APPLICABILITY OF DISPERSION MODEL TO A PACKED BED REACTOR WITH AN IRREVERSIBLE CHEMICAL REACTION OF THE 2ND ORDER*

KEI MIYANAMI, MUNETAKE SATO AND TAKEO YANO

Department of Chemical Engineering, University of Osaka Prefecture, Sakai, Japan

Applicability of the one-dimensional dispersion model as a flow model of a packed-bed chemical reactor is discussed for the hydrolysis of ethyl acetate by sodium hydroxide. An experimental technique, easily applied by purging one of the reactants concerned from a flow system with the other, is developed to study fluid mixing effectively in a flow system accompanying chemical reaction. Called dual-step response method, it is proved to be an effective method.

Introduction

Fluid mixing in a packed bed is macroscopically expressed by a dispersion model, and the degree of mixing in the bed is represented by a model parameter, the longitudinal dispersion coefficient. Various studies of fluid mixing in a variety of packed beds have been made experimentally and theoretically. Dynamic and static characteristics of the packed bed as a chemical flow reactor, however, have been studied only theoretically by applying various flow models^{4,5,8}.

In this paper, applicability of the one-dimensional dispersion model (1-DDM)¹⁰ to a packed-bed chemical reactor is studied experimentally for cases where an irreversible chemical reaction of the 2nd order occurs in the bed.

Experimental

Fig. 1 shows a schematic flow diagram of the apparatus. The details of the packed-bed reactor are given in **Fig. 2**. The reactor consists of glass tubes of 50 mm i.d. and lengths of 250, 500 and 1000 mm, packed randomly with 10mm ceramic Raschig rings or 7mm glass spheres. The void fractions were 0.537 when packed with the Raschig rings and 0.399 with the spheres.

Three independent liquid pumping systems were prepared for circulation of liquids. Flow rates of the liquids were adjusted by needle valves V_1 , V_2 and V_3 , measured by flow meters (rotameters) R_1 , R_2 and R_3 , respectively, and then the liquids were fed into the reactor.

To apply step inputs of the concentrations in the fluid flow to the reactor, the liquids from each of the three pumping systems into the reactor were interchanged through solenoid valves V_4 , V_5 and V_6 , which can be activated simultaneously. To avoid any change of flow rates on the introduction of the step inputs, variable-height overflow tubes O_4 and O_5 were attached to the outlets of flow meters R_1 and R_2 , respectively. While the liquid from tank T_1 is flowing into the reactor, the liquid from T_2 is overflowing at a predetermined rate through O_5 until the solenoid valves are activated. After activation, the liquid from T_1 in turn overflows through O_4 and the liquid of T_2 enters the reactor.

The liquid leaving the reactor is exhausted through overflow tube O_6 .

1. Tracer step response

Fluid mixing in the packed bed was observed by means of tracer step responses and identified with the 1-DDM.

Potassium chloride solution (KCl) of 0.01 N was used for the tracer. Water was stored in T_1 and the KCl solution in T_2 . The step change of KCl concentration was introduced into the reactor by activating or deactivating the solenoid valves simultaneously. The KCl concentrations of entering and leaving solutions were determined continuously by measuring the electric conductivities of the solutions with instruments similar to the one described by Cairns and Prausnitz². The conductivity cell consists of a pair of platinum wires of 2 mm diameter with 7 mm aperture. Two such cells, C_1 and C_2 , are installed at the inlet and the outlet of the reactor, respectively.

2. Dual-step response with the 2nd order irreversible chemical reaction¹¹

To test whether the 1-DDM can be used to interpret the dynamic behavior of the packed bed as a chemical

* Received on September 23, 1971

Presented at the 32nd Annual Meeting of the Soc. of Chem. Engrs., Japan, at Tokyo, April, 1967.

- B : packed-bed reactor
 C₁, C₂: electric conductivity cell
 M : pre-mixer
 P₁₋₃: pump
 R₁₋₃: flow-rate meter
 T₁₋₃: liquid-storage tank
 V₁₋₃: needle valve
 V₄₋₆: solenoid sliding valve
 O₁₋₆: overflowing tube

Fig. 1 Schematic diagram of the experimental apparatus

flow reactor, the reaction

was performed in the bed. This reaction is 2nd order irreversible, and the rate equation is given by¹⁴⁾

$$\frac{d[\text{NaOH}]}{dt} = -k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{NaOH}]$$

$$\log_{10} k = -1780/T_r + 0.00754T_r + 2.75 \quad (2)$$

Ethyl acetate solution of 0.1 mol/l was stored in T₁ and sodium hydroxide solution in T₂. The concentration of the NaOH solution was varied from 0.005 to 0.2 N. By simultaneous activation or deactivation of the solenoid valves, the fluid stream into the reactor was changed from the ester solution to the NaOH solution (input-B in Fig. 3), or *vice versa* (input-A in Fig. 3). With this procedure, step changes of the concentrations of both ester and sodium hydroxide occur in the fluid stream into the reactor, as shown in Fig. 3 by the solid lines. Consequently, this method may be called the "dual-step response method". The responses were followed in terms of NaOH concentration at the outlet of the reactor by measuring the electric conductivity of the leaving solution. The responses are shown in Fig. 3 by dotted lines.

3. Conversion of NaOH at steady state

Static characteristics of the packed bed as a chemical flow reactor are also important to estimate the conversion of a reaction. Steady-state experiments were done as follows: Ethyl acetate solution was stored in T₁ and sodium hydroxide solution in T₃. These two liquids were well mixed by the premixer M and then fed into the reactor. When the indications of the electric conductivity meters at the inlet and the outlet of the reactor became constant under a constant flow rate of the reactants, the output voltages were recorded. The liquid flow was then stopped. After the indications became constant again, they were also recorded.

- 1: glass tube
 2: covers
 3: sieve plates
 4: liquid distributor
 5: platinum electrodes
 6: sponge rubber
 7: flange supporters
 8: gaskets

Fig. 2 Details of the packed-bed chemical reactor

Fig. 3 Inputs applied to the reactor (dual-step input)

From these voltages with the inlet concentrations of NaOH and ester, the conversion of NaOH at the outlet of the reactor can be calculated⁶⁾.

Results and Discussion

1. Tracer step response (calculations of the flow model parameters)

The variance σ^2 (the 2nd order moment around the mean) of the residence time distribution of fluid in the reactor is defined as

$$\sigma^2 = \frac{\overline{t^2}}{(\bar{t})^2} - 1 \quad (3)$$

where

$$\bar{t} = \int_0^\infty \Psi(t) dt, \quad \bar{t^2} = 2 \int_0^\infty t \Psi(t) dt \quad (4)$$

$$\Psi(t) = 1 - F(t) \quad (5)$$

The value of σ^2 was calculated by numerical integration of the normalized tracer step response, $F(t)$ ¹³⁾.

The model parameter Pe of the 1-DDM was evaluated from the relation:

$$\sigma^2 = 2(Pe - 1 + e^{-Pe})/Pe^2 \quad (6)$$

by means of the Newton-Raphson method.

The tracer step response of the 1-DDM was calculated by means of Brenner's procedure¹⁾ with the authors' modification¹²⁾.

In Fig. 4, a comparison is made between typical experimental and model responses. The extent in Fig. 4

Fig. 4 Tracer step responses of the packed-bed reactor

Fig. 5 Longitudinal dispersion coefficient of the packed-bed chemical reactor

to which the model response was in agreement with the experimental one did not depend on changes of packing materials, length of the packed bed reactor or flow rate of the liquid.

Cairns and Prausnitz²⁾ arranged their experimental results as plots of the longitudinal dispersion coefficient E against $4m\bar{u}$. E is calculated from the relation

$$E = \bar{u}l/Pe, \quad (7)$$

where $\bar{u}$ is given as

$$\bar{u} = 4f/\pi D^2 \varepsilon \quad (8)$$

and $4m$ is the hydraulic radius of the packing. Fig. 5 shows the relation between E and $4m\bar{u}$. In this figure, the results by Cairns & Prausnitz²⁾, Carberry & Bretton³⁾ and Strang & Geankoplis⁹⁾ are also included for comparison. The present results are in good agreement with the data already published, and E is approximately proportional to $4m\bar{u}$. E can be correlated with $4m\bar{u}$ by the relation

$$E = 3.70 [4m\bar{u}]^{1.12} \quad (9)$$

Fig. 6 Dual-step responses of the packed-bed chemical reactor with the 2nd order reaction

This correlation is based on the experimental data of about 150 runs. The maximum deviation between the values of E calculated from Eq. (9) and the experimental ones is about ± 30 percent.

2. Dual-step response with the 2nd order irreversible chemical reaction

It appears from the results in 1) that fluid mixing in the packed bed could be expressed by the 1-DDM. If the fluid entering the bed is changed instantaneously from a solution of species A to that of species B and there occurs an irreversible reaction of the 2nd order between A and B, the responses of A and B are governed by Eq. (10):

$$\left. \begin{aligned} \frac{\partial c_A}{\partial \tau} &= \frac{1}{Pe} \frac{\partial^2 c_A}{\partial \xi^2} - \frac{\partial c_A}{\partial \xi} - \kappa_B c_A c_B \\ \frac{\partial c_B}{\partial \tau} &= \frac{1}{Pe} \frac{\partial^2 c_B}{\partial \xi^2} - \frac{\partial c_B}{\partial \xi} - \kappa_A c_A c_B \\ \text{at } \xi=0+, & \quad -\frac{1}{Pe} \frac{\partial c_A}{\partial \xi} = 1 - c_A \\ & \quad -\frac{1}{Pe} \frac{\partial c_B}{\partial \xi} = -c_B \\ \text{at } \xi=1-, & \quad \frac{\partial c_A}{\partial \xi} = 0, \quad \frac{\partial c_B}{\partial \xi} = 0 \\ \text{at } \tau=0, & \quad c_A=0, \quad c_B=1 \end{aligned} \right\} \quad (10)$$

In deriving Eq. (10), it is assumed that no fluid mixing occurs outside the bed. The parameters Pe , κ_A and κ_B in Eq. (10) can be evaluated from the experimental conditions. κ_A and κ_B were varied as $\kappa_A = 0.434 \sim 4.46$, $\kappa_B = 0.107 \sim 7.50$ for input-A and

$\kappa_A = 0.182 \sim 8.36$, $\kappa_B = 0.500 \sim 4.97$ for input-B.

Pe was estimated by Eq. (9). Eq. (10) was solved numerically by means of the quasilinearization method⁷⁾. In Fig. 6, a comparison is made between typical experimental responses and model responses.

If A and B were completely segregated, no reaction between them would take place. Then the experimental dual-step response might become the same as the tracer step response and deviate from the solution of Eq. (10). The deviation also occurs if the

Fig. 7 The definitions of τ_d and τ_r

Fig. 8 Comparison of τ_{de} with τ_{dm}

actual mechanism of fluid mixing in the bed differs from that assumed in the 1-DDM. To discuss the applicability of the 1-DDM to the interpretation of the dual-step responses, the characteristics of the response τ_r and τ_d , shown in Fig. 7 schematically, were evaluated from the experimental responses (they are denoted by τ_{re} and τ_{de}) and the corresponding responses of the model (τ_{rm} and τ_{dm}). τ_r is the time interval between the points where the tangent line drawn at the inflection point of the response curve intersects the lines of c_A or $c_B=0$ and c_A or $c_B=1$, respectively, and τ_d is the time at which the tangent intersects the line of c_A or $c_B=0$. Hence, τ_r represents the rise time of the response and τ_d , the dead time. A pair of τ_r and τ_d can characterize a dual-step response. In Fig. 8, a comparison is made between τ_{dm} and τ_{de} , and τ_{rm} is compared with τ_{re} in Fig. 9. From these two figures, it is clear that, although the estimates of τ_d by the model are in agreement with the observed ones to a precision of ± 10 percent, the estimates of τ_{re} deviate from the observed ones by ± 30 percent.

By the dual-step response method, the applicability of the 1-DDM to the packed bed reactor can easily be examined more strictly than by the tracer step response method.

3. Steady-state conversion of NaOH

Recording of the output voltages from the electric conductivity meters is shown in Fig. 10. Since these

Fig. 9 Comparison of τ_{re} with τ_{rm}

Fig. 10 Recording of the output voltages of the electric conductivity meters at steady state

voltages, e_0 , e and e_∞ are proportional to the electric conductivities of the respective solutions, the conversion of NaOH η_e can be calculated by⁶⁾

$$\eta_e = \frac{e_0 - e}{e_0 - e_\infty} \alpha \quad (11)$$

if the gains of the meters are adjusted to a certain identical level in advance.

Now, if one assumes the 1-DDM for fluid mixing in the packed bed, the model equation of the steady state becomes

$$\begin{aligned} \frac{1}{Pe} \frac{d^2 c_A}{d\xi^2} - \frac{dc_A}{d\xi} - \kappa_A c_A (c_A - 1 + \alpha) &= 0 \\ \text{at } \xi=0+, \quad \frac{1}{Pe} \frac{dc_A}{d\xi} &= c_A - 1 \\ \text{at } \xi=1-, \quad \frac{dc_A}{d\xi} &= 0 \end{aligned} \quad (12)$$

Eq.(12) was solved numerically by the finite-difference method and the multi-dimensional Newton-Raphson method. The conversion of NaOH is given by

$$\eta_m = 1 - c_A|_{\xi=1} \quad (13)$$

In Fig. 11, the experimental results η_e are compared with the conversions calculated η_m . Agreement between them is obtained within ± 5 percent deviation except for small conversions, where the measure-

Fig. 11 Comparison of η_e with η_m

ment error in electric voltage becomes appreciable. This better agreement than the above described results shows that the 1-DDM can be applied to predict steady-state conversion of the reaction at the outlet of a packed-bed reactor.

In the steady-state experiments, a mixture of reactants concerned, say A and B, is fed into the packed-bed reactor, and fluid mixing in the reactor contributes partly to the steady-state conversion at the outlet. On the other hand, in the dual-step response method, the reactant A already present in the process is replaced gradually with the reactant B, for example. Therefore, A and B are mixed only in the packed bed, so that fluid mixing in the reactor fully affects the dual-step responses at the outlet. In effect, the contribution of fluid mixing in the bed to steady-state conversion is different from that to the transient dual-step response.

Conclusion

The applicability of the one-dimensional dispersion model to the packed-bed chemical reactor is investigated through the results of experiments regarding tracer step responses, dual-step responses with 2nd order irreversible chemical reaction (a saponification of ethyl acetate) and steady-state conversions of the reaction.

The steady-state conversion of the reactor can be well estimated by the model. The model, however, fails to interpret the dynamic behavior of the packed bed with reaction. It is also noted that the dual-step response method is a useful method of testing the applicability of a flow model to a continuous flow system when a chemical reaction is involved.

Acknowledgement

All the numerical calculations in this paper were carried out at the Computer Center, University of Tokyo. This

study was financially supported in part by the foundation of the Ministry of Education of Japan.

Nomenclature

c	= concentration of a chemical species, normalized by the respective inlet concentration	[—]
C_{A0}	= inlet concentration of ethyl acetate (input-A) or sodium hydroxide (input-B)	[mol/l]
C_{B0}	= inlet concentration of sodium hydroxide (input-A) or ethyl acetate (input-B)	[mol/l]
e	= output electric voltage of the electric conductivity meter, defined in Fig. 10	[volt]
E	= longitudinal dispersion coefficient	[cm ² /sec]
f	= volumetric flow rate	[cm ³ /sec]
$F(t)$	= normalized response of reactor to step input of tracer, integral of residence time distribution	[—]
k	= rate constant of the 2nd order chemical reaction, defined in Eq.(2)	[l/mol·sec]
l	= axial length of the packed bed	[cm]
Pe	= $\bar{u}l/E$, Peclet number	[—]
t	= time	[sec]
$\bar{t}$	= mean residence time, $l/\bar{u}$	[sec]
T_r	= temperature	[°K]
$\bar{u}$	= interstitial velocity	[cm/sec]
x	= axial coordinate in the packed bed	[cm]
α	= ratio of the inlet concentration of ethyl acetate to that of sodium hydroxide	[—]
ε	= void fraction	[—]
$\Psi(t)$	= $1 - F(t)$	[—]
κ_A	= $kC_{A0}l/\bar{u}$	[—]
κ_B	= $kC_{B0}l/\bar{u}$	[—]
σ^2	= variance of the residence time distribution	[—]
τ	= $t/\bar{t}$	[—]
η	= conversion of sodium hydroxide	[—]
ξ	= x/l	[—]
<Subscripts>		
A	= ethyl acetate (input-A) or sodium hydroxide (input-B)	
B	= sodium hydroxide (input-A) or ethyl acetate (input-B)	
e	= experimental	
m	= model	

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