

DME 합성을 위한 고정층 반응기의 모델링 및 모사
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MODELING AND SIMULATION OF FIXED BED REACTOR FOR DME
SYNTHESIS

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1. INTRODUCTION

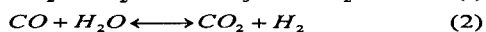
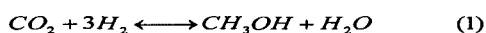
Dimethyl ether (DME), the simplest ether, is a colorless, non-toxic, environmentally benign compound. DME is traditionally produced by dehydration of methanol, which is in turn produced from syngas, products of natural gas reforming. This traditional process is thus called two-step or indirect method of DME preparation. However, DME can be prepared directly from syngas (single-step or direct method). Single-step method needs only one reactor for DME synthesis, instead of two for two-step process. It can also alleviate thermodynamic limitation of methanol synthesis by converting it as produced into DME, thereby potentially enhancing overall conversion of syngas to DME. Catalysts are required for the conversion of syngas to DME. Control of reactor temperature is very critical as DME synthesis is strongly exothermic.

In a fixed bed reactor the main difficulty would be the prevention of the occurrence of hot spot. Catalysts can be irreversibly deactivated once exposed to above certain temperatures. One simple way of limiting temperature rise is controlling conversion, but this is not desirable economically. It is thus necessary to be able to understand and predict the behaviour of reactor at various conditions for the design and scale-up of the DME synthesis process. But it is not practical to gather all the data experimentally, and numerical simulation will be very valuable in the process development. In this study we developed a mathematical model to simulate a pilot-plant scale, shell and tube type DME reactor.

2. REACTOR MODEL DEVELOPMENT

2.1 Reaction kinetics

Preparation of DME from syngas can be represented by three catalytic reactions as shown below. (Ng, *et al*, 1999)



Reaction (1) is methanol synthesis reaction from carbon dioxide and hydrogen. Reaction (2) is water gas shift reaction. These two reactions are catalyzed by methanol synthesis catalyst (CuO/ZnO/Al₂O₃). The last reaction is methanol dehydration reaction: DME synthesis reaction catalysed by an acidic catalyst

(-alumina). Combinations of these three reactions can explain other schemes of DME preparation from syngas. And we use reaction rate equations as follows: (Bushe, *et al*, 1996; Bercic, *et al*, 1992)

$$r_{CO_2 \text{hydrogenation}} = \frac{k_1(P_{H_2}, P_{CO_2})[1 - (1/K_{eqm1})(P_{CH_3OH}P_{H_2O})/(P_{CO_2}P_{H_2}^3)]}{(1 + K_2(P_{H_2O}/P_{H_2}) + \sqrt{K_3P_{H_2} + K_4P_{H_2O}})^2}$$

$$\Delta Hr = -49.47 \text{ kJ/mol}$$

$$r_{RWGS} = \frac{k_5 P_{CO_2} [1 - K_{eqm2} (P_{CO} P_{H_2O} / P_{CO_2} P_{H_2})]}{1 + K_2 (P_{H_2O} / P_{H_2}) + \sqrt{K_3 P_{H_2} + K_4 P_{H_2O}}}$$

$$\Delta Hr = 41.17 \text{ kJ/mol}$$

$$r_{MeOH \text{dehydration}} = \frac{k_6 K_{CH_3OH}^2 [\frac{C_{CH_3OH}^2 - (C_{H_2O} C_{DME} / K_{eqm3})}{(1 + 2\sqrt{K_{CH_3OH} C_{CH_3OH} + K_{H_2O} C_{H_2O}})^4}]}{(1 + 2\sqrt{K_{CH_3OH} C_{CH_3OH} + K_{H_2O} C_{H_2O}})^4}$$

$$\Delta Hr = -21.003 \text{ kJ/mol}$$

These three reactions are all exothermic. The adiabatic temperature rise can be more than 1000K if the reactions could be sustained to completion. Therefore handling of reaction heat is very important for the control of reactions. Values of kinetic parameters in the above kinetic expressions are summarized in Table 2.1.

Table 2.1. kinetic parameters

	A(i)	B(i)	parameter
k ₁	1.65	36696	4846.92537
K ₂	3610	0	3610
K ₃	0.37	17197	15.61050021
K ₄	7.14E-11	124119	38.34028362
k ₅	10900000000	-94765	12.06676023
K _{eqm1}			1.23622E-05
K _{eqm2}			52.015
K _{eqm3}	0.00079	70500	3633.132926
k ₆	37000000000	-105000	4.416718591
K _{eqm3}	0.084	41100	643.3761003
K _{eqm3}			59429.21586

$$\text{parameter} = A(i) \exp(B(i)/RT)$$

$$\log_{10} K_{eqm1} = \frac{3066}{T} - 10.592$$

$$\log_{10} \frac{1}{K_{eqm2}} = -\frac{2073}{T} + 2.029$$

$$\log_{10} K_{eqm3} = \frac{10194}{T} - 13.91$$

Equilibrium constant of each reaction is taken from literature. (Twigg, 1986; Stull, *et al*, 1969)

2.2 Heat and Mass Transfer on the surface of the catalyst

Due to highly exothermic nature of the reactions temperature of the catalyst pellets can be different from bulk stream of the reactants. Likewise there could be difference in reactants concentration between the bulk and catalyst pellets surface. Therefore, we investigated heat and mass transfer on the surface of the catalyst pellets. We employed conventional expressions for the heat transfer coefficient: (Kunii, *et al*, 1990)

$$N_{nu} = \frac{h_p d_p}{k_g} = 2 + 0.6 N_{Re \text{ sph}}^{0.5} N_{pr}^{1/3}$$

$$N_{Re \text{ sph}} = \frac{d_p v \rho}{\mu}$$

$$N_{pr} = \frac{C_p \mu}{k_g}$$

For the cylindrical pellets we adopted equivalent diameter in order to account for the difference in shapes (Fig. 2.1). The temperature of the catalyst particle should satisfy energy balance of heat transfer and heat of reaction:

$$\sum_i r_i \Delta H_r g_{cat} = h_p A_p (T_{p1} - T_f)$$

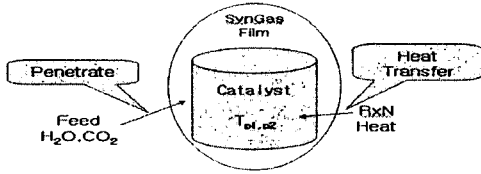


Fig. 2.1 Heat & Mass transfer on the surface of the catalyst

2.3 Effectiveness factor

Intrinsic reaction rate can be different from global reaction rate because of pore diffusion in the catalyst pellet when diameter of the catalyst pellet is several millimeters. For spherical catalyst pellets, if concentrations of reactants on catalyst surface are C_0 , radius of a particle is R , concentration of reactants and products can be obtained by solving the following equations (Fig. 2.2):

$$\begin{aligned} \frac{d^2 C_{H_2} + 2}{dr^2} \frac{dC_{H_2}}{dr} &= \frac{3\rho_p}{D_{eff,H_2}} r_{CO_2} + \frac{\rho_p}{D_{eff,H_2}} r_{RWGS} \\ \frac{d^2 C_{CO} + 2}{dr^2} \frac{dC_{CO}}{dr} &= -\frac{\rho_p}{D_{eff,CO}} r_{RWGS} \\ \frac{d^2 C_{CO_2} + 2}{dr^2} \frac{dC_{CO_2}}{dr} &= \frac{\rho_p}{D_{eff,CO_2}} r_{CO_2} + \frac{\rho_p}{D_{eff,CO_2}} r_{RWGS} \\ \frac{d^2 C_{H_2O} + 2}{dr^2} \frac{dC_{H_2O}}{dr} &= -\frac{\rho_p}{D_{eff,H_2O}} r_{CO_2} - \frac{\rho_p}{D_{eff,H_2O}} r_{RWGS} - \frac{\rho_p}{2D_{eff,H_2O}} r_{MeOH} \\ \frac{d^2 C_{DME} + 2}{dr^2} \frac{dC_{DME}}{dr} &= -\frac{\rho_p}{2E_{eff,DME}} r_{MeOH} \\ \frac{d^2 C_{MeOH} + 2}{dr^2} \frac{dC_{MeOH}}{dr} &= -\frac{\rho_p}{D_{eff,MeOH}} r_{CO_2} + \frac{\rho_p}{D_{eff,MeOH}} r_{MeOH} \end{aligned}$$

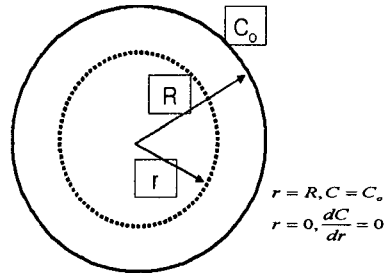


Fig. 2.2 Consideration of intra-phase mass transfer resistance in the catalyst pellet

Effective diffusivity of gases through porous catalyst pellets was estimated from molecular diffusivity, porosity and tortuosity of pores:

$$D_{eff,i} = D_i \frac{\epsilon}{\tau}$$

$\epsilon = \text{void_fraction(porosity)}$
 $\tau = \text{tortuosity}$

We employed 0.603 for porosity and 3 for tortuosity, respectively (Bercic, *et al*, 1992). Solutions of these equations provide the concentration profiles of gas species in the catalyst pellets together with the global reaction rates.

2.4 Heat transfer between tubes and shell

Heat generated from the chemical reactions in the catalyst is transferred to the gases flowing through reactor tubes, and then to cooling medium in the shell side of the reactor. The overall heat balance can be summarized as follows:

$$\left(\sum_i r_i \Delta H_r g_{cat} - UA_i (T_f - T_o) \right) = C_{p,fluid} m_f \Delta T_f$$

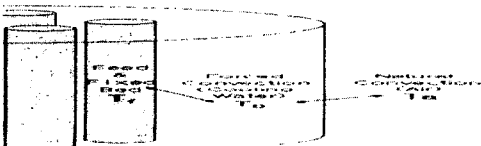


Fig. 2.3 Heat Transfer between reactants in the tubes and coolant in the shell.

In order to estimate the heat transfer coefficient, U, we should know both the of shell side and tube side heat transfer coefficients. The common method of heat transfer coefficient calculation procedures can be employed for the estimation of shell side heat transfer coefficient as heat transferring liquid or boiling water is used as cooling medium in the shell. But the presence of catalyst pellets makes the estimation of heat transfer coefficient on the tube side much complicated. Although several correlations are available in the literature, their reliability should be experimentally verified. As we do not have experimental values for the tube side heat transfer coefficient, we selected the following correlation for the estimation of tube side heat transfer coefficient. (Kunii, *et al*, 1990)

$$h = \left(\frac{1}{\frac{1}{h_r + 2k_{sw}^0/d_p + a_w C_{pg} \rho_g v} + \frac{1}{h_{packet}}} \right)$$

$$h_{packet} = 1.13 \left(\frac{k_s^0 \rho_p (1 - \epsilon_{mf}) C_{ps}}{\tau_p} \right)^{0.5}$$

$$k_{sw}^0 = \epsilon_w k_g + (1 - \epsilon_w) k_s \left(\frac{1}{\phi_w (k_s / k_g) + 1/3} \right)$$

$$k_s^0 = \epsilon_{mf} k_g + (1 - \epsilon_{mf}) k_s \left(\frac{1}{\phi_o (k_s / k_g) + 2/3} \right)$$

$$a_w = 0.05, h_r (\text{radiation}) = 0$$

The simulator can simulate the performance of the fixed bed reactor taking into account of chemical reaction kinetics, heat and mass transfer between catalyst pellets and bulk fluid, effects of mass transfer inside each catalyst (effectiveness factor), heat transfer between fluid in the tubes and cooling medium in the shell. It can also calculate change of chemical species concentration as reactants gas stream move downward through catalyst pellets in the reactor tubes. Radial variation across tube diameter was neglected, as ratio of tube diameter to length is small.

3. RESULTS AND DISCUSSION

Using the simulator we developed behavior of a pilot-scale DME reactor was studied. Reaction condition of the reactor for simulation is as follows: GHSV 1000 hr⁻¹, feed temperature 280°, reactor pressure 50 bar, H₂:CO ratio 2:1.

Figure 3.1 and 3.2 show profiles of reaction rate within catalyst pellets for the case of mixture of pellets. In this case catalyst pellets for the synthesis of methanol from syngas (CuO/ZnO/Al₂O₃, 6mm pellets for reaction 1 and 2) and catalyst pellets for the synthesis of DME by dehydration of methanol ((-alumina, 7.7mm pellets for reaction 3) are present as a mixture inside the reactor tubes. As expected we can observe strong influence of pore diffusion on reaction rate. Reaction rate of water gas shift decreased in the catalyst core by pore diffusion effect of CO. But, reaction rates of methanol synthesis showed maximum value in the region about 2.5~3mm from the catalyst surface. It was caused by CO₂ increase by water gas shift reaction.

Note that methanol dehydration occurs only on the methanol dehydration catalyst in the case of mixture of pellets. Thus, Fig. 3.2 shows effects of pore diffusion on reaction rate. However, quite a different picture emerges in the case of hybrid catalyst (Fig. 3.3). Here all three reactions occur in the same catalyst pellet. Although reaction rate of water gas shift reaction decreases toward the center of the catalyst pellet as a result of pore diffusion effects, reaction rates of methanol synthesis and DME synthesis in the core region of the catalyst pellets are higher than those of near pellet surface. As the reactions (1), (2) and (3) involved in the synthesis of methanol and DME are interrelated in a complex way including pore diffusion, their rates within the catalyst pellet reflect inter-play of mass transfer and chemical reactions as

well as variations of species concentration within the catalyst. Therefore effectiveness factor can be over 100% under some circumstances for hybrid catalysts. We evaluated effectiveness factor for three reactions along the reactor length and found that effectiveness factor for DME synthesis reaction is well over 100% in the entrance zone of the reactor, and that for methanol synthesis above 100% in the first half of the reactor (Fig. 3.4). Effectiveness factor for water shift reaction shows very unusual trend. It swings from negative and positive values. In order to investigate this further we calculated effectiveness factors for various sizes of catalyst pellet.

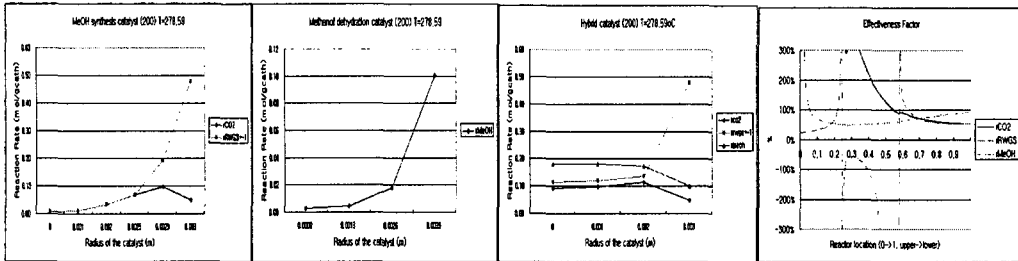


Fig. 3.1

Fig. 3.2

Fig. 3.3

Fig. 3.4

Fig. 3.7 shows reactor behaviour for the case of mixture of pellets. It shows the temperature of reactant stream rises rapidly (290 to 321 °C) and then falls slowly as it moves down through reactor tube. It means cooling is not sufficient in the entrance region of the reactor where chemical reactions are fast due to high concentration of reactants. In the case of mixture of catalyst pellets CO conversion is 36% and DME productivity is 8.54 gmol/kg-cat h. Reactor performance for hybrid catalyst is shown in Fig. 3.8. Maximum temperature is higher than that of mixture of catalyst pellets. In this case, CO conversion is 69%, DME productivity is 20.6 gmol/kg-cat h.

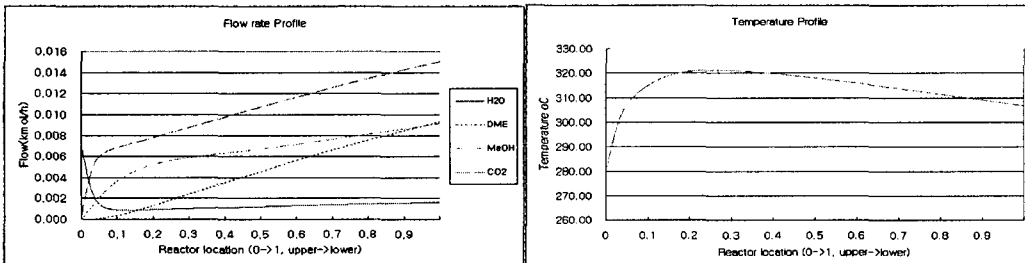


Fig 3.7 Flow rate and Temperature profile in the fixed bed reactor for DME synthesis. (Effectiveness factor is applied.)

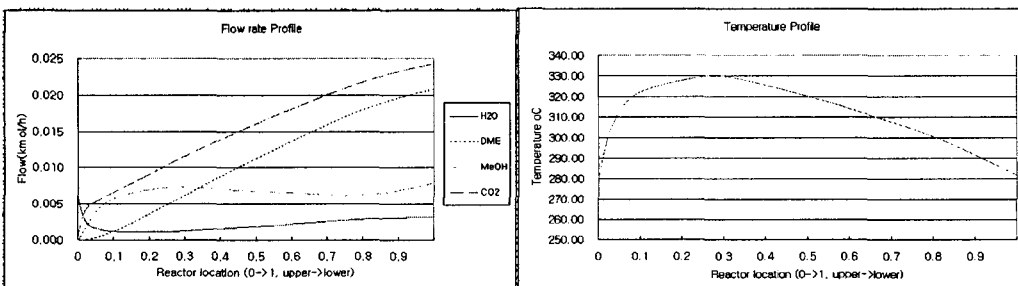


Fig 3.8 Flow rate and Temperature profile of the reactor filled by hybrid catalyst

4. CONCLUSION

We developed a simulator of the fixed bed reactor for single-step DME synthesis from syngas, and examined behavior of reactor at various conditions. We found that complex reactions coupled with pore diffusion within the catalyst pellet affects can show unusual values of effectiveness factor. Employing hybrid catalyst yielded higher productivity compared with using mixture of catalyst pellets. But, more careful cooling of reactor is needed as more reaction heat is released near reactor entrance.

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NOMENCLATURE

$C_{A0,i}$ Concentration of component i in fluid [kmol/m³]

D_{AB} Binary diffusivity [cm²/s]

$D_{eff,i}$ Binary effective diffusivity of component i in the catalyst pellet [m²/h]

$dHr, \Delta Hr$ Reaction Heat [kJ/mol]

K_i Adsorption constants

$K_{eqm,j}$ Equilibrium constant of reaction j

r particle radius [m]

r_{CO_2} Reaction rate of the methanol synthesis reaction [mol/gcat·h]

r_{RWGS} Reaction rate of the reverse water gas shift reaction [mol/gcat·h]

r_{MeOH} Reaction rate of the methanol dehydration(DME synthesis) reaction [mol/gcat·h]

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