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NUMERICAL SIMULATION OF FIXED-BED CATALYTIC REACTOR FOR ISOPROPYL ALCOHOL SYNTHESIS

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Abstract—The mathematical model and the method of its numerical analysis for fixed-bed catalytic reactors were developed and were applied to the pilot reactor of isopropyl alcohol (IPA). The experimental results from pilot test runs were used to test and verify the simulation results. The numerical simulation gives the IPA concentration and temperature profiles in the reactor. The production of IPA from a commercialized ethanol reactor was examined. The operation conditions of IPA synthesis were established.

INTRODUCTION

Isopropyl alcohol (IPA) is commercially synthesized by direct hydration process. Direct hydration is brought by simultaneously contacting a solid or liquid catalyst with propylene and water. According to the phase of reactants, the direct hydration is classified into three basic processes: vapor-phase hydration, mixed vapor-liquid phase hydration, and liquid-phase hydration.

This paper is concerned with vapor-phase hydration process where propylene and water react in the vapor phase. In the vapor-phase hydration process developed by Veba-Chemie [1], a vaporized stream of propylene and water is passed through an acidic catalyst bed(H_3PO_4 supported on SiO_2) at 180-260 °C and 25-40 atm. The gas stream from the reactor is cooled and fed to a scrubber where isopropyl alcohol is removed. Isopropyl alcohol selectivity is about 96% and propylene conversion is 5-6 % [2,3].

KRICT(Korea Research Institute of Chemical Technology) and Korea Alcohol Co. performed the feasibility study for the production of isopropyl alcohol in 1985[4], and carried out the pilot test from 1986 to 1987 in order to obtain the basic data for scale-up[5,6].

In this paper, the experimental results of pilot test runs are analyzed by the numerical simulation of fixed-bed catalytic reactors. The possibility of IPA synthesis with a commercialized ethanol reactor and the scale-up from the pilot plant are also investigated.

THEORY

1. Equation of reaction rate

In vapor-phase hydration, propylene and water are chemically combined over a phosphoric acid-on-silica catalyst to produce isopropyl alcohol[7].

$$C_3H_6+H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (CH_3)_2CHOH \tag{1}$$

This reaction is exothermic, and the heat of reaction, ΔH, is about -12,000 cal/gmol.

Small amounts of by-products such as diisopropyl ether, acetone, propane and polymer are formed. In this study, only the main reaction, Eq.(1), is considered in numerical simulation for reactor analysis, the side reactions for small amounts of impurities being neglected.

The equilibrium constant of Eq.(1), K_p(atm^{-1}), is expressed as follows[7].

$$\ln K_p = \frac{6043}{T} - 17.466 \tag{2}$$

When the partial pressures of propylene, water, and isopropyl alcohol in the reactor are let to be P_P, P_W, and P_{IA}, respectively, and the reaction rates are assumed to be the first-order to reactants, the reaction rate, R_P(gmol IPA/hr·kg cat), may be written:

$$R_p = k_1 P_p \cdot P_w - k_2 P_{IA} \tag{3}$$

where k_1(gmol/hr·atm^2·kg cat) and k_2(gmol/hr·atm·kg cat) are the constants of forward and reverse reactions, respectively.

On the other hand, the equilibrium constant K_P, is as follows:

$$K_p = \frac{k_1}{k_2} = \frac{P_{IA}}{P_p \cdot P_w} \tag{4}$$

The equation of reaction rate of Eq.(3) can be written in the form of Eq.(5):

$$R_p = k_1 (P_p \cdot P_w - \frac{1}{K_p} P_{IA}) \tag{5}$$

Let the mole ratio of water to propylene and the propylene concentration in the feed of reactor be α and C_0 (gmol/*l*), respectively, and assuming that the reactants be ideal-gas mixture, the partial pressures of respective reactants can be expressed as follows:

$$P_p = P \frac{1 - C/C_0}{1 + \alpha - C/C_0} \tag{6}$$

$$P_w = P \frac{\alpha - C/C_0}{1 + \alpha - C/C_0} \tag{7}$$

$$P_{IA} = P \frac{C/C_0}{1 + \alpha - C/C_0} \tag{8}$$

where P is the total pressure(atm) in the reactor.

2. Mathematical model of fixed-bed catalytic reactors

The schematic diagram of a fixed-bed catalytic reactor is shown in Fig. 1. The silica catalyst impregnated with phosphoric acid is packed in the reactor. Although the actual reaction is a heterogeneous catalytic reaction, we consider it as a pseudo-homogeneous reaction provided that plug-flow behavior is a valid assumption. We also assume that the activity of catalyst does not decrease, but is constant during the reaction, and that the pressure drop in the reactor can be neglected.

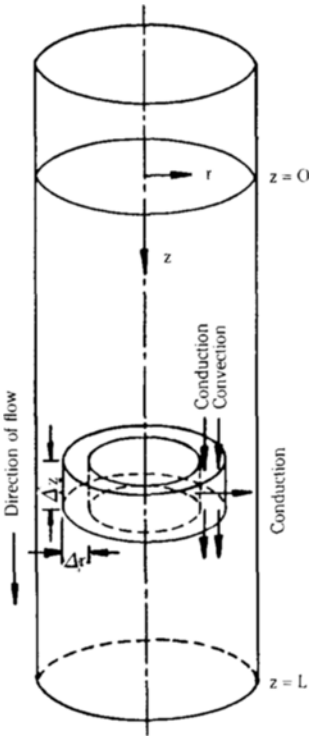


Fig. 1. Schematic diagram of a fixed-bed catalytic reactor.

The mass and energy balances for the above fixed-bed catalytic reactor at steady state can be written by Eq.(9) and Eq.(10), respectively:

$$\frac{1}{r}\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} - \frac{P_{er}}{d_p}\frac{\partial C}{\partial z} + \frac{P_{er}}{P_{ez}}\frac{\partial^2 C}{\partial z^2} + \frac{R_p}{u}\frac{\rho_B \cdot P_{er}}{d_p} = 0 \tag{9}$$

$$\frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} - \frac{\rho \cdot C_p}{k_e} \cdot u \frac{\partial T}{\partial z} - \frac{\rho_B \cdot R_p \cdot \Delta H}{k_e} = 0 \tag{10}$$

In the derivation of Eq.(9), it is assumed that the effective diffusivities (D_r & D_z) are not very sensitive to r or z and the velocity is not a function of z. The Eq.(10) is derived by assuming that the axial effective thermal conductivity is neglected since its contribution is negligible except for very shallow beds and low velocities [8].

The boundary conditions of Eq.(9) and Eq.(10) are as follows:

$$C = 0 \ \& \ T = T_0 \quad \text{at } z = 0 \text{ for all } r \tag{11}$$

$$\frac{\partial C}{\partial z} = \frac{\partial T}{\partial z} = 0 \quad \text{at } z = L \text{ for all } r \tag{12}$$

$$\frac{\partial C}{\partial r} = \frac{\partial T}{\partial r} = 0 \quad \text{at } r = 0 \text{ for all } z \tag{13}$$

$$\frac{\partial C}{\partial r} = 0 \ \&$$

$$-k_e \frac{\partial T}{\partial r} = U(T_b - T_s) \quad \text{at } r = R \text{ for all } z \tag{14}$$

Radial Peclet No. (P_{er}) is independent of flow rate and has a magnitude of about 10 above a modified Reynolds No. ($d_p \cdot \rho \cdot u/\mu$) of about 40. We estimate P_{er} using the following equation (9):

$$P_{er}/[1 + 19.4(\frac{d_p}{2R})^2] = \beta \tag{15}$$

where β is a constant ranging from 5 to 10. For axial Peclet No. (P_{ez}), the value of $P_{ez} = 2.0$ proposed by McHenry and Wilhelm[10] is used.

In Eq.(10) the effective thermal conductivity, k_e, has been assumed to be independent of radial direction. It is suggested that k_e decreases somewhat as the reactor wall is approached. We shall use an average value in our discussions for simplicity. Owing to the many mechanisms in the heterogeneous system, k_e is not an ordinary thermal conductivity, but a property of the bed that depends on a large number of variables such as gas flow rate, particle diameter, porosity, true thermal conductivity of the gas and of the solid phases, and temperature level. Therefore, the most logical method of correlating data is to divide k_e into separate contributions corresponding to a mechanism of heat transfer. Methods are well developed in several literatures [8,9]. We also use this method for the prediction of k_e.

In this dicussion, it is also assumed that the superficial velocity profile in the radial direction conforms to the semi-empirical equation proposed by Schwartz and Smith [11]:

$$\ln\left[\frac{u+(u^2-u_o^2)^{1/2}}{u_o}\right]=k'\left(\frac{r}{R}\right)^{3/2} \tag{16}$$

where,

$$k'=33.3\left(\frac{d_p}{2R}\right) \text{ at } 0\leq\frac{d_p}{2R}<0.06 \tag{17}$$

$$\text{and } k'=2.0 \quad \text{at} \quad \frac{d_p}{2R}\geq 0.06. \tag{18}$$

At low values of $d_p/2R$, k' approaches 0 and Eq. (16) would predict a flat profile.

The overall heat-transfer coefficient, U, between the inside wall surface of reactor and the surroundings is 0 for an adiabatic reactor, and has "+" value when the reactor is cooled. The reactor analysis has to be performed by estimating the value of U according to the type of heat-transfer in the reactor.

NUMERICAL ANALYSIS

The partial differential equations from Eq.(9) to Eq.(14) are converted to the finite difference equations of explicit form. By solving these equations simultaneously with Eq.(2),(5),(6),(7), and (8) using a digital computer, the radial and axial profiles of product concentration and temperature in the reactor are found. For this calculation, the parameters such as P_{er}, P_{ez}, u and U are estimated as mentioned above.

The input data for the simulation of IPA pilot reactor is shown in Table 1. The data for reaction temperature, pressure, and mole ratio of water to propylene were established from the pilot plant tests [5,6]. The properties of reactants are estimated for the conditions of 215 °C and 31 atm with the assumption of ideal gas mixture.

Table 1. Input data for the simulation of pilot reactor

1. Reactor dimension:	
Diameter	15 cm
Length	56.6 cm
2. Catalyst:	
Pellet diameter	0.362 cm
Thermal conductivity	0.756 Btu/hr·ft·°F
Bed porosity	0.4
Bed density	1.0 kg/*l*
Emissivity	0.79
3. Initial reaction conditions:	
Temp.	210°C
Pressure	31 atm
H_2O/Propylene mole ratio	0.94
Propylene concentration	0.515 gmol/*l*
IPA concentration	0 gmol/*l*
4. Average physical properties of reactants:	
Density	0.047 g/cm³
Heat capacity	0.504 Btu/lb °F
Viscosity	0.015 c.p
Thermal conductivity	0.176 Btu/hr·ft·°F
Average mol wt	30.4

RESULTS AND DISCUSSION

The IPA concentrations and temperatures at reactor outlet for the case shown in Table 1 are calculated as a function of k_1 by the previously mentioned method of numerical analysis. Comparing these calculated results with the experimental ones, the best fitted

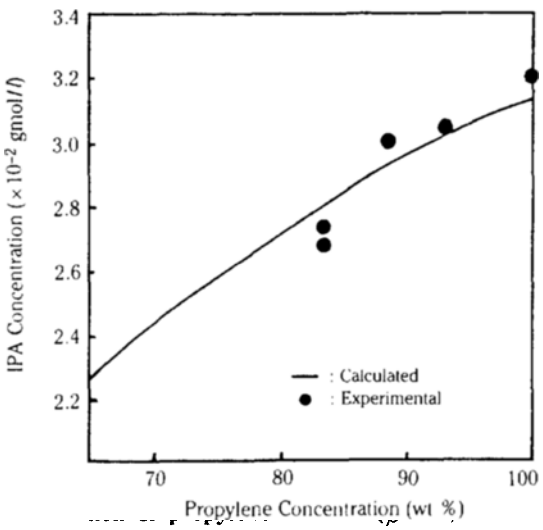
Table 2. Estimation of reaction rate constant, k_1

Propylene feed rate (kgmol/hr)	0.185	0.277	0.370	0.416	0.462	0.554
IPA concentration at reactor outlet (mol/*l*)	0.0360	0.0335	0.0301	0.0319	0.0319	0.0258
Estimated k_1 (gmol/hr·atm²·kg cat)	10.5×10^{-3}	9.10×10^{-3}	8.88×10^{-3}	11.5×10^{-3}	13.3×10^{-3}	10.9×10^{-3}
Estimated temp. at reactor outlet (°C)	222.5	222.8	222.4	223.1	223.5	222.0

(β = 10, U = 0.2 Btu/hr·ft²·°F for numerical analysis)

k_1 that may be the reaction rate constant for the simulated reaction conditions is found. In Table 2, the experimental results and the reaction rate constants found as mentioned above are presented. The overall heat-transfer coefficient, U, used in these simulations has been estimated for the glass wool insulation of 10 cm thickness. The reaction rate constant depends on the reaction conditions such as temperature, pressure, reactant feed rate, and etc. From the results of Table 2, it can be seen that the reaction rate constant increases somewhat as the reactant feed rate increases. This may be due to the increasing mass-transfer rate around the catalyst pellets. However, the values of reaction rate constant in Table 2 do not vary significantly within the experimental scope of feed rates. Therefore, the average value of reaction rate constants in Table 2 could be assumed to be the reaction rate constant for this system. The calculated average value is 10.7×10^{-3} gmol/hr·atm^2·kg cat, and used in the following simulation. The calculated temperatures at reactor outlet agree well with the experimental results of 220-230 °C.

Space velocity is one of the most important variables in reactor design. In Fig. 2, the variation of IPA concentration at reactor outlet as a function of reactant feed rate(space velocity) is illustrated. It can be seen that the calculated concentrations agree well with the experimental ones and IPA concentration at reactor outlet decreases linearly with increasing propylene feed rate (space velocity) within the scope of experiments. From this, it is deduced that propylene feed rate should be maintained below 0.430 kgmol/hr in order to obtain IPA yield of above 6.0 mole %(0.0309 gmol/l) in the reactor of 15 cm diameter packed with catalysts of 56.6 cm depth.



Btu/hr·ft^2·°F for numerical analysis).

In the vapor-phase process the conversion of propylene to IPA is as low as about 6 mole %. Therefore, in the commercialized plant, most of the unreacted propylene should be recovered and reused. When recycling the unreacted propylene to the reactor, the propylene concentration at reactor inlet decreases since the complete separation of impurities is not possible. In order to investigate the effect of propylene concentration at reactor inlet on the reaction and to find the optimum propylene concentration, the results of pilot plant test performed with the reactants in which propylene concentration is varied by mixing propylene and propane (KRICT, 1986) are compared with the simulated results in Fig. 3. Propane is the most probable impurity formed during the reaction. The IPA concentrations calculated and experimentally measured coincide well. The IPA concentration (or yield) at reactor outlet decreases rapidly as the propylene concentration in feed decreases. From the figure, it may be concluded that the propylene concentration in dry feed should be maintained above 83 wt %(propylene concentration in wet feed = 0.470 gmol/l) so as to obtain propylene conversion to IPA above 6 mole %. The reason why IPA yield decreases with decreasing propylene concentration is that the partial pressure of propylene in the reactants becomes lower.

In the following discussion, the possibility of utilizing a comercialized ethanol reactor of 260 cm diameter

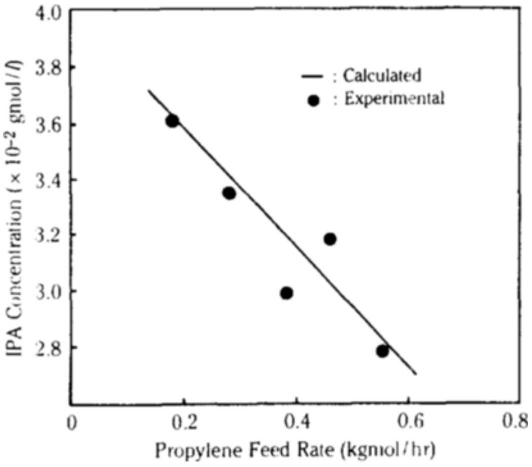


Fig. 3. IPA concentration at reactor outlet as a function of propylene concentration in dry feed ($\beta = 10$, U = 0.2 Btu/hr·ft^2·°F for numerical analysis).

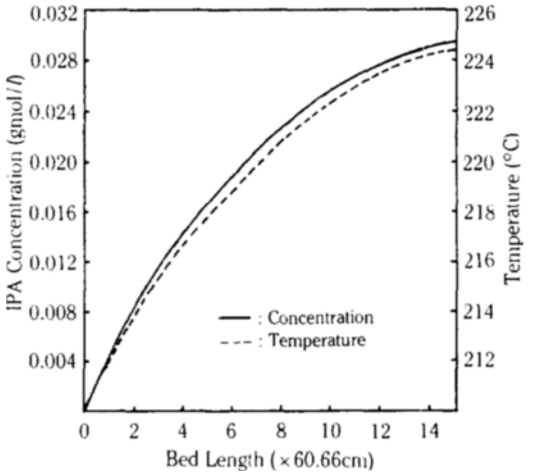


Fig. 4. Axial profiles of IPA concentration and temperature (β = 10, U = 0.2 Btu/hr·ft^2·°F & k_1 = 10.7 × 10^{-3} gmol/hr·atm^2·kg cat).

and 910 cm packing length for IPA production will be investigated. The catalyst for the production of both ethanol and IPA is composed of silica impregrated with phosphoric acid. The propylene feed rate for the commercialized ethanol reactor can be estimated from the pilot reactor discussed above to be 20,800 kgmol/hr. In this case, the capacity of IPA production is about 30,000MT/yr based on 6.0 mole % yield.

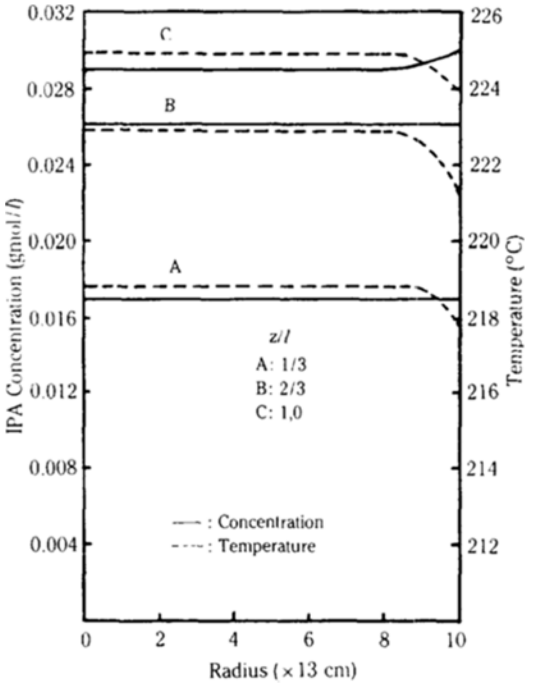


Fig. 5. Radial profiles of IPA concentration and temperature (β = 10, U = 0.2 Btu/hr·ft^2·°F & k_1 = 10.7 × 10^{-3} gmol/hr·atm^2·kg cat).

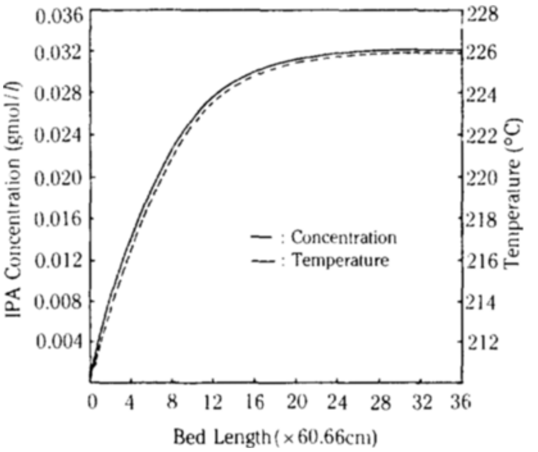


Fig 6. Equilibrium concentration and temperature (β = 10, U = 0.2 Btu/hr·ft^2·°F & k_1 = 10.7 × 10^{-3} gmol/hr·atm^2·kg cat).

In Fig. 4 and Fig. 5, the profiles of IPA concentration and temperature in the reactor are illustrated for the case of utilizing the above ethanol reactor for IPA production. The IPA concentration and temperature at reactor outlet are 0.030 gmol/*l* (about 6.0 mole % yield) and 224.5 °C, respectively. These two figures also show that the hot spot where the temperature is especially high is not formed in the reactor. Although the heat of reaction of IPA synthesis (12 kcal/gmol) is larger than that of ethanol synthesis (10 kcal/gmol) by about 20%, it can be concluded that there will be no problem in temperature control for producing IPA with ethanol reactor.

To investigate the equilibrium concentration and temperature, the above ethanol reactor is simulated by enlarging the reactor length. Its results are shown in Fig. 6. The equilibrium concentration and temperature are found to be 0.032 gmol/*l* (about 6.4 mole % yield) and 226 °C, respectively. In the production of IPA using the above ethanol reactor, the IPA concentration at reactor outlet reaches to about 93 percent of equilibrium concentration. The present reactor length may be said to be well justified by considering the investment cost and utility cost. In order to obtain the equilibrium concentration, a reactor whose length is at least twice as large as that of the ethanol reactor should be used.

CONCLUSION

The mathematical model for fixed-bed catalytic reactors was numerically simulated for the pilot reactor of IPA synthesis, and the results of experiments and simulations were compared. The two results were found to agree well. This provides us with more confidence in our pilot work.

This profiles of IPA concentration and temperature in the reactor for the production of IPA from a commercialized ethanol reactor were analyzed by the numerical simulation, and the problem in scale-up from pilot plant being investigated. It was found that the ethanol reactor can be used without problems for IPA synthesis. The operation conditions of IPA synthesis were established.

NOMENCLATURE

C : product concentration (gmol/l)
C_o : initial concentration of reactant (gmol/l)
C_p : specific heat (cal/g·°C)
D_r : radial diffusivity (cm^2/sec)
D_z : axial diffusivity (cm^2/sec)
d_p : diameter of catalyst pellet (cm)
K_p : equilibrium constant (atm^{-1})
k_e : effective thermal conductivity (cal/sec·cm·°C)
k_1 : reaction rate constant (gmol/hr·atm^2·kg cat)
k_2 : reaction rate constant (gmol/hr·atm·kg cat)
k' : constant for the equation of velocity profile
L : reactor length (cm)
P_{IA} : partial pressure of IPA (atm)
P_P : partial pressure of propylene (atm)
P_W : partial pressure of water (atm)
P_{er} : radial Peclet No.
P_{ez} : axial Peclet No.
R : radius of reactor (cm)
R_p : reaction rate (gmol/hr·kg cat)
r : distance from the axis to the wall of reactor (cm)
T : temperature (°K)
T_b : bulk temperature of the reactants (°K)
T_o : initial temperature (°K)
T_s : temperature of the coolant or heating medium (°K)
U : overall heat transfer coefficient (cal/sec·cm^2·°C)
u : superficial velocity (cm/sec)
u_o : average superficial velocity (cm/sec)
z : distance from the reactor inlet (cm)

Greek Letters

α : mole ratio of water to propylene
β : constant
ΔH: heat of reaction (cal/gmol)
ρ : reactant density (g/cm^3)
ρ_B : bed density (g/cm^3)
μ : reactant viscosity (g/cm·sec)

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