Nonisothertmal Design of Fluid Segments for Precise Temperature Control in Microreactors

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Abstract

The present paper discusses effects the fluid segments size on temperature profile as well as mixing performance in microreactors under nonisothermal conditions. In the reactors, exothermic parallel-series reaction systems having different ratio of activation energy proceeds with the cooling through walls of a fixed temperature. Reactant fluids are fed by the form of fluid segment. The width of fluid segment determines the diffusive mixing rate, and the height of fluid segment affects the cooling rate of reactant fluids. When the activation energy of the reaction producing the desired product is higher than that of the by-product, an optimum height to maximize the yield of the desired product exists with a fixed fluid segment width. This result indicates that the fluid segment size can be determined from the mixing rate and cooing rate. The fluid segment height is then changed on the half way of reactor channel. Reactors where the height is small near the inlet region and enlarged suddenly after the region provides higher yield of the desired product than those where the height is fixed.

Keywords: microreactor, arrangements and shapes of fluid segments, mixing by molecular diffusion, yield and selectivity of multiple reactions

Introduction

Mixing in microreactors is mainly driven by molecular diffusion. Reduction of diffusion length is required for fast mixing in microreactors. To reduce diffusion length, reactant fluids are split into many laminated fluid segments at the mixer section. The interdigital mixer (Ehrfeld et al., 1999), the static V-micro-jetmixer (Ehlers et al., 2000), the SuperFocus mixer (Löb et al., 2004), the K-M mixer (Nagasawa et al., 2005), and the dual pipe mixer (Daito et al., 2006) are examples of the micromixers using this mixing principle. We have investigated the design factors of fluid segment such as arrangement and shape under the isothermal condition (Aoki et al., 2004; Aoki and Mae, 2006). Precise temperature control is also an advantage of microreactors because of high surface-to-volume ratios due to small dimensions and an essential issue for a high yield and selectivity of a desired product (Jensen, 2001). To leverage this advantage, a proper design of fluid segment is needed from the viewpoint of temperature control as well as mixing performance. Thus, we extended the previous study by including effects of heat generation by reactions and heat removal from walls and studied effects of the sizes of fluid segment having rectangular cross section on product yield and temperature profile in microreactors using computational fluid dynamics (CFD) simulations. First, we examined effects of activation energy of parallel-series reactions on the design of fluid segments. Then, we studied effects of changing the fluid segment height on the half way of reactor channel on the improvement of temperature control and product yield.

Effects of Activation Energy and Reaction Heat on the Design of Fluid Segments

Methods of CFD simulations

We used Fluent 6.2 as a CFD code. This code solves the flow field in the reactors by the finite-volume method (Fluent inc., 2005). The laminar flow and the finite-rate models are applied in the modeling of reactors. Fig. 1 shows the reactor settings for CFD simulations. We assumed that each reactant fluid is split fluid segments at the reactor inlet; the cross-sectional shape of fluid segments is rectangle; and the fluid segments are aligned in a line. The flow in reactors was assumed to be laminar flow, and the reactants A and B mix only by molecular diffusion. From the interface between each reactant fluid, reactions take place and heat is generated by reactions. The reactant fluids were assumed to be cooled by the reactor wall where temperature was fixed at 300 K, which is the reference temperature.

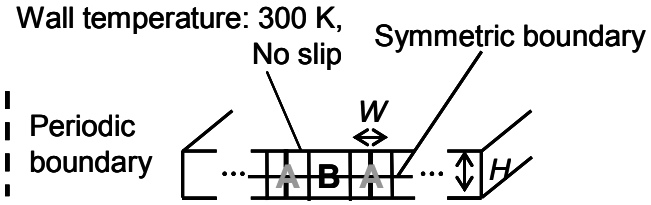

Fig. 1. Settings of reactors for CFD simulations

The reaction formulas and the reaction rates, r_1 and r_2, of multiple reactions proceeding in reactors are as follows:

$$\begin{aligned} &\mathrm{A}+\mathrm{B}\rightarrow\mathrm{R},\ r_1=k_1C_\mathrm{A}C_\mathrm{B},\ k_1=k_{10}\exp(-E_1/RT),\ \Delta H_1=-100\ \mathrm{kJ/mol},\\ &\mathrm{B}+\mathrm{R}\rightarrow\mathrm{S},\ r_2=k_2C_\mathrm{B}C_\mathrm{R},\ k_2=k_{20}\exp(-E_2/RT),\ \Delta H_2=-100\ \mathrm{kJ/mol} \end{aligned} \quad (1)$$

where R is the desired product, and S is the by-product; k_1 and k_2 are the rate constants (k_1 is 1 $m^3 \cdot kmol^{-1} \cdot s^{-1}$ at 300 K); C_i is the concentration of component i, and C_{A0} = 5 kmol/m^3 and C_{B0}/C_{A0} = 2 at the reactor inlet; and ΔH_1 and ΔH_2 are the heats of reactions and have a fixed value. To study effects of he ratio of activation energy E_2/E_1, we chose the ratio of 3 (E_1 = 50 kJ/mol, E_2 = 150 kJ/mol) or 1/3 (E_1 = 150 kJ/mol, E_2 = 50 kJ/mol). At the reference temperature, the ratio of rate constants at 300 K, $(k_2/k_1)_{300\ \mathrm{K}}$, which is the index of selectivity, is 0.1 at E_2/E_1 = 3 or 2 at E_2/E_1 = 1/3. We also assumed that all the components take the common physical properties and that the properties of the components are independent of temperature and as follows: thermal conductivity, k, is 0.1 $W \cdot m^{-1} \cdot K^{-1}$; the specific heat, c_p, is 1000 $W \cdot kg^{-1} \cdot K^{-1}$; the diffusion coefficient D is 10^{-9} m^2/s. The inlet velocity of the reactant fluids u was fixed at 0.001 $m \cdot s^{-1}$, and the reactor length, L, was set at 1 cm; that is, the mean residence time of the reactants in the reactors was 10 s. The dimensionless numbers, D/uL and $k/\rho c_p uL$ are equal to 10^{-4} and 10^{-2}, respectively. Thus, the influence of axial dispersion and thermal conductivity are negligible.

Using the above settings, we examined effects of fluid segment sizes on product yield and temperature profile in microreactors. The segment width, W, was 32, 55, or 100 μm, and at 300 K, the corresponding Damköhler number, $\phi_0 = (k_1)_{300\ \mathrm{K}} C_{B0} W^2/D$, which represents the ratio of reaction rate to diffusive mixing rate, was 10, 30, or 100, respectively (Paul et al., 2004). The fluid segment height, H, was 50, 100, 200, or 300 μm.

Using the settings mentioned above, we conducted the CFD simulations to obtain concentration and temperature profiles of the components in the reactors and then calculated the yield of the desired product R, Y_R and temperature T as a reactor

performance measure. The yield of R and temperature is obtained from the mass-weighted average concentration of each component on the plane perpendicular to the axial direction.

Results and discussion

Fig. 2 shows the maximum yield of R, $Y_{R,max}$, and the maximum temperature, T_{max}, in the reactor of each fluid segment size for the two E_2/E_1. When E_2/E_1 = 3, the ratio of k_2/k_1 increases and the selectivity of R decreases with increasing temperature. In addition, at elevated temperature, the reactions tend to proceed under a diffusion controlled condition, leading to a low selectivity of R. The reduction in W and ϕ_0 provides fast mixing. The fast mixing leads to fast reaction and fast heat generation. Thus, at low value of ϕ_0, the heat generation rate is larger than the heat removal rate through the reactor wall, and temperature greatly increases. At elevated temperatures, the rate constants increase, and the reactions take place under diffusion controlled conditions, resulting in decreased Y_R. This is especially true for a large value of fluid segment height, since the heat removal is enhanced by reducing the height. At H = 50 μm, nearly isothermal conditions are realized for each ϕ_0, and ϕ_0 = 10 gives $Y_{R,max}$ equal to that for the reaction controlled condition. Fast mixing by the reduction of W also leads to fast reaction and fast heat generation, which is expected to increase T_{max}. At H = 200 and 300 μm, T_{max} for ϕ_0 = 10 are the highest. At these H, $Y_{R,max}$ for ϕ_0 = 10 is lower than that for ϕ_0 = 100. The results indicate that fluid segment sizes can be determined from the trade-off between fast mixing and large temperature rise by fast heat generation.

When E_2/E_1 = 1/3, the ratio of k_2/k_1 decreases and the selectivity of R increases with increasing temperature. However, at elevated temperature, the reactions tend to proceed under a diffusion controlled condition by the increased k_i. In this reaction system, temperature rise, thus, has both effects of increasing and decreasing Y_R. In the range of $H \leq$ 100 μm for ϕ_0 = 10 and $H \leq$ 200 μm for ϕ_0 = 30, Y_R increases with temperature. These results

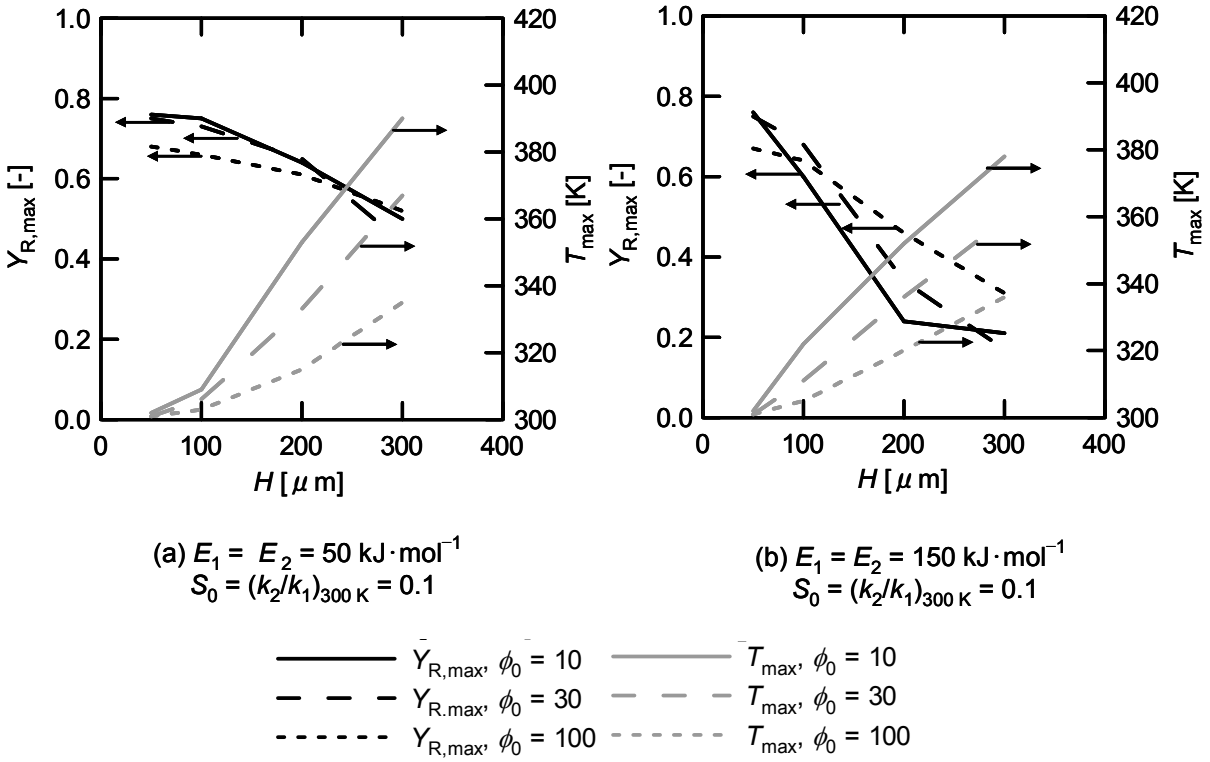

Fig. 2. $Y_{R,max}$ and T_{max} in the reactor of each fluid segment size for the two E_2/E_1.

indicate that the effect of decreasing k_2/k_1 dominates that of reaching diffusion controlled

condition by temperature rise. For these value of ϕ_0, further increase in H reduces $Y_{R,max}$. For ϕ_0 = 100, $Y_{R,max}$ gradually increases. At this ϕ_0, decreasing k_2/k_1 has the larger effect than reaching diffusion controlled condition. From these results, we need to choose the optimum fluid segment size to maximize Y_R based on the mixing rate and the heat removal rate.

Effects of changing the Fluid Segment Height on the half way of the Reactor Channel

To further improve temperature control and product yield in the reaction system of $E_1 > E_2$, we then discuss effects of the change of fluid segment height on the half way of the reactor channel. In the reaction system shown in Eq. 1 of E_1 = 150 kJ/mol, E_2 = 50 kJ/mol, when reactions takes place isothermally, and ϕ_0 =10, $Y_{R,max}$ maximizes around 315–320 K as shown in Fig. 3. Keeping the temperature in a reactor around 315–320 K is effective to enhance $Y_{R,max}$.

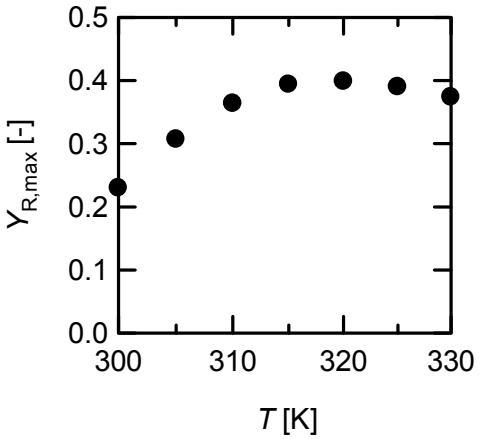

Fig. 3. Relation between $Y_{R,max}$ and reaction temperature for the reaction system shown in Eq. 1 of E_1 = 150 kJ/mol, E_2 = 50 kJ/mol. ϕ_0 = 10. T is the fixed temperature.

Methods of CFD simulations

In this study, we apply the reaction system shown in Eq. 1 of E_1 = 150 kJ/mol, E_2 = 50 kJ/mol in the CFD simulations. The fluid segment width W is fixed at 32 μm; that is, ϕ_0 = 10. Fig. 4 shows a schematic of the side view of the reactor with the change of fluid segment height on the way of the channel. The height is changed at 0.0001 m from the reactor inlet. The fluid velocity is 0.001 m·s^{-1} at the reactor inlet. The height change is, thus, occurs when the mean residence time is 0.1 s. The way to change the height is as follows:

Pattern 1) The height is 100 μm (H_1) in the first axial region. This height is optimum for enhancing $Y_{R,max}$ as shown in Fig. 2b. Then, the height is enlarged into 150, 200, 250, or 300 μm (H_2). This enlargement is for preventing the decrease in temperature in the last half of the reactor. In this region, reaction and heat generation rate is slow, and the cooling through the wall dominates the reactor temperature.

Pattern 2) The height is 50 μm (H_1) in the first axial region. Then, the height is enlarged into 100, 200, 250, or 300 μm (H_2). The objective of the combination of the heights is to mix reactants at low temperature and to react them at high

temperature.

Pattern 3) The height is 110, 130, or 150 μm (H_1) in the first axial region. Then, the height is reduced into 100 μm (H_2). The objective of wide channel near the inlet is to increase temperature rapidly.

The other settings for the CFD simulations is the same as those mentioned earlier.

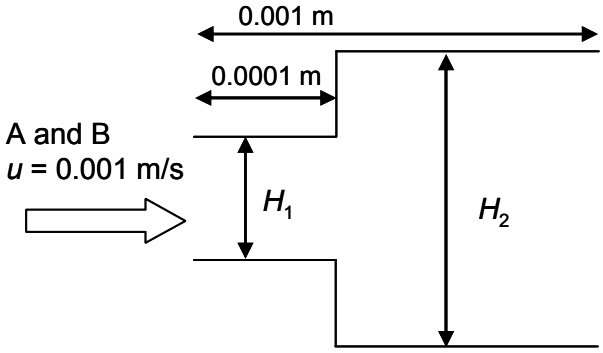

Fig. 4. Side view of the reactor

Results and discussion

Table 1 summarizes $Y_{R,max}$ and T_{max} for each combination of H_1 and H_2. $Y_{R,max}$ for pattern 1 is larger than that for the reactor whose segment height is fixed. However, the difference in $Y_{R,max}$ for both patterns and the effect of H_2 on $Y_{R,max}$ are small. The reason is as follows. T_{max} increase with H_2. By the temperature rise, the reaction condition reaches to a diffusion controlled condition, leading to a decrease $Y_{R,max}$ On the other hand, temperature decrease in the last half of the reactor is alleviated by increasing H_2. This effect has a contribution to increase $Y_{R,max}$. These effects compensate, and the increase in $Y_{R,max}$ with H_2 is thus small.

Table 1. $Y_{R,max}$ and T_{max} for each combination of H_1 and H_2

Pattern	H_1 [μm]	H_2 [μm]	$Y_{R,max}$ [-]	T_{max} [K]
	100	100	0.396	323.3
1	100	150	0.400	324.4
		200	0.403	325.0
		250	0.404	325.9
		300	0.404	327.3
2	50	150	0.452	315.8
		200	0.463	317.3
		250	0.467	318.0
		300	0.469	318.5
3	110	100	0.394	325.9
	130		0.384	330.2
	150		0.375	333.5

$Y_{R,max}$ for pattern 2 is larger than that for the reactor whose segment height is fixed. The small height of fluid segment near the reactor inlet suppress temperature rise, and the channel enlargement then bring T into the optimum temperature range for maximizing $Y_{R,max}$ as shown in Fig. 5. In the low temperature region ($H = H_1$), mixing proceeds compared with reaction. In the region of $H = H_2$, the mixed reactants produce R rapidly at elevated temperature by the channel enlargement. In other words, this change of fluid segment height leads to mixing that proceed mainly in low temperature and reaction in high temperature, resulting in increase in $Y_{R,max}$. This temperature profile is suitable for the reaction system that the activation energy of the reaction producing a desired product is higher that of a by-product. The effect of H_2 on $Y_{R,max}$ is small for this pattern.

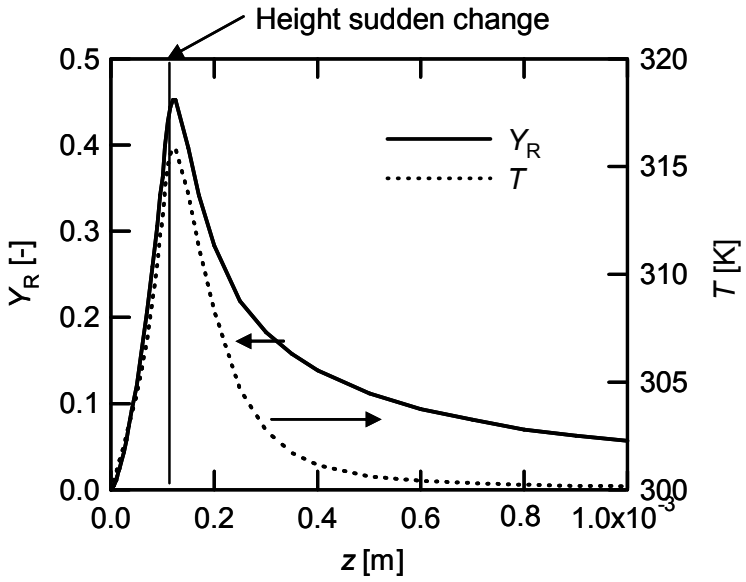

Fig. 5 Profile of Y_R and T in the reactor of H_1 = 50 μm. H_2 = 150 μm. z is the axial position.

$Y_{R,max}$ for pattern 3 is smaller than that for the reactor whose segment height is fixed, and decreases with increasing H_1. T_{max} highly increases with H_1. This result indicate that the fluid segment size near the reactor inlet dominates $Y_{R,max}$.

Conclusions

We studied effects of the sizes of fluid segment having rectangular cross section on product yield and temperature profile in microreactors under a nonisothermal condition using CFD simulations. We also examined effects of the ratio of activation energy. In the reactors, exothermic parallel-competitive reaction systems having different ratio of activation energy proceeds with the cooling through walls of a fixed temperature. Reactant fluids are fed by the form of fluid segment. The width of fluid segment determines the diffusive mixing rate, and the height of fluid segment affects the cooling rate of reactant fluids. When the activation energy of the reaction producing the desired product is higher than that of the by-product, an optimum height to maximize the yield of the desired product exists with a fixed fluid segment width. This result indicates that the fluid segment size can be determined from the mixing rate and cooing rate. We have also changed the fluid segment height on the half way of reactor channel. Reactors where the height is small near the inlet region and enlarged suddenly after the region provides higher yield of the desired product than those where the

height is fixed. This change of fluid segment height leads to mixing that proceed mainly in low temperature and reaction in high temperature. The temperature profile is suitable for the reaction system that the activation energy of the reaction producing a desired product is higher that of a by-product.

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