

New methods for increasing productivity by using microreactors of planar pumping and alternating pumping types

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Abstract

Two methods for increasing productivity of microreactors themselves ((1) planar pumping and (2) alternating pumping types) are presented without using numbering-up processes. As for method 1, two thin liquid layers can react each other in the vicinity of their interface. The reaction yield was about 10% greater than that in conventional batch reaction using mechanical stirrer. Method 2 is based upon the diffusive mixing through the liquid–liquid successive interfaces which are perpendicular to the flow direction. At the very low frequencies less than 1 Hz, the reaction yield for the addition reaction of phenylisocyanate and ethanol in the water/oil phases increased linearly with alternating frequencies. At higher frequencies, however, the yield of their direct reaction did not change with increasing frequencies which is assumed to be not diffusion-controlled reaction, but activation-controlled reaction of second order.

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1. Introduction

A microreactor is a reactor whose dimension is of the order of 100 μm , and which makes use of diffusive mixing in the laminar flow state by large surface to volume ratio. Mixing time due to molecular diffusion is proportional to the square of the characteristic length scale (typically the width of the reactor channel). If one halves the size of a reactor, the mixing time becomes a quarter, and it is expected that realization of very quick homogenization would make possible the production of high quality chemical and pharmaceutical products.

The advantages of microreactors, therefore, are (1) the facility of rapid and precise control of temperature, which is helpful in obtaining heat-unstable compounds, (2) high reaction rates, (3) high yield of reaction products and (4) ease of scale-up of reaction volume by numbering-up procedures of each microreactor element without complicated calculations in chemical engineering. The increase of productivity

of chemical compounds by microreactors is very helpful for the cost-effective production of fine chemicals.

There are two directions in increasing the productivity of reaction products, or in scale out process: (a) the construction of reaction modules, so-called numbering-up, and (b) the improvement of a reactor itself. This paper concerns the latter direction. Two methods are proposed for this, (i) a planar pumping method, and (ii) an alternating pumping method.

2. Planar pumping-type microreactor [1]

Falling film microreactors have been reported by IMM [2], and CPC [3] for gas–liquid reactions. Why does the reactor require micro-channels of several hundred micrometers? We have developed a planar pumping-type microreactor having no grooved micro-channels for liquid–liquid reaction. As long as the size of the reactor in the direction of diffusive mixing, perpendicular to the interface between two layers is kept small, the other dimension can be allowed to have a larger size in the order of mm, or cm. A meandering stream within each plane is also permitted as long as it is within the range of laminar flow condition. Fig. 1 shows the equipment in which the reaction field is 200 μm thick, 50 mm wide, and 110 mm long and is composed of two lay-

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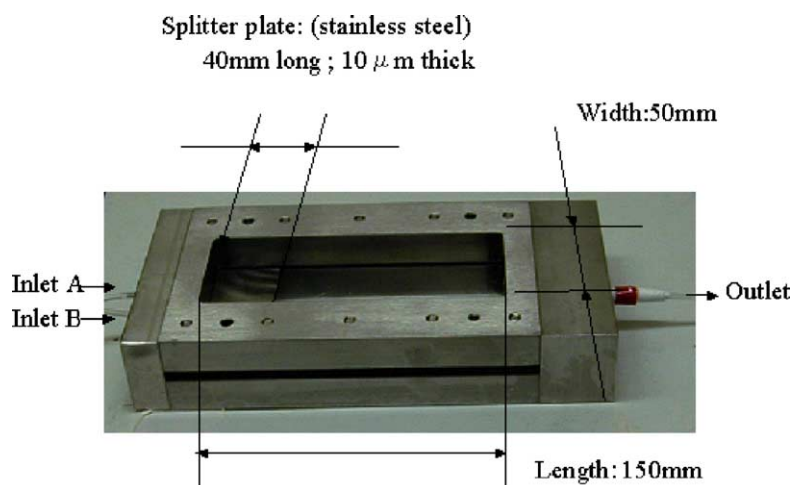


Fig. 1. Planar-type microreactor.

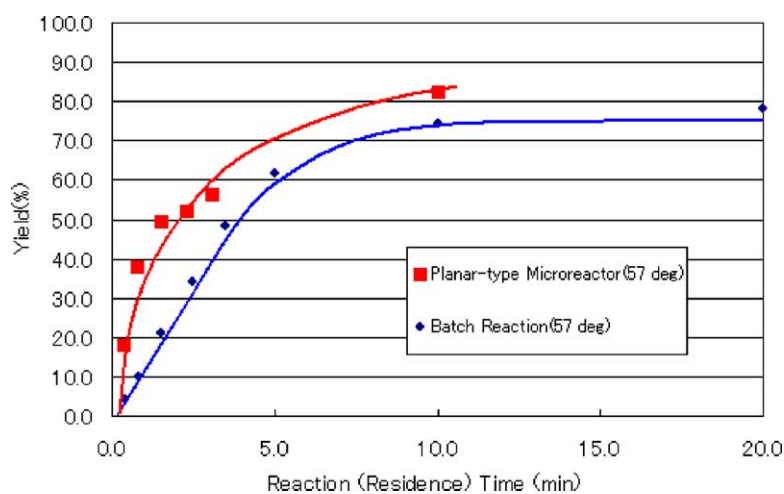


Fig. 2. Reaction yield for planar-type microreactor in the reaction of phenylisocyanate and ethanol.

ers. The know-how is to insert a splitter plate made of stainless steel of 10 μm thickness to stabilize the laminar flow from the inlet. Fig. 2 shows the experimental results for an addition reaction of phenylisocyanate and 42 wt% of ethyl alcohol in toluene in equimolar concentration. The reaction yield by the microreactor is about 10% greater than that in the conventional batch reaction using mechanical stirrer under the same experimental conditions (57 °C) and for the same residence time. That is the one of advantages of our new method. If micro-channels are not used, cost overruns in the manufacturing of microreactors can be avoided.

3. Alternating pumping-type reactor [4]

One of the characteristics for microreaction technology for liquid–liquid reaction is attributed to the reaction in the vicinity of the liquid–liquid interfaces which are parallel to the direction of laminar flow, typically seen in Y-shaped reactors.

There are many ways to obtain good mixing for liquid–liquid reaction as shown in Fig. 3. The key point for such mixing is to increase the area of the interface.

If one could create successive multi-layers perpendicular to the flow direction, surely the reaction yield will be increased compared to the parallel feeding method (Fig. 3(c)). Tracy et al. [5] reports on the alternative introduction of liquid slugs into a microfluidic channel, but the authors do not mention chemical reactions when mixing by diffusion. In the present study, we propose and examine methods of pumping two reactants alternately into a microreactor. This is expected to shorten mixing time drastically as well as reduce the reactor channel length. Conventional microreactor have often been rather long, and of a folded patterned channel. Fig. 3(d) is the ideal goal which we are aiming at, where perfect mixing can be performed.

Alternating pumping of two different liquids was realized by (3.1) a piezoelectric driven system, and (3.2) a mechanically pumping system.

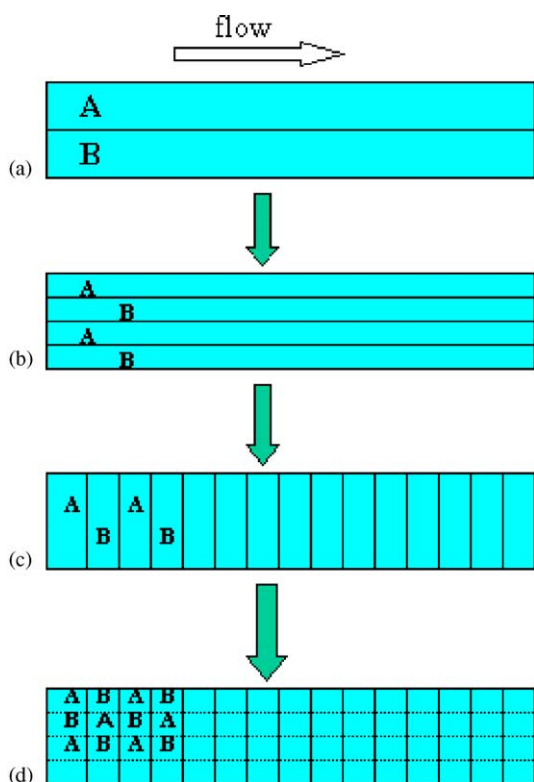


Fig. 3. Various methods of diffusion processing for good mixing.

3.1. Piezoelectric pumping system

Two thin tubes with outer diameter of 300 μm were inserted into a straight tube typically with a 1 mm inner diameter and two liquids were alternatively pumped in the frequency range of 0.01–1.53 Hz manually, and from 0.5 to 20 Hz automatically. The piezoelectric pump of NS-06D Master/Slave pump of Nippon Keiki Works Ltd. was used. The system was applied to the following three kinds of reactions of:

- (1) phenylisocyanate (hereafter abbreviated to PIC) and ethyl alcohol (abbreviated to EtOH);
- (2) dimethylphenylisocyanate and ethyl alcohol, and
- (3) dimethylphenol and iodine as shown in Fig. 4.

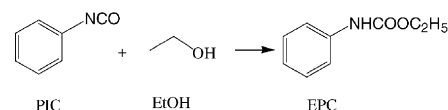
Fig. 5 shows the typical parabolic dynamic profile of EtOH when dyed with methylene blue. With increasing the pumping frequency from 0.5 to 20 Hz, the distance between the two layers (liquid interfaces) is getting closer.

3.2. Mechanical pumping system

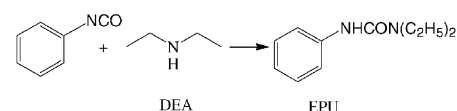
The typical specification of the microreactor used is a channel width of 200 μm and a flow speed of 1 cm/s as shown in Fig. 6. The kinematic viscosity of the test liquids were assumed to be the same as that of water. We aim at developing alternating pumping system operating at 1 kHz, which produces a lamellar structure of 10 μm in layer thick-

(1) Phenyl isocyanate + Ethanol

Reaction

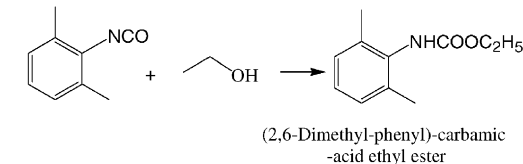


Quenching

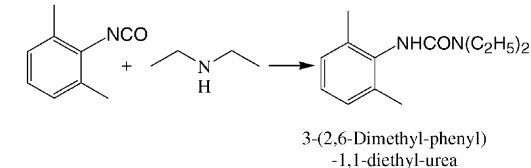


(2) Dimethylphenyl isocyanate + Ethanol

Reaction

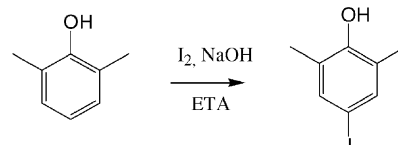


Quenching



(3) Iodination of 2,6-Dimethyl-phenol

Reaction



Quenching

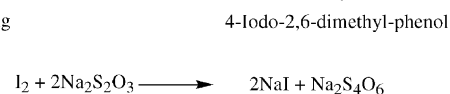


Fig. 4. Reaction applied in the experiments.

ness. This improves the mixing time by 10 times that of the conventional concurrent pumping system, because the mixing time is proportional to the square of the diffusive length scale, which is now along the flow direction.

In order to investigate whether an alternating pumping system could create thin lamellar structure in a microreactor channel, a scale-up model was made by using Reynolds similarity. This is a rather back-to-front approach since tradi-

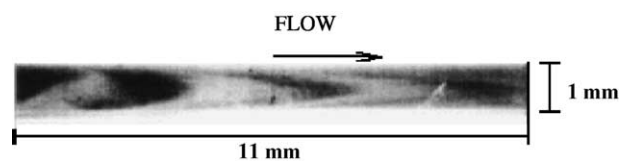


Fig. 5. Actual pumping status for (methylene blue in EtOH)/EtOH (alternating frequency: 3 Hz).

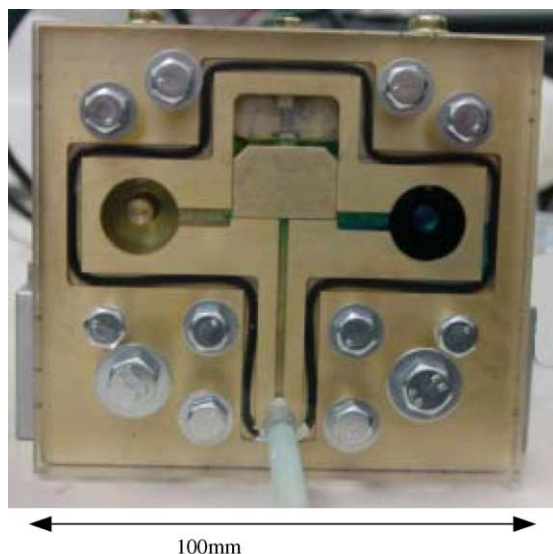


Fig. 6. Experimental apparatus of alternating pumping system (mechanical pumping).

tional chemical engineering design is for scale-up but not for scale-down. The size of the experimental channel is 10 times as large as the reactor mentioned above. Therefore, it is relatively easy to make a channel without relying on a micro-fabrication technology. Furthermore, because of Reynolds similarity, time scale becomes 100 times larger. It becomes easier to observe formation of the lamellar structure. The experimental apparatus is shown in Fig. 6. Syringes are embedded next to the channel, so as to minimize any damping effect with regards to the alternating feed flow. The liquids are fed into the channel through the displacement of piston by a stepping motor.

As is shown in Fig. 7 for preliminary numerical simulation, mere high frequency operation could not create thin lamellar (or stack) structure. Optimal way of alternating feeding, with changing the momentum of feeding, in the experiment of mechanical pumping system has been investigated.

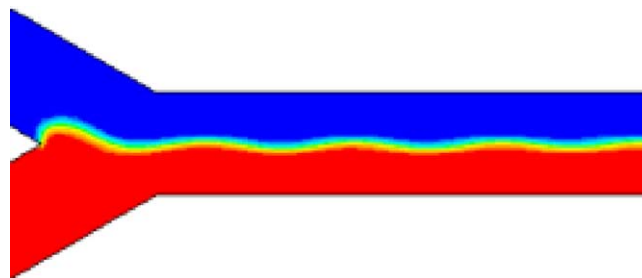


Fig. 7. Preliminary results of numerical simulation (flow rate 0.1 m/s, channel width 200 μm , operational frequency 500 Hz).

4. Results

The results obtained from the piezoelectric alternative pumping system are mainly reported. To evaluate the effectiveness of alternative mixing, neat PIC and MeOH in toluene were used with the same molar concentrations and also the same flow rate.

Toluene and water are immiscible. The two liquids form a clear interface due to their immiscibility with each other and they diffuse through the interface. In order to verify the concept of alternating pumping, i.e. the increase in interface area, 10 wt% of PIC in toluene and 50 wt% of EtOH in water in equivolume were fed alternately at very low frequencies from 0.01 to 1.53 Hz, whilst keeping the flow rate constant (120 $\mu\text{l}/\text{min}$). Fig. 8 is the typical of such “block pumping”. The length of the mixing pipe is 500 mm and it took liquids 196 s to pass through the pipe. At the exit, the reaction of the two reagents was immediately quenched by diethylamine as shown in Fig. 4, and the reaction yield was analyzed by HPLC. Fig. 9 shows that at very low frequencies the reaction yield increase linearly with the frequency. It proves that an increase in the interface area improves the mixing. However, the effectiveness of the increase in the interfacial area on the mixing gets weaker at higher frequencies. Increase in frequency decrease the length of blocks in the flow direction. At frequencies of 2 Hz, the length of each block is about

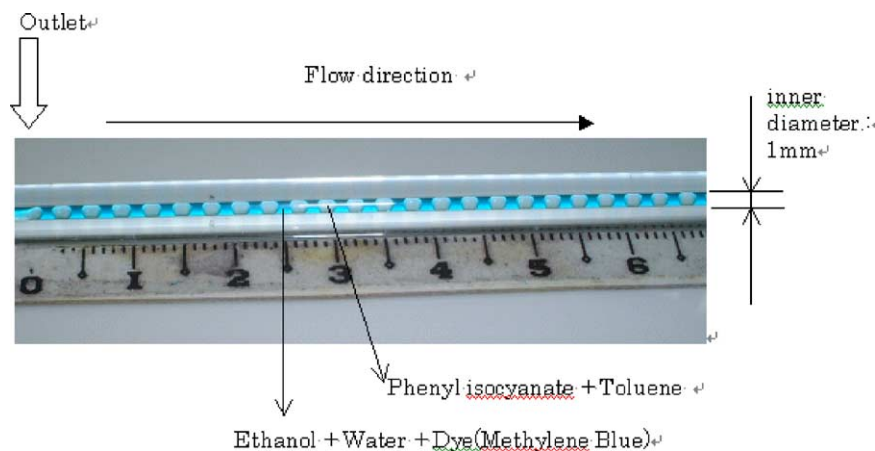


Fig. 8. Pulsative alternating pumping system (block pumping) for (PIC/toluene) + (ethanol/water) reaction. The pumping frequency is 3 Hz.

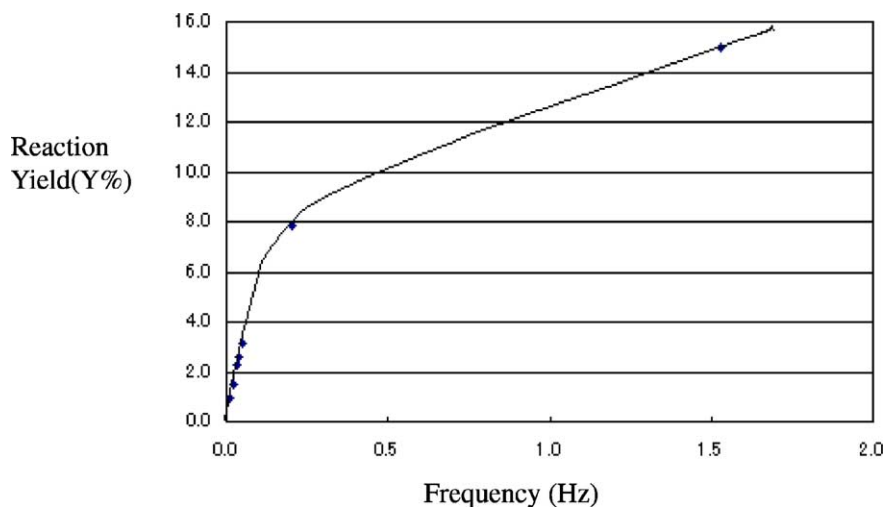


Fig. 9. Reaction yield dependency on alternative frequency for the reaction of (PIC/toluene) + (ethanol/water).

2 mm and at the exit diffusive mixing could saturate a block. Assuming that the reaction takes place instantly, that is, the diffusive mixing controls the reaction yield, the prediction of the reaction yield would be about 90% with linear extrapolation from the results at low frequencies. It was not examined if the reaction yield increases at even higher frequency, since it was not successful to make a smaller size of block inverse proportional to the specified frequency probably due to the interfacial tension. Although, the results from the mechanical pumping system, it shows that creating lamellar structure by alternating pumping depends on initial condition.

In order to verify the effectiveness of an increase in the interfacial area on mixing and reaction yield at even higher frequencies, neat PIC and EtOH were mixed directly with toluene. Three different experimental conditions are shown in Table 1. Under each experimental condition, the reaction yield was measured at various operating frequencies. The results shown in Fig. 10 demonstrate that the reaction yield does not depend on the operational frequency.

Table 1
Reaction conditions in Fig. 10

	Experiment number			
	1	2	3	4
Reactor				
i.d. (mm)	1.0	1.0	0.5	1.0
Length (mm)	464	464	155	500
Flow rate, μ (l/min per one channel)	60	20	5	8
Residence time (min)	3.04	9.1	27 ^a	24.5
Diffusion time (min) vs. frequency (Hz)				
0.5 Hz	108	12	12	1.92
3	3	0.33		0.053
10	0.27	0.03	0.03	0.005
20			0.008	

^a The residence time includes the reaction time at the outlet reservoir, 24 min.

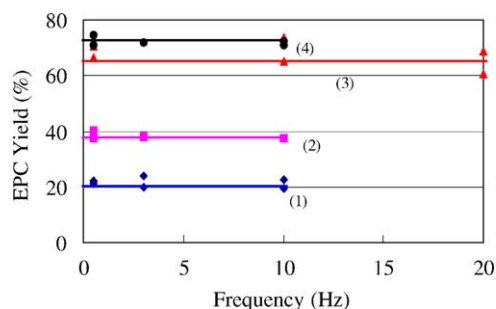


Fig. 10. Frequency-dependency of reaction yield for phenylisocyanate and ethanol (piezopumping) (see the experimental conditions in Table 1).

The same dependency was observed in the reaction of both dimethylphenylisocyanate and ethyl alcohol, and dimethylphenol and iodine as shown in Fig. 4.

5. Discussion

Two different types of experimental results have been obtained regarding the dependency of reaction yield on alternative frequency shown in Figs. 9 and 10. Let us consider the dependency of reaction yield on residence time. A schematic representation of alternative pumping is illustrated in Fig. 11. In the case of diffusion reaction, the diffusion time, t is described according to the diffusion equation as follows:

$$t = \frac{L^2}{D}, \quad (1)$$

where L is the half of the distance between the interfaces of liquid A and B, and D the mutual diffusion constant. In diffusion-controlled process, molecules A and B can react instantly when they encounter. The reaction yield Y , therefore, can be assumed to be

$$Y = 100 \left(\frac{L}{L^*} \right), \quad (2)$$

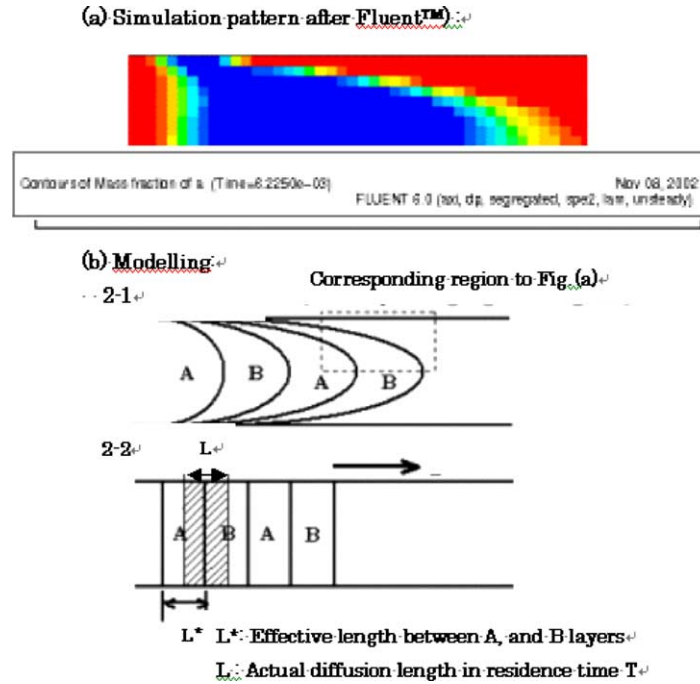


Fig. 11. Schematic diagram of alternating pumping.

where L^* is the maximum diffusion distance for the reaction which can be determined from the reactor shape, flow rate, and alternative frequency of pumps applied (see Fig. 11). From Eqs. (1) and (2), we can get the following equation:

$$Y = \frac{100(Dt)^{1/2}}{L^*} \quad (3)$$

On the other hand, in the case of the activation-controlled reaction, the increase of reaction yield is proportional to the quantity of the unreacted portion. For second-order reactions, this is expressed as

$$\frac{dY}{dt} = C(100 - Y)^2, \quad (4)$$

where C is constant. From this differential equation, we can obtain the following:

$$\frac{0.01Y}{100 - Y} = Ct. \quad (5)$$

The curves of Eqs. (3) and (5) are illustrated in Fig. 12. The dotted curve of Fig. 13 coincides with Eq. (5) that is to say the activation-controlled equation for the value of $C = 8.38 \times 10^{-4}$. That is the reason why the reaction yield in Fig. 10 does not depend on the alternating frequency, which is a characteristic particularly to diffusion reactions. One of the reason for this may be attributed to that the shear enhances the diffusive mixing away from the center of the tube, since the distance of the interface near the wall-tube depresses at the rate of $(1/St)$, where S is the shear rate and t the time. The reason for this is still being investigated.

If we choose adequately a typical diffusion-controlled reaction out of radical reactions, or photo-chemical reactions,

we can expect much higher reaction yields by increasing alternating pumping frequency.

Criteria for distinction, therefore, between diffusion-controlled process, and activation-controlled process has been proposed as shown in Fig. 14. Suppose, for instance, two liquids are injected into a tube reactor alternatively. If the reaction yield of the reaction system is proportional to the

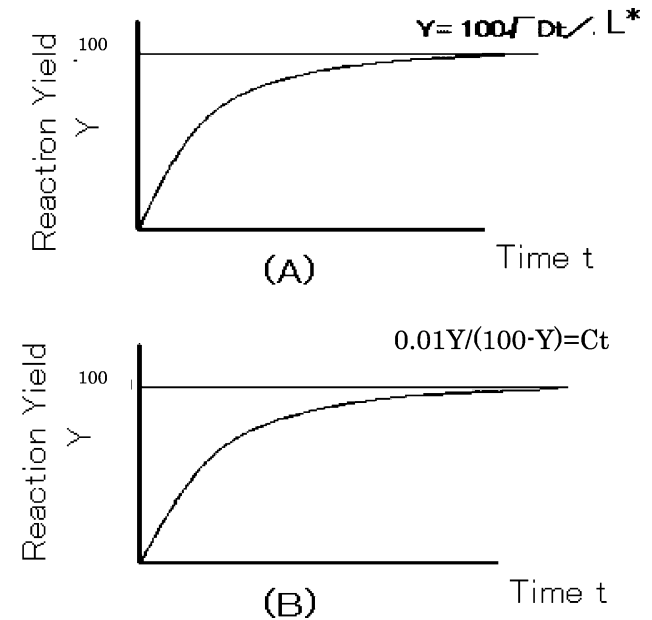


Fig. 12. Reaction time (t) dependency on reaction yield (Y) for: (A) diffusion-controlled process, and (B) activation-controlled process (second-order reaction).

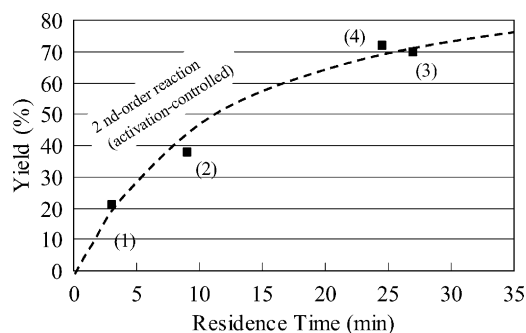


Fig. 13. Residence time (t) dependency of reaction yield (Y) for phenylisocyanate and ethanol at room temperature (a dotted line shows the curve based on second-order reaction theory).

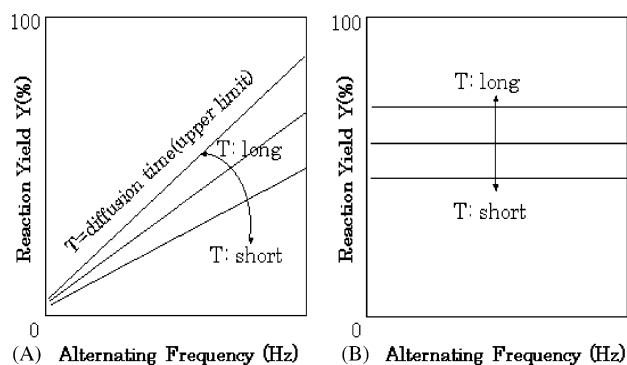


Fig. 14. Criteria for distinction between (A) diffusion-controlled process, and (B) activation-controlled process; T: residence time.

frequency of the alternating pumping, the reaction can be assumed to be diffusion-controlled reaction. On the other hand, if the yield does not change according to the increase of alternating frequency, the reaction is assumed to be activation-controlled reaction.

The importance of feeding liquids alternately is to make lamellar structure perpendicular to the flow direction, which incorporate the shear-thinning effect to enhance the diffusive mixing. This does not appear in the concurrent flowing system. The practical advantages of the alternative pumping type of microreactor are a possible increase in reaction yield and an increase in productivity. Also the characteristic sizes such as the radius of the reactor can be increased to the order of centimeters (which is not strictly a microreactor) as long as the flow is maintained in laminar flow.

Thus, the possibilities of the increasing productivity of a microreactor itself are proposed, which is a different approach from numbering-up process.

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