. Effect of $H_2/CO$ in feed gas on reaction results: $SV = 3000 \text{ml/gcat/h}$, $P = 3 \text{MPa}$, $T = 260^\circ\text{C}$.

Fig. 7. Effect of pressure on reaction results: $SV = 3000 \text{ml/gcat/h}$, $H_2/CO = 1$, $T = 260^\circ\text{C}$.

Fig. 8. Effect of temperature on reactor performance $H_2/CO = 1$, $SV = 3000 \text{ml/gcat/h}$, $P = 3 \text{MPa}$.

5.4. Effect of reactor pressure ($P$)

As is shown in Fig. 7, increasing the pressure results in an increase in CO conversion and DME productivity, because the increase of pressure accelerates the reaction of methanol synthesis especially and the whole reaction as well. In addition, because methanol dehydration reaction approaches to equilibrium catalyzed by HZSM-5 catalyst, DME selectivity keeps a high level with the increase in pressure.

5.5. Effect of reaction temperature ($T$)

The effect of temperature is shown in Fig. 8, which reveals that with the increase of temperature, there exists an optimum temperature for CO conversion and DME productivity between 280 and 290°C. The existence of optimum is partly due to the declining equilibrium value of CO conversion with temperature increasing, and more due to the synergy of the different methanol synthesis and methanol dehydration catalyst component with different active temperature region. But it should be noted that the catalyst has to be exposed to lower temperatures, less than 270°C, to avoid excessive deactivation.

Moreover, DME selectivity increases a little, because higher temperature is more favorable for the activity of methanol dehydration catalyst rather than methanol synthesis catalyst.

5.6. Effect of space velocity ($SV$)

Fig. 9 shows that, with the increase of space velocity, CO conversion keeps decreasing, and DME productivity remains increasing. In addition, DME selectivity slightly decreases, because higher space velocity means shorter residence time of reactants in contact with the catalysts, and short residence time is unfavorable for DME selectivity because DME is the final product of the consecutive reactions of methanol synthesis and methanol dehydration.

6. Conclusions

The preliminary experimental results in this work have shown that fluidized bed technology is more efficient for...
When \( \text{H}_2/\text{CO} = 1.0 \), the CO conversion and DME selectivity are 48.5% and 97% in a fluidized-bed reactor, compared to the values of 17% and 70% in a slurry reactor under the same conditions, and those of 10.7% and 91.9% in a fixed-bed reactor under its normal conditions.

A new mechanism and kinetics model for DME synthesis are established and have been applied for the simulation of fluidized-bed reactor. Two two-phase models are used to simulate DME synthesis in the lab fluidized-bed reactor with the bubble phase assumed to be in plug flow, and the dense phase in plug flow (P–P model) and in fully back-mixed flow (P–M model). Comparison between calculated and experimental results shows P–M is more valid than P–P model.

Then, based on P–M model, the influences of different factors, such as pressure, temperature, \( \text{H}_2/\text{CO} \) ratio in feed gas and space velocity are simulated and analyzed. The results include that the optimum \( \text{H}_2/\text{CO} \) ratio in feed gas is about 1.4, and enhancement of pressure and space velocity improve DME productivity remarkably. There exists an optimum temperature value between 280 and 290\(^\circ\)C, but high temperature may lead to excessive deactivation of the catalysts.

### Notation

- \( A \): cross-sectional area of bed, \( \text{m}^2 \)
- \( d \): diameter, \( \text{m} \)
- \( d_c \): reactor diameter, \( \text{m} \)
- \( D_{im} \): diffusivity of component \( i \) in gas mixture, \( \text{m}^2/\text{s} \)
- \( D_{ij} \): diffusivity of component \( i \) in component \( j \), \( \text{m}^2/\text{s} \)
- \( H \): reactor height, \( \text{m} \)
- \( (H_{bd})_b \): interphase heat-transfer coefficient between bubble and dense phase based on bubble volume, \( \text{J}/\text{m}^2\text{sK} \)
- \( (K_{bd})_{ib} \): overall mass-transfer coefficient (bubble phase–dense phase) based on bubble volume, \( \text{s}^{-1} \)
- \( N \): gas flow rate, \( \text{mol/s} \)
- \( P \): reactor pressure, bar
- \( P_{DME} \): DME productivity, \( \text{g/g/h} \)
- \( Q \): gas volumetric flow, \( \text{m}^3/\text{s} \)
- \( r \): reaction rate, \( \text{mol/gcat/s} \)
- \( S_{DME} \): DME selectivity in organic products, dimensionless
- \( SV \): space velocity, \( \text{ml/g/h} \)
- \( T \): reaction temperature, \( ^\circ\text{C} \)
- \( u \): gas velocity, \( \text{m/s} \)
- \( u_0 \): superficial gas velocity, \( \text{m/s} \)
- \( x \): mole fraction, dimensionless
- \( X_{\text{CO}} \): CO conversion, dimensionless
- \( z \): distance along bed height, \( \text{m} \)
- \( \Delta H \): heat of reaction, \( \text{J/g mol} \)

### Greek letters

- \( \alpha_{ij} \): stoichiometric coefficient of component \( i \) in reaction \( j \), dimensionless
- \( \beta \): equilibrium degree, dimensionless
- \( \delta \): bubble-phase volume as a fraction of total bed volume, dimensionless
- \( \epsilon \): dense-phase voidage, dimensionless
- \( \rho \): density, \( \text{kg/m}^3 \)
- \( \mu \): viscosity, \( \text{Pa} \text{s} \)

### Subscripts

- \( b \): bubble phase
- \( d \): dense phase
- \( f \): gas flow
- \( mf \): minimum fluidization
- \( p \): catalyst particle

### References


