Proceedings of The 1995 Regional Symposium on Chemical Engineering
Bangkok, October 1995

Application of *tert*-Butanol Dehydration Reaction to Chemical Heat Transport

Yuji Kiguchi, Hidetoshi Sekiguchi, Takayuki Watanabe
and Atsushi Kanzawa

Dept. of Chem. Eng., Tokyo Institute of Technology
O-okayama, Meguro-ku, Tokyo 152, Japan

ABSTRACT

The reaction system of *tert*-butanol/isobutene/water has been applied to chemical heat transport. In this study, the heat transfer with endothermic *tert*-butanol dehydration reaction at the heat supply side was investigated. This reaction converts *tert*-butanol into isobutene and water in liquid phase. The produced isobutene is vaporized as this reaction proceeds. The heat transport is attributed to the heat of reaction and the latent heat of isobutene in this reaction system.

The experiments were carried out obtaining the conversion and the heat flow in a catalyst bed reactor of a heat exchanger type. The initial composition of heating medium was pure *tert*-butanol. It was noticed that the heat flow with this reaction was much higher than without reaction. These results indicate that the dehydration reaction promotes the heat transfer rate. This is due to an increase in the temperature difference between the heating medium and the wall because of the reaction. The possibility of the effective heat transport with this reaction system was suggested.

1. INTRODUCTION

Heat recovery systems are very important in connection with environmental problem. A chemical heat transport system (chemical heat pipe) has been proposed to make good use of waste heat.

A chemical heat transport system is using a cyclic thermochemical process for transporting heat. A schematic description of chemical heat transport system is given in Fig. 1. The thermal energy is converted into chemical energy by an endothermic chemical reaction at the heat supply side. The energy is transported in the form of chemical substances. The transported chemical energy is reconverted into thermal energy releasing the reaction heat by an exothermic reverse reaction at the heat demand side. Several chemical reaction systems have been considered to be used for heat

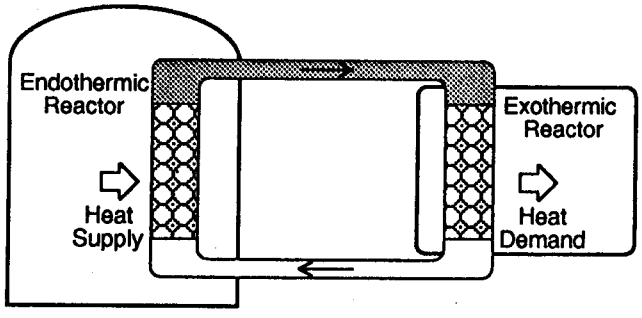

FIGURE 1. Schematic description of chemical heat transport system.

transport, for example, CH_4-H_2O/CO-H_2 system [1], CH_4-CO_2/CO-H_2 system [2,4], SO_2/SO_3 system [6,7] and N_2O_4/NO_2 system [5]. These systems are gas phase reactions at high temperature level. However, few studies have ever been tried to use chemical reaction system with liquid phase. Energy density in liquid is greater than in gas.

The reaction system of *tert*-butanol/isobutene/water has been applied to chemical heat transport[3].

$$(CH_3)_3COH\ (l) \rightleftharpoons (CH_3)_2CCH_2\ (l) + H_2O\ (l) \qquad (1)$$
$$\Delta H_R = 38.0\times10^3\ J\cdot mol^{-1}$$

tert-Butanol dehydration reaction is endothermic, and reverse reaction is exothermic. In this study, the heat transfer with endothermic *tert*-butanol dehydration reaction at the heat supply side was investigated. This reaction converts *tert*-butanol into isobutene and water in liquid phase. The produced isobutene is vaporized as this reaction proceeds. It was considered that the vaporization of isobutene influenced the heat transport.

$$(CH_3)_2CCH_2\ (l) \rightleftharpoons (CH_3)_2CCH_2\ (g) \qquad (2)$$
$$\Delta H_V = 18.6\times10^3\ J\cdot mol^{-1}$$

The experiments were carried out using a catalyst bed reactor of a heat exchanger type. Numerical calculations based on a two-dimensional model were carried out and the results were compared with the experimental ones. The purpose was to estimate the heat transfer characteristics in this reaction under the condition of extremely small temperature difference between heat source and heating medium.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental apparatus is shown in Fig. 2. The catalyst bed reactor, the inner tube, was made of copper tube with 12 mm O.D., 10 mm I.D. The catalyst was Amberlyst 15E. The bed length was 0.25 to 1 m. The outer tube was made of vinyl chloride tube with 32 mm O.D., 24 mm I.D., and was wrapped in insulating material.

The water as heat source flowed into the outer tube. The heating medium flowed into the catalyst bed reactor after steady state condition of the water. The initial composition of heating medium was pure *tert*-butanol. The water temperature Tw and the initial temperature of heating medium T_{in} were 70 ℃ in this experiment. The temperatures of heating

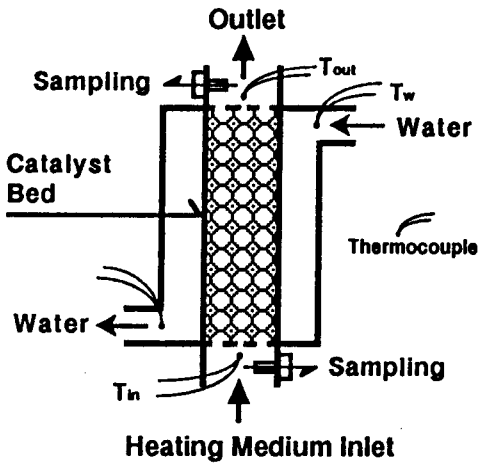

FIGURE 2. Experimental apparatus.

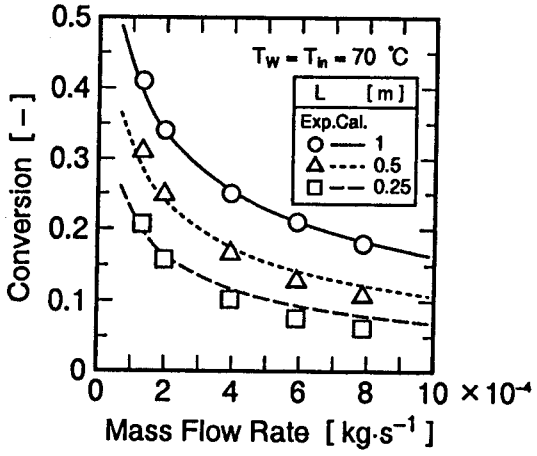

FIGURE 3. Effect of mass flow rate of heating medium on conversion.

medium were measured by copper-constantan thermocouples at the inlet and the outlet of the catalyst bed. The heating medium was sampled from the outlet the catalyst bed, and was analyzed by a gas chromatograph.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The conversion is estimated by measuring the heating medium composition change in the catalyst bed. The effect of mass flow rate of heating medium on conversion is shown by keys in Fig. 3. The calculated results showed by lines are explained later. The conversion increases with decreasing mass flow rate of heating medium because of increasing the residence time of heating medium in the catalyst bed.

In this experiment, a generation of gas was observed. The gas was analyzed by a gas chromatograph. Most of the gas composition was isobutene. The generated gas is assumed to be only isobutene in this study.

The heat transport is attributed to the heat of reaction and the latent heat of isobutene in this reaction system. The heat of reaction and the latent heat of isobutene are estimated by the composition change of heating medium in the catalyst bed.

$$Q_R = \dot{m} X_A \frac{\Delta H_R}{M_A} \tag{3}$$

$$Q_V = \dot{m} X_A Y_B \frac{\Delta H_V}{M_B} \tag{4}$$

where Y_B is the vapor fraction of isobutene. The sensible heat is estimated by the temperature change of heating medium in the catalyst bed.

$$Q_S = \dot{m} c_p (T_{out} - T_{in}) \tag{5}$$

The heat flow of this reaction system is defined as:

$$Q_T = Q_S + Q_R + Q_V \tag{6}$$

The effect of mass flow rate of heating medium on heat flow is shown by keys in Fig. 4. The heat flow increases with length of catalyst bed. Representative results with the detail of the heat flow are shown in Fig. 5. The outlet temperature of heating medium was about 2 to 5 degrees lower than the inlet one because of the influence of the endothermic reaction and the vaporization of isobutene. Thus, the sensible heat was negative in the case of same temperature both T_W and T_{in}.

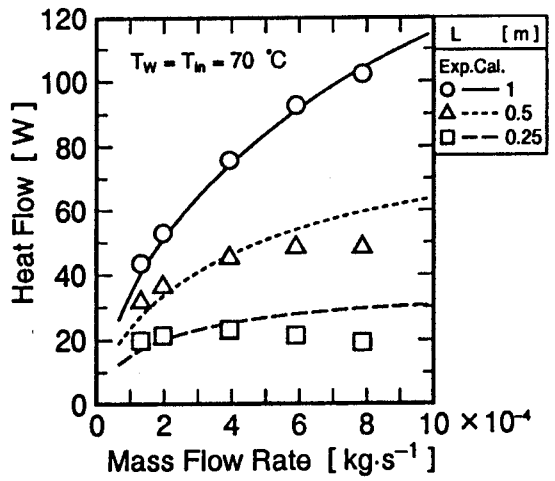

FIGURE 4. Effect of mass flow rate of heating medium on heat flow.

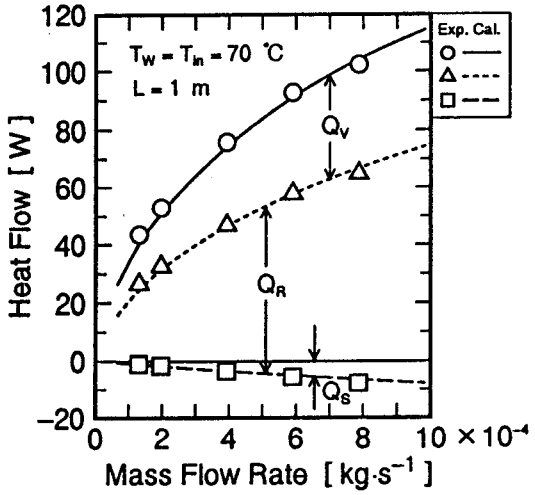

FIGURE 5. Detail of heat flow.

4. NUMERICAL CALCULATION

The numerical model of heating medium is presented in Fig. 6. The numerical calculation were based on the following assumptions: 1)The temperature of heating medium flowing through the catalyst bed is same as the catalytic particles at each location; 2)Axial conduction of heat and diffusion of mass can be neglected; 3)The flow of heating medium in the catalyst bed is piston flow; 4)In gas phase, heat transfer and reaction are ignored; and 5)The pressure is 1 atm and constant. The mass and energy balances are given by:

$$\rho u \frac{\partial X_A}{\partial z} = \frac{\alpha \rho D_r}{r} \frac{\partial}{\partial r}\left(r \frac{\partial X_A}{\partial r}\right) + \frac{\alpha \rho_b (-R_A) M_A}{C_{A0}} \tag{7}$$

$$\rho c_p u \frac{\partial T}{\partial z} = \frac{\alpha k_{er}}{r} \frac{\partial}{\partial r}\left(r \frac{\partial T}{\partial r}\right) + \alpha \rho_b (-R_A)(-\Delta H_R) + \alpha R_V (-\Delta H_V) \tag{8}$$

where α is the liquid fraction of heating medium. α is defined from mass of components in liquid and gas phase. The boundary conditions associated with equations 7 and 8 are as follows:

$$z = 0 \; ; \; T = T_0(r) \; , \; X_A = X_{A0}(r) \tag{9}$$

$$r = 0 \; ; \; \frac{\partial T}{\partial r} = 0 \; , \; \frac{\partial X_A}{\partial r} = 0 \tag{10}$$

$$r = r_W \; ; \; -k_{er}\left(\frac{\partial T}{\partial r}\right) = h_W (T - T_W) \; , \; \frac{\partial X_A}{\partial r} = 0 \tag{11}$$

where Tw used same expression of water temperature is wall temperature. In the experiment, water temperature difference between inlet and outlet of the heat exchanger was extremely small. Thus, the wall temperature is presumed to be constant in this calculation.

The conversion and temperature of heating medium can be calculated from the finite difference form by use of the explicit method.

5. CALCULATED RESULTS AND DISCUSSION

The results are presented by lines in Figs. 3~5. These results show good agreement with experimental ones. The validity of the numerical model is checked by comparisons of calculated and experimental results.

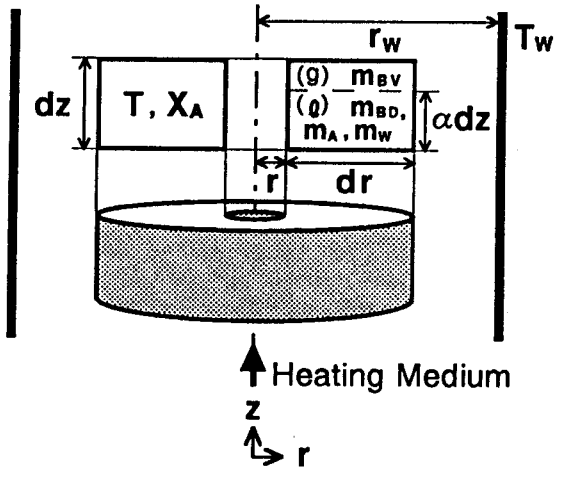

FIGURE 6. Numerical calculation model.

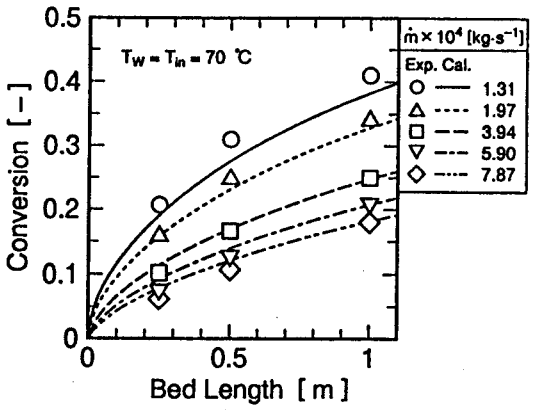

FIGURE 7. Conversion distribution in the axial direction of the catalyst bed.

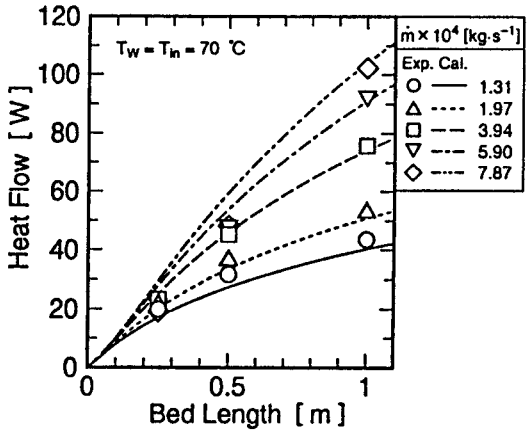

FIGURE 8. Heat flow distribution in the axial direction of the catalyst bed.

The calculated results for the conversion and the heat flow distributions in the axial direction of the catalyst bed are shown in Figs. 7 and 8, respectively. The heat flow increases with mass flow rate of heating medium in spite of low conversion. This is because mass flow rate of heating medium contributes much to the heat flow.

The typical results with the detail of the heat flow distribution in the axial direction of the catalyst bed are shown in Fig. 9. The sensible heat has a minimum value at the vicinity of 0.15 m point of the catalyst bed. The heat of reaction and the latent heat of isobutene increase with length of catalyst bed because of proceeding reaction.

The heat transfer mechanism of this reaction system was considered by comparisons of the case with and without reaction.

The heat flow of differential length dz can be written as:

$$dQ = 2\pi r_w \cdot dz \cdot h_z (T_w - T_m) \qquad (12)$$

where h_z is apparent local heat transfer coefficient and T_m is mean temperature of heating medium. In the case without reaction, no heat transfer will occur under the condition of no temperature difference

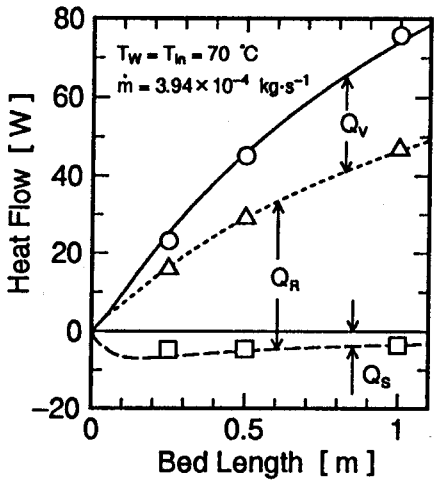

FIGURE 9. Detail of heat flow distribution in the axial direction of the catalyst bed.

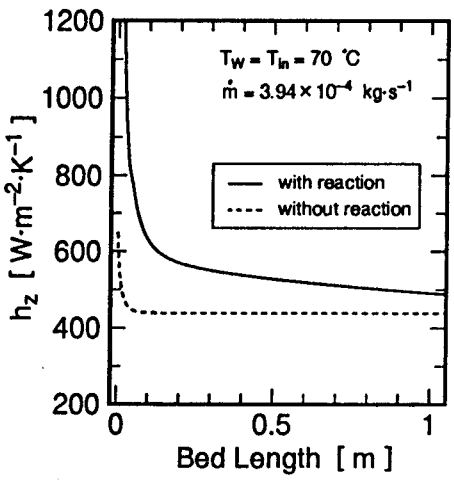

FIGURE 10. Local heat transfer coefficient distribution in the axial direction of the catalyst bed : comparison between the results with and without chemical reaction.

between heat source and heating medium. In the case with reaction, the endothermic reaction causes a drop of heating medium temperature. The vaporization of isobutene causes more drop of the temperature in this reaction system. Because of a promoting force of the temperature difference between heat source and heating medium will be generated, heat transfer will occur in the case with reaction.

The typical calculated results for the apparent local heat transfer coefficient are represented in Fig. 10. The results without reaction were calculated under the condition that the initial temperature of heating medium was 69.9 ℃. In the case with reaction, h_z was influenced by reaction. The apparent local heat transfer coefficient with chemical reaction was higher than without reaction.

These results indicate that the dehydration reaction promotes the heat transfer rate. This is due to an increase in the temperature difference between the heating medium and the wall because of the reaction. For reasons mentioned above, it was possible to apply this reaction system to effective heat transport.

ACKNOWLEDGEMENTS

This research was supported by a grant from Tanikawa Fund Promotion on Thermal Technology.

NOMENCLATURE

C_i = mass fraction of i species [-]
c_p = specific heat at constant pressure [$J \cdot kg^{-1} \cdot K^{-1}$]
D_r = diffusion coefficient in the radial direction [$m^2 \cdot s^{-1}$]
ΔH_R = heat of reaction [$J \cdot mol^{-1}$]
ΔH_V = latent heat of isobutene [$J \cdot mol^{-1}$]
h_w = apparent heat transfer coefficient at the wall [$W \cdot m^{-2} \cdot K^{-1}$]
h_z = apparent local heat transfer coefficient [$W \cdot m^{-2} \cdot K^{-1}$]
k_{er} = effective thermal conductivity in the radial direction [$W \cdot m^{-1} \cdot K^{-1}$]
L = bed length [m]
M_i = molecular weight of i species [$kg \cdot mol^{-1}$]
m = mass [kg]
$\dot{m}$ = mass flow rate [$kg \cdot s^{-1}$]
Q = heat flow [W]
R_A = reaction rate [$mol \cdot (kg\text{-}cat)^{-1} \cdot s^{-1}$]
R_V = vaporization rate of isobutene [$mol \cdot m^{-3} \cdot s^{-1}$]
r = distance in radial direction [m]
T = temperature [℃]
T_m = mean temperature of heating medium [℃]
u = axial velocity [$m \cdot s^{-1}$]
X_A = conversion [-]
Y_B = vapor fraction of isobutene [-]
z = distance in axial direction [m]

<Greek letters>

α = liquid fraction of heating medium [-]
ρ = density of heating medium [$kg \cdot m^{-3}$]
ρ_b = apparent density of catalyst in packed bed [$kg \cdot m^{-3}$]

<Subscripts>

A = *tert*-butanol
B = isobutene
D = dissolution
in = inlet
out = outlet
R = reaction
S = sensible heat
T = total
V = vaporization
W = water or wall

REFERENCES

1. Fedders,H. and Hohlein,B. : *Int.J.Hydrogen Energy*,7,793 (1982).
2. Fraenkel,D., Levitan,R. and Levy,M. : *Int.J.Hydrogen Energy*,11,267 (1986).
3. Kiguchi,Y., Watanabe,T. and Kanzawa,A. : *Kagaku Kogaku Ronbunshu*,21,746 (1995).
4. Levy,M., Levitan,R., Meirovitch,E., Segal,A., Rosin,H. and Rubin,R. : *Solar Energy*, **48**,395 (1992).
5. Ragaini,V. : *Solar Energy*,**29**,535 (1982).
6. Zeng,W.P., Matsuda,H. and Hasatani,M. : *Nippon Kagaku Kaishi*,**8**,1267 (1988).
7. Zeng,W.P., Matsuda,H. and Hasatani,M. : *Kagaku Kogaku Ronbunshu*,**17**,441 (1991).