

Heat-Transfer Characteristics in *tert*-Butanol Dehydration Reaction Used for Heat Transport

Yuji Kiguchi, Takayuki Watanabe, and Atsushi Kanzawa
Department of Chemical Engineering
Tokyo Institute of Technology

The reaction system of *tert*-butanol/isobutene/water was considered for use in chemical heat transport. In this study, the heat-transfer characteristics in an endothermic *tert*-butanol dehydration reaction which occurred in the heat-supply side of this reaction system was investigated. The heat flow was obtained by measuring the reactant composition change and temperature change in the catalyst bed. The heat flow consists of reaction heat, the latent heat of isobutene, and sensible heat in this reaction system. Numerical calculations based on a two-dimensional model were carried out and the results showed good agreement with experiment. It was noticed that the heat flow with chemical reaction was much higher than without reaction. These results indicated that the dehydration reaction promoted the heat-transfer rate, because of the increase in temperature difference between the heating medium and the wall by making use of chemical reaction for a heat transport. The apparent local heat-transfer coefficient with chemical reaction was higher than without reaction. The possibility of a high efficiency heat transport which used this reaction system was suggested.

Key words: Heat transfer, chemical reaction, heat transport, catalyst bed, endothermic reaction, 2-methyl-2-propanol

1. Introduction

Heat-recovery systems are very important in connection with global environmental problems. Chemical processes have advantages of an effective utilization of thermal energy. Chemical heat-transport systems (chemical heat pipes) have been proposed to make good use of waste heat.

A chemical heat-transport system uses a cyclic thermochemical process for transporting heat. In this system, 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. There is little en route heat loss from the heat transport in this system. A chemical heat pipe can transport much thermal energy for a long distance as compared with a conventional transport system, for example using sensible heat and latent

heat [12]. Several chemical reaction systems have been considered to be used for heat transport; the well-known $\text{CH}_4\text{-H}_2\text{O}/\text{CO-H}_2$ system EVA-ADAM [2], the $\text{CH}_4\text{-CO}_2/\text{CO-H}_2$ system [3, 8], the SO_2/SO_3 system [13, 14] and the $\text{N}_2\text{O}_4/\text{NO}_2$ system [9]. These systems have gas-phase reactions at high temperature levels. However, few studies have ever been tried to utilize a chemical reaction system with a liquid phase, even though the energy density in a liquid is greater than in a gas.

The reaction system of *tert*-butanol/isobutene/water has been applied to chemical heat transport. In this study, the heat-transfer characteristics in an endothermic dehydration reaction of *tert*-butanol at the heat-supply side of this system were investigated by experiments and numerical calculations based on a two-dimensional model. The possibility of heat transport with this reaction system was examined by comparisons with a system without reaction.

Nomenclature

\bar{C}_i	: concentration of i species	$[\text{mol} \cdot \text{m}^{-3}]$
C_i	: mass fraction of i species	$[-]$
c_p	: specific heat at constant pressure	$[\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}]$
D_r	: diffusion coefficient in the radial direction	$[\text{m}^2 \cdot \text{s}^{-1}]$
ΔH_R	: heat of reaction	$[\text{J} \cdot \text{mol}^{-1}]$
ΔH_V	: latent heat of isobutene	$[\text{J} \cdot \text{mol}^{-1}]$
h_W	: apparent heat-transfer coefficient at the wall	$[\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}]$
h_z	: apparent local heat-transfer coefficient	$[\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}]$
K	: equilibrium constant	$[\text{m}^3 \cdot \text{mol}^{-1}]$
k_2	: apparent reaction rate constant	$[\text{m}^3 \cdot (\text{kg-cat})^{-1} \cdot \text{s}^{-1}]$
k_{er}	: effective thermal conductivity in the radial direction	$[\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}]$
L	: bed length	$[\text{m}]$
M_i	: molecular weight of i species	$[\text{kg} \cdot \text{mol}^{-1}]$
m	: mass	$[\text{kg}]$
\dot{m}	: mass flow rate	$[\text{kg} \cdot \text{s}^{-1}]$
Pe	: Peclet number	$[-]$
Q	: heat flow	$[\text{W}]$
R	: gas constant	$[\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]$
R_A	: reaction rate	$[\text{mol} \cdot (\text{kg-cat})^{-1} \cdot \text{s}^{-1}]$
R_V	: vaporization rate of isobutene	$[\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}]$
r	: distance in radial direction	$[\text{m}]$
T	: temperature	$[\text{°C}]$
T_m	: mean temperature of heating medium	$[\text{°C}]$
u	: axial velocity	$[\text{m} \cdot \text{s}^{-1}]$
W_i	: production rate of i species	$[\text{kg} \cdot \text{m}^{-3} \cdot \text{s}^{-1}]$
X_A	: conversion	$[-]$
Y_B	: vapor fraction of isobutene	$[-]$
z	: distance in axial direction	$[\text{m}]$
ρ	: density of heating medium	$[\text{kg} \cdot \text{m}^{-3}]$
ρ_b	: apparent density of catalyst in packed bed	$[\text{kg} \cdot \text{m}^{-3}]$

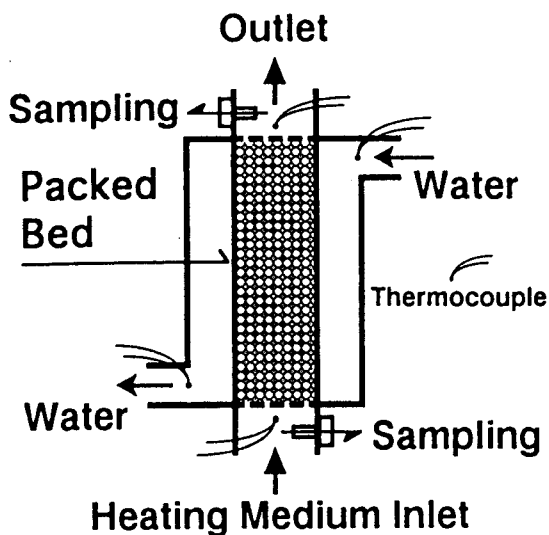


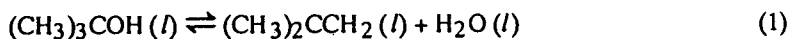
Fig. 1. Experimental apparatus.

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

2. Reaction System

A reaction system used for a heating medium in this study is shown in Eq. (1) [1, 7] (IUPAC name: 2-methyl-2-propanol/2-methylpropene/water).



$$\Delta H_R = 38.0 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$$

The dehydration reaction of *tert*-butanol is endothermic, and the reverse reaction is exothermic. Both reactions take place over acid catalysts in the liquid phase. In this study, the heat transfer

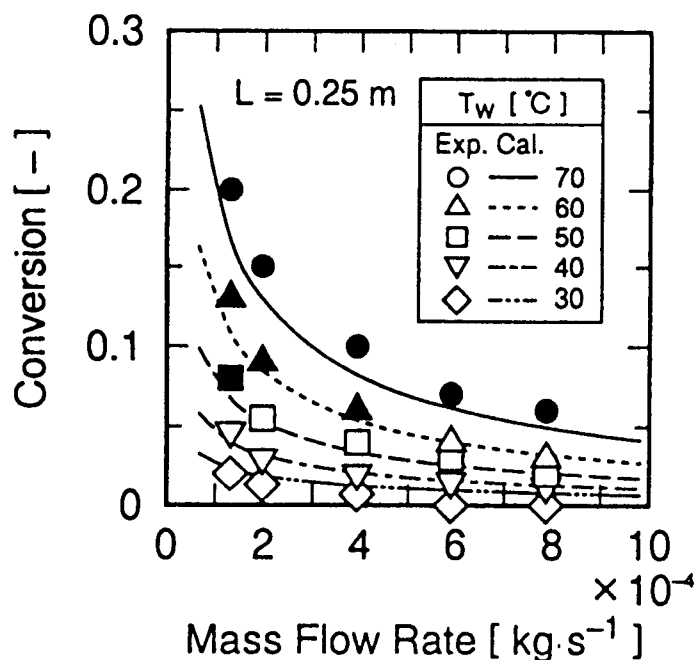
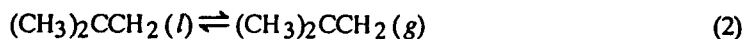


Fig. 2. Effect of mass flow rate of heating medium on conversion: comparison between the results of the experiments and the calculations (closed symbols: with vaporization of isobutene).

with endothermic dehydration reaction of *tert*-butanol has been investigated. The produced isobutene is vaporized as this reaction proceeds, because the vapor pressure of isobutene is higher than of *tert*-butanol and water. It is considered that the vaporization of isobutene influences the heat transport.



$$\Delta H_V = 18.6 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$$

3. Experiment

3.1 Experimental apparatus

Experiments were carried out using a catalyst bed reactor of a double-pipe heat-exchanger type. The experimental apparatus is shown in Fig. 1. The catalyst bed reactor, the inner tube, was made of a copper tube with 12-mm O.D. and 10-mm I.D. The bed length was 0.25 or 0.5 m. The outer tube was a PVC tube with 32 mm O.D. and 24 mm I.D., and was wrapped with an insulating

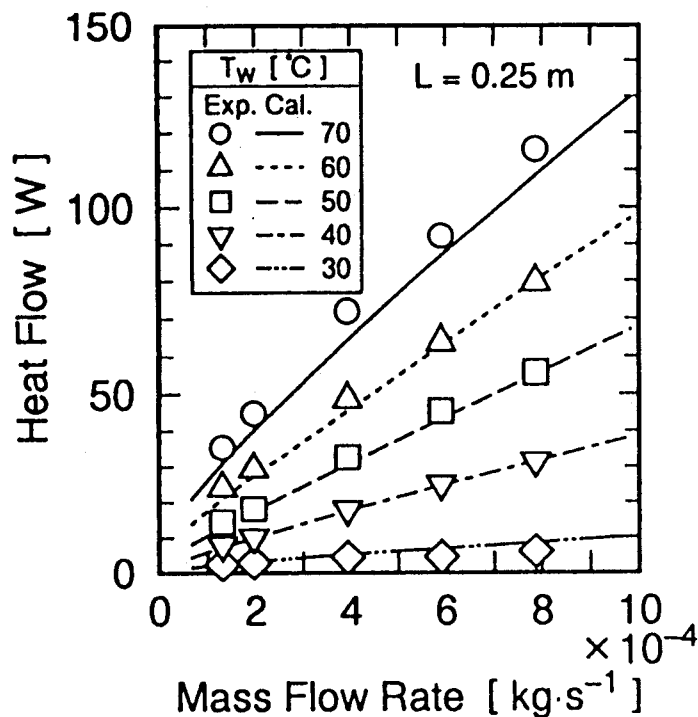


Fig. 3. Effect of mass flow rate of heating medium on heat flow: comparison between the results of the experiments and the calculations.

material. Solid acid catalysts were packed in the inner tube. The catalyst was Amberlyst 15E having a mean diameter of 0.7 mm.

The heating medium flowed into the catalyst bed reactor. The water as a heat source flowed through the outer tube in counterflow with the heating medium. The temperatures of the heating medium and the water were measured by T type (copper-constantan) thermocouples at the inlet and the outlet of the heat exchanger. The heating medium was sampled from the outlet of the catalyst bed and was analyzed by a gas chromatograph (Porapak Type N).

3.2 Experimental procedure

The water having a constant temperature flowed through the outer tube. The water temperature ranged from 30 to 70 °C. The heating medium having an initial temperature at 27 °C flowed into the catalyst bed reactor at a constant flow rate, after the water flowing outside of the catalyst bed reactor obtained a steady-state condition. The initial heating medium was pure *tert*-butanol. Temperatures and compositions of the heating medium were measured at the outlet of the catalyst bed. The experiments were carried out by changing the mass flow rate of the heating medium. The experiments without chemical reactions were also carried out by packing inert particles in the inner tube.

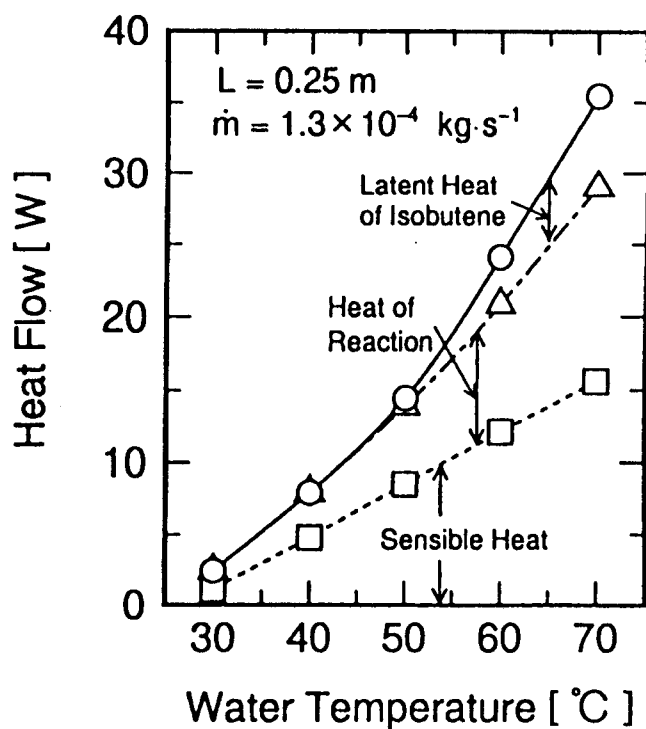


Fig. 4. Effect of water temperature on heat flow.

3.3 Experimental results

The conversion is estimated by measuring the heating medium composition change in the catalyst bed. The effect of mass flow rate of the heating medium on the conversion are shown in Fig. 2. The bed length is 0.25 m. The calculated results shown by lines in this figure are explained later. The conversion increases with increasing the water temperature and with decreasing the mass flow rate of the heating medium. Under some conditions, gas generation was observed. The closed symbols denote the reaction with gas generation. The generated gas was analyzed by a gas chromatograph. Most of the gas composition was isobutene. Hence the generated gas was assumed to be only isobutene when the heat flow was estimated.

The heat transport is attributed to the heat of reaction, the latent heat of isobutene and the sensible heat in this reaction system. The sensible heat was estimated by the temperature change of the heating medium in the catalyst bed.

$$Q_s = \dot{m}c_p(T_{out} - T_{in}) \quad (3)$$

The heat of reaction and the latent heat of isobutene were estimated by the composition change of the heating medium in the catalyst bed.

$$Q_R = \dot{m}X_A \frac{\Delta H_R}{M_A} \quad (4)$$

$$Q_V = \dot{m}X_A Y_B \frac{\Delta H_V}{M_B} \quad (5)$$

where X_A is the conversion and Y_B is the vapor fraction of isobutene. The total heat flow of this reaction system is defined as

$$Q_T = Q_S + Q_R + Q_V \quad (6)$$

The effect of mass flow rate of the heating medium on the heat flow are shown in Fig. 3. The heat flow increases with the water temperature and the mass flow rate of the heating medium. Representative results with the detail of the heat flow are shown in Fig. 4. The lines in this figure are the experimental ones drawn to make the mechanism of the heat flow more clear. The fraction of the heat of reaction or of the latent heat of isobutene to the total heat flow increases with the water temperature.

4. Numerical Calculation

4.1 Calculation procedure

Numerical calculations based on a two-dimensional model were carried out. The numerical model for solving the temperature and the conversion of the heating medium is presented in Fig. 5 [5]. The numerical calculations are based on the following assumptions: (1) The temperature of the heating medium flowing through the catalyst bed is the same as the catalytic particle temperature at each location; (2) the heat conduction and the mass diffusion in the axial direction are neglected; (3) the flow condition of the heating medium in the catalyst bed is piston flow; and (4) the pressure is constant at 1 atm. In the experiment, the water temperature difference between the inlet and the outlet of the heat exchanger was extremely small. Thus the wall temperature as the heat source is presumed to be constant. And the same expression of the water temperature T_w is used for the wall temperature in this calculation.

A mass conservation equation is given by

$$\rho\mu \frac{\partial C_i}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left(\rho D_r r \frac{\partial C_i}{\partial r} \right) + W_i \quad (7)$$

Equation (7) can be expressed in terms of the conversion.

$$\rho\mu \frac{\partial X_A}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left(\rho D_r r \frac{\partial X_A}{\partial r} \right) + \frac{\rho_b (-R_A) M_A}{C_{AO}} \quad (8)$$

where D_r is the diffusion coefficient in the radial direction, and is estimated from the Peclet number Pe . The Peclet number is assumed to be 26 because of the liquid phase reaction [4, 10] in this study.

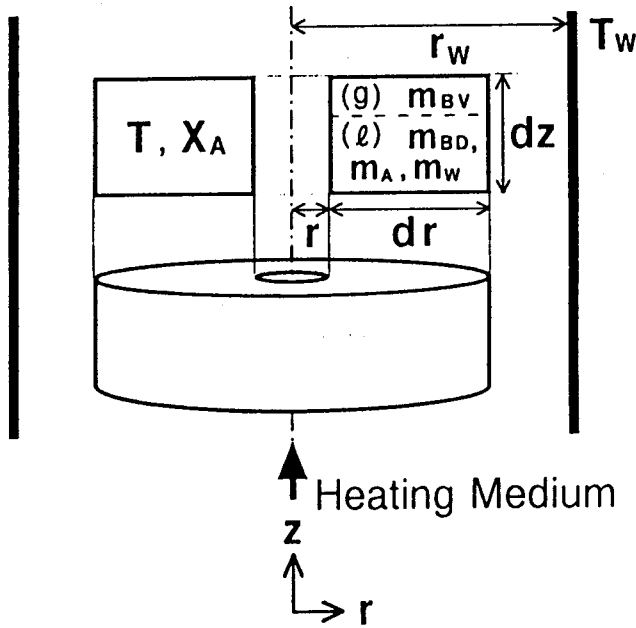


Fig. 5. Numerical calculation model.

The energy equation considering the heat of reaction and the latent heat of isobutene is given by

$$\rho c_p \mu \frac{\partial T}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left(r k_{er} \frac{\partial T}{\partial r} \right) + \rho_b (-R_A) (-\Delta H_R) + R_V (-\Delta H_V) \quad (9)$$

where k_{er} is the effective thermal conductivity in the radial direction. The boundary conditions associated with Eqs. (8) and (9) are as follows:

$$z = 0; T = T_0(r), X_A = X_{A0}(r) \quad (10)$$

$$r = 0; \frac{\partial T}{\partial r} = 0, \frac{\partial X_A}{\partial r} = 0 \quad (11)$$

$$r = r_w; -k_{er} \left(\frac{\partial T}{\partial r} \right) = h_w (T - T_w), \frac{\partial X_A}{\partial r} = 0 \quad (12)$$

where h_w is the apparent heat-transfer coefficient at the wall, and h_w and k_{er} are estimated from Yagi-Kunii's equations [11].

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

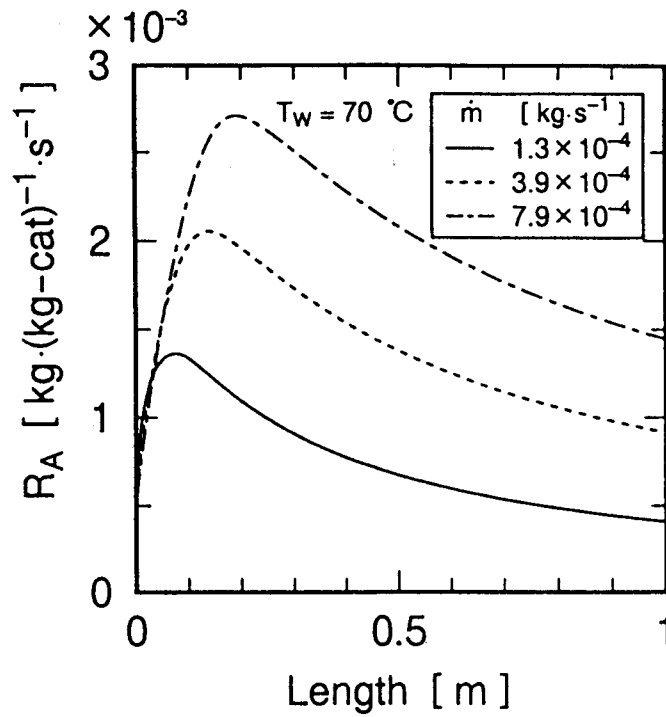


Fig. 6. Calculated reaction rate distribution in the axial direction of the bed.

The reaction rate R_A , after Kato [6], is used.

$$-R_A = \frac{k_2 \bar{C}_A}{(1 + K_B \bar{C}_B + K_W \bar{C}_W)^2} \quad (13)$$

$$k_2 = 4.39 \exp\left(\frac{-56.62 \times 10^3}{RT}\right) \quad (14)$$

$$K_B = 8.254 \times 10^{-11} \exp\left(\frac{41.93 \times 10^3}{RT}\right) \quad (15)$$

$$K_W = 1.128 \times 10^{-11} \exp\left(\frac{49.73 \times 10^3}{RT}\right) \quad (16)$$

The vaporization of isobutene has been evaluated from the following procedures. The mass of produced isobutene m_B is estimated from the conversion. The mass of isobutene in liquid phase m_{BD} is estimated by calculating the solubility of isobutene in aqueous solution of *tert*-butanol. In

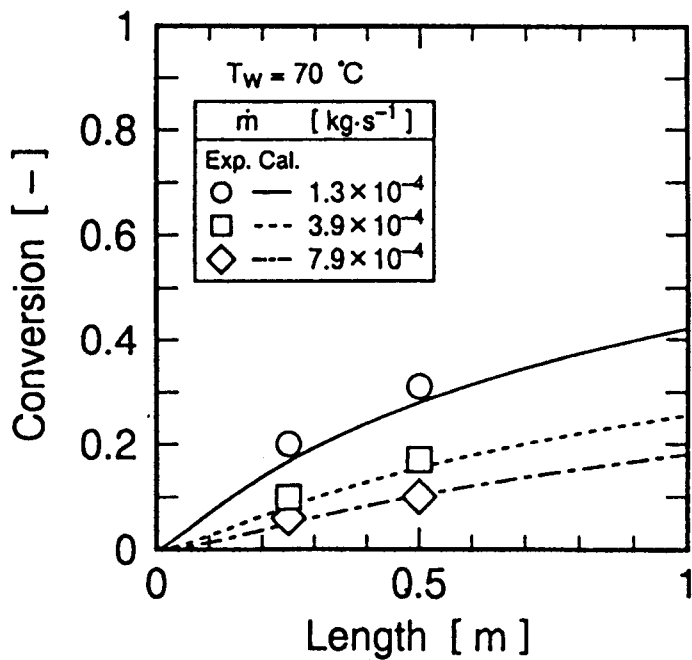


Fig. 7. Calculated conversion distribution in the axial direction of the bed.

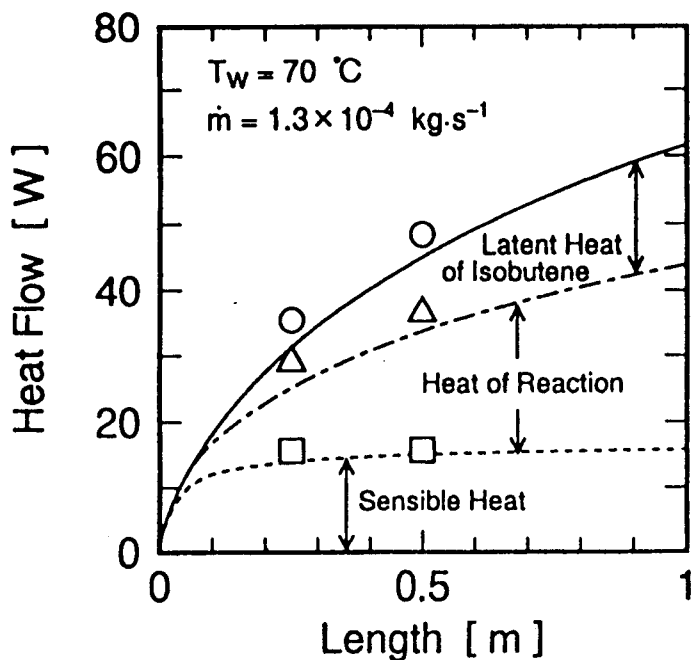


Fig. 8. Calculated heat-flow distribution in the axial direction of the bed.

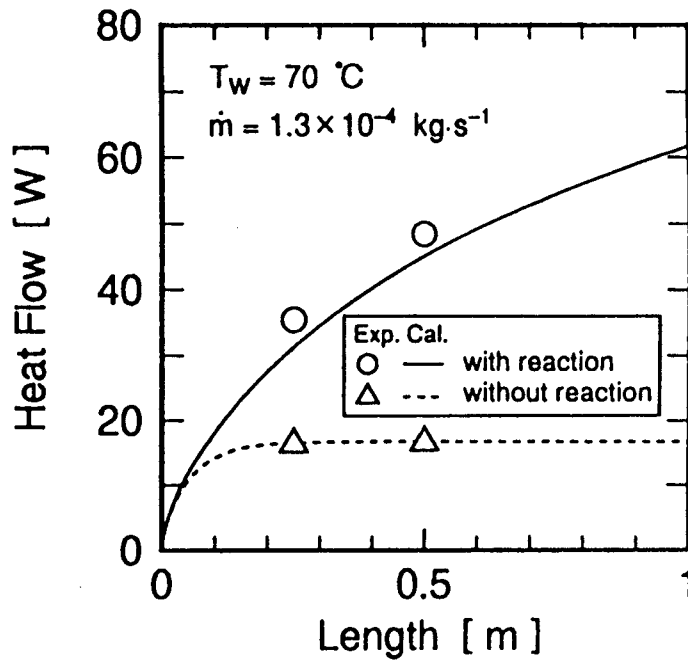


Fig. 9. Calculated heat-flow distribution in the axial direction of the bed: comparison between the results with and without chemical reaction.

this numerical calculation, isobutene is assumed to be vaporized when m_B is larger than m_{BD} . The mass of vaporized isobutene m_{BV} is given by

$$m_{BV} = m_B - m_{BD} \quad (17)$$

Thus the vaporization rate of isobutene is defined as

$$R_V = \rho_b (-R_A) \frac{m_{BV}}{m_B} \quad (18)$$

The influence of the vaporized isobutene on the reaction rate and the flow condition of heating medium is assumed to be little in the numerical calculations.

4.2 Comparison between the results of the experiments and the calculations

The calculated results of the conversion and the heat flow are presented by lines in Figs. 2 and 3, respectively. The bed length is 0.25 m. These results show good agreement with experimental ones. Similar results were obtained when the bed length was 0.5 m. These agreements indicate the validity of the numerical model.

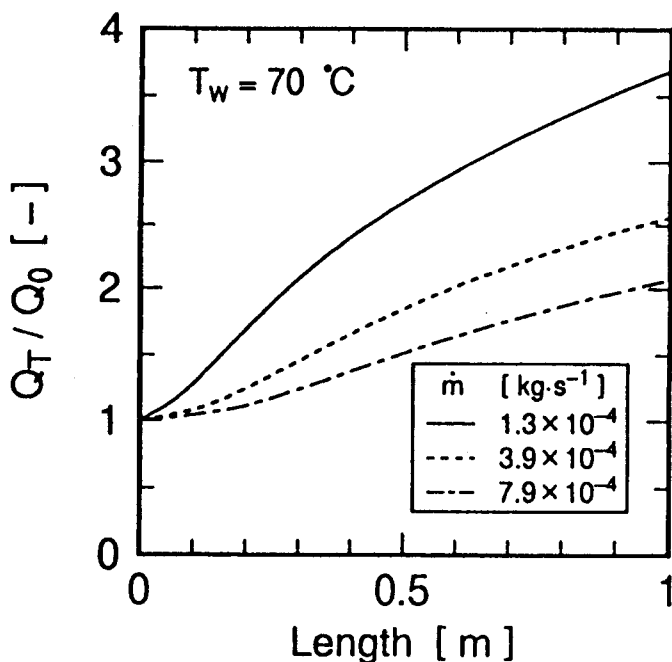


Fig. 10. Ratio of heat flow with reaction to heat flow without reaction.

5. Simulation

Simulations were carried out by investigating the behavior of the heating medium in the catalyst bed which was difficult to be investigated in the experiments. The heat transfer and the reaction characteristics in this reaction were examined.

The calculated results of the reaction rate in the axial direction of the catalyst bed are shown in Fig. 6. The reaction rate is averaged over the cross section. The reaction rate increases with the temperature of the heating medium because of endothermic reaction. The adsorption of water in the catalyst inhibits the *tert*-butanol dehydration reaction. The reaction rate has a maximum, and it decreases rapidly as this reaction proceeds owing to that inhibition. The conversion increases with decreasing the mass flow rate of the heating medium because of increasing the residence time of the heating medium in the catalyst bed. Thus the inhibition appears larger with decreasing the mass flow rate of the heating medium. The reaction rate is influenced by the mass flow rate because the reaction rate is dependent on the temperature and the composition of the heating medium.

The calculated results of the conversion distributions in the axial direction of the catalyst bed are shown by lines in Fig. 7. Even though the mass flow rate of the heating medium becomes 3 or 6 times (a dotted line or a dash-dot one) of the case of the solid line, the conversion does not become one-third or one-sixth of that case owing to the influence of the reaction rate.

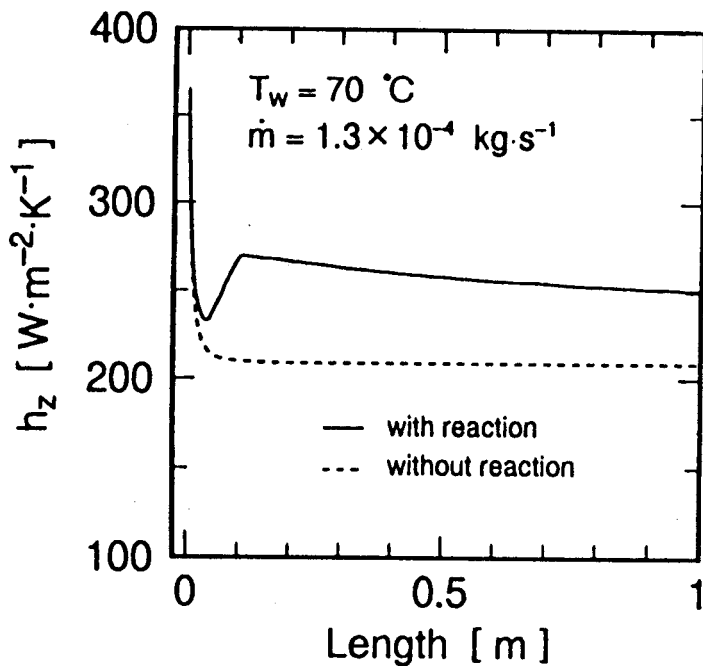


Fig. 11. Local heat-transfer coefficient distribution in the axial direction of the bed: comparison between the results with and without chemical reaction.

Typical results of the heat-flow distribution in the axial direction of the catalyst bed are shown in Fig. 8. The sensible heat approaches a constant value with increasing bed length. The heat of reaction and the latent heat of isobutene increase with the length of the catalyst bed because of increasing the conversion.

The typical calculated results of the heat-flow distributions in the axial direction of the catalyst bed are shown in Fig. 9. The calculated heat flow with the reaction is compared to the results without the chemical reaction. In the case without the reaction, the heat transport is attributed only to the sensible heat. Because the temperature of the heating medium approaches the heat source temperature with increasing bed length, the heat flow approaches a constant value. In the case with reaction, the heat flow increases with bed length provided that the reaction proceeds.

The calculated results of the ratio of the heat flow with the reaction (Q_T) to the heat flow without the reaction (Q_0) are shown in Fig. 10. The heat flow with reaction is much larger than that without reaction at 1 m of the catalyst bed.

Therefore this reaction system can be applied be effective heat-transport system.

6. Discussion

The heat-transfer mechanism of this reaction system was discussed from comparisons of the cases with and without the reaction.

The heat flow of differential length dz can be written as

$$dQ = 2\pi r_W \cdot dz \cdot h_z(T_W - T_m) \quad (19)$$

where h_z is the apparent local heat-transfer coefficient and T_m is the mean temperature of the heating medium. The difference between T_W and T_m is the driving force for the heat transfer. The heat transfer is influenced by the apparent local-transfer coefficient and the driving force of the temperature difference between the heat source and heating medium. In the case without a reaction, the driving force of the temperature difference approaches 0, because the temperature of the heating medium becomes nearly equal to the heat source temperature with increasing bed length. In the case with a reaction, the endothermic reaction causes a decrease in the heating medium temperature. Moreover, the vaporization of isobutene causes a decrease in the temperature in this reaction system. Thus the driving force of the temperature difference between heat source and heating medium with the chemical reaction is larger than that without the reaction.

Typical calculated results of the apparent local heat-transfer coefficient are represented in Fig. 11. The result without the reaction is presented by a dotted line. In the case without reaction, the apparent local heat-transfer coefficient is shown by a solid line. The influences of the entrance region and the reaction rate cause h_z to have a minimum and a maximum. The apparent local heat-transfer coefficient with the chemical reaction was higher than without the reaction.

These results indicate that the dehydration reaction of *tert*-butanol enhances the heat-transfer rate, because of increases in the apparent local heat-transfer coefficient and the driving force of the temperature difference between the heating medium and the wall by utilizing a chemical reaction.

7. Conclusion

The reaction system of *tert*-butanol/isobutene/water has been applied to chemical heat transport. In this study, the heat-transfer characteristics in an endothermic dehydration reaction of *tert*-butanol at the heat-supply side of this reaction system were investigated. The heat flow with the chemical reaction was much higher than without reaction. These results indicated that the dehydration reaction promoted the heat-transfer rate, because of increases in the apparent local heat-transfer coefficient and the driving force of the temperature difference between the heating medium and the wall by utilizing the chemical reaction. This reaction system can be applied to an effective heat-transport system.

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Translated by Yuji Kiguchi, Department of Chemical Engineering, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152, Japan.