

Simultaneous Reaction-Separation in a Microchannel Reactor with the Aid of a Guideline Structure

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Abstract—A microchannel with two inlets and two outlets was tested as a potential reactor to carry out two-phase catalytic phase transfer reaction with phase separation at the exit of the microchannel. The catalytic phase transfer reaction between benzyl chloride and sodium sulfide was chosen as a model reaction. The effect of operational time on the conversion was studied. By utilizing a multiphase parallel flow inside the microchannel reactor with the aid of a guideline structure, the catalytic phase reaction followed by phase separation could be ensured. The organic phase could be separated completely from one exit and part of the aqueous phase was separated purely and could be reused with slightly affecting the catalytic phase transfer reaction.

Keywords—Green engineering, microchannel reactor, multiphase reaction, process intensification.

I. INTRODUCTION

PROCESS intensification is defined as any chemical engineering development that leads to a substantially smaller, cleaner and more energy-efficient technology [1]. Process intensification aims at increasing the productivity as defined by the relationship between production of an output and all the resource inputs used in accomplishing the assigned task [2]. Many approaches can be adopted for process intensification in the chemical and process industry. The development of novel equipments and/or methods is the key activities for process intensification.

Aqueous-organic reactions are characterized by extremely low solubility of the organic reactants in the aqueous phase. This problem can be overcome by incorporating a phase transfer catalyst (PTC). A PTC is added to the system to transfer a functional reactant ion or group from one phase to another phase where it can rapidly react with another reactant. Thus, phase transfer catalysis was viewed as a process-intensifying technique via which a variety of liquid-liquid and liquid-solid reactions have been intensified [3].

Miniaturization is another way of achieving process intensification [4]. The miniaturization of chemical reactors has many benefits. These include: minimal environmental hazards and enhanced safety as a result of smaller volume (reagents holdup), enhanced reactivity as a result of high

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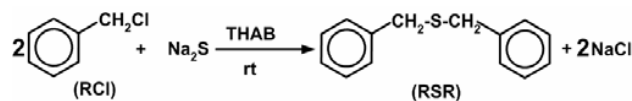
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surface area-to-volume ratio which will allow for efficient contact between reagents, low manufacturing, operating, and maintenance costs [5]. Microreactors have been utilized to perform various functions, from mixing to catalytic reactions, heat exchange or separation [1]. A rapidly emerging area of microreactor applications rests on the integration of both reaction and separation in one single unit. In phase transfer catalysis systems, it is intriguing to perform the reaction with continuous removal of the aqueous phase. This enhances the process performance as well as the green context of the system through the reusability of this phase.

In this work, we attempt to conduct a phase transfer catalyzed reaction in a biphasic system in a microchannel reactor with continuous phase separation at the exit of the microchannel.

The reaction under investigation is the phase transfer catalyzed reaction between benzyl chloride (RCl) and sodium sulfide (Na_2S) to produce dibenzyl sulfide (RSR) in the presence of tetrahexylammonium bromide (THAB) as a phase transfer catalyst (see Scheme 1).



Scheme. 1 Phase transfer catalysis of benzyl chloride with sodium sulfide

II. EXPERIMENTAL

Fig. 1 shows a schematic view of the microchannel reactor apparatus.

The microchannel reactor is purchased from IMT (Institute of Microchemical Technology, Japan). The microchannel reactor is fixed between two aluminum holders and it is positioned under the lens of a microscope. The microscope is equipped with a digital camera to make snapshots. The microchannel reactor used in the experiments has a guideline structure to stabilize and maintain a parallel multiphase flow pattern. Experiments of the microchannel reactor are conducted at room temperature. The organic phase feed is made of (0.4M RCl, 0.04M THAB, 0.1M n-docane as internal standard and toluene). The aqueous phase feed is made of (1M $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$). The aqueous phase reactants and the organic feed reactants are fed to the microchannel at the same volume flow rate through two separate inlets. Phase flow rate are varied from (0.25 ml/min to 0.005ml/min). The

products are analyzed by GC.

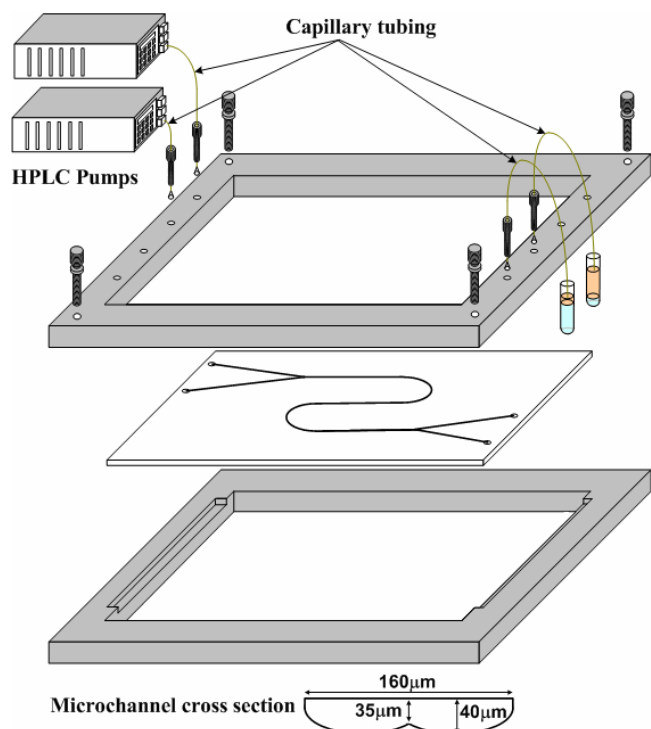


Fig. 1 Microchannel reactor apparatus

III. RESULTS AND DISCUSSION

A. Flow Pattern of the Aqueous – Organic Binary System in the Microchannel

Multiphase flows in microchannels, is largely dominated by the interfacial effects. It is believed that viscosity or surface tension often dominate other effects that can be present in general [6]. For immiscible liquid-liquid two-phase flows inside microchannels, wide range of flow patterns could be identified; such as: slug flow, parallel flow and parallel flow that breaks into slug flow.

From a practical point of view it is desired to have two-phase parallel flow inside the microchannel in order to facilitate the separation of phases at the exit of the microchannel. To achieve this goal, a number of approaches have been investigated to engineer the interaction between the aqueous –organic systems within the microchannel.

One possible option is by incorporating surfactants into the multiphase system. Surfactants might adjust the physical properties of the flowing fluids by reducing the surface tension in the system [7].

Another possible option is by adding microtextures in the microchannel. These so called guideline structure can guide the flow and parallel flow can be obtained [8].

Fig. 2 shows snapshots for the multiphase parallel flow at different locations in the microchannel.

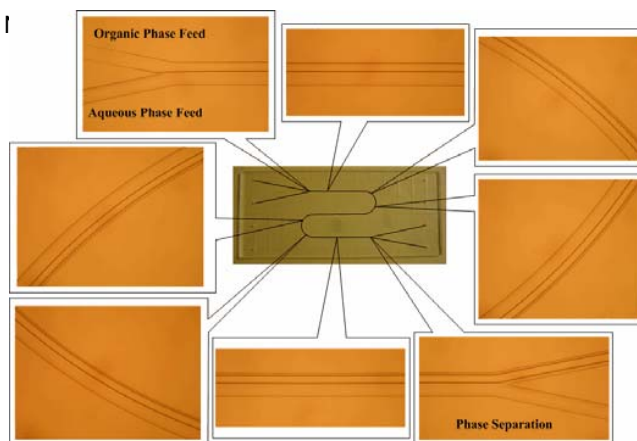


Fig. 2 Microchannel reactor apparatus

The promotion effect of such guideline structure is attributed to their influence on the interfacial and viscous forces associated with the multiphase flow inside the microchannel. Basically, a stable elongated interface between the two phases occurs when the viscous forces are equal to or greater than the interfacial forces [9]. Incorporating a guideline structure into the microchannel will reduce the contact area between the flowing phases. The interfacial force will be reduced as a result of the confined space where the organic phase must minimize itself inside it to keep a minimum interfacial energy. At the same time the viscous force will be increased as a result of the increased phase velocity in smaller confinements.

The multiphase flow stability was examined under different phase flow rates. Flow rates larger than 0.007ml/min (organic phase) + 0.007ml/min (aqueous phase) has resulted in the formation of parallel multiphase flow inside the microchannel. At lower flow rates, other flow patterns could be identified; namely: slug flow and parallel flow that breaks into slug flow.

The degree of separation at the exit of the microchannel was function of the operated flow rates. Figure 3 shows the contents at the organic outlet. Figure 4 shows the contents at the aqueous outlet.

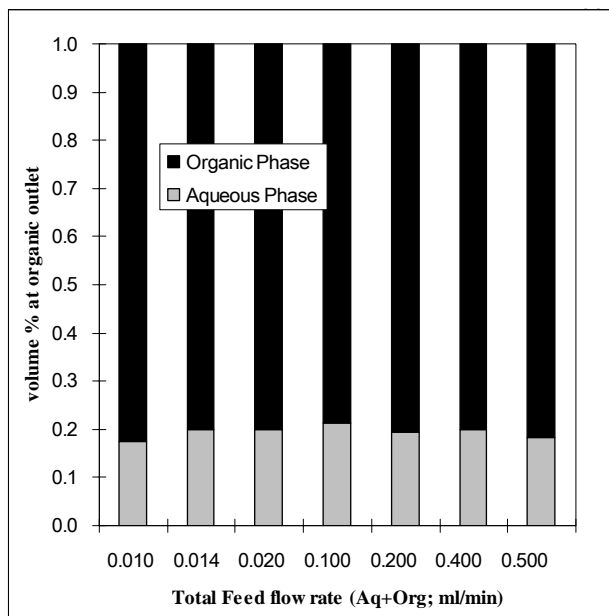


Fig. 3 Contents of the collected liquid from the organic outlet

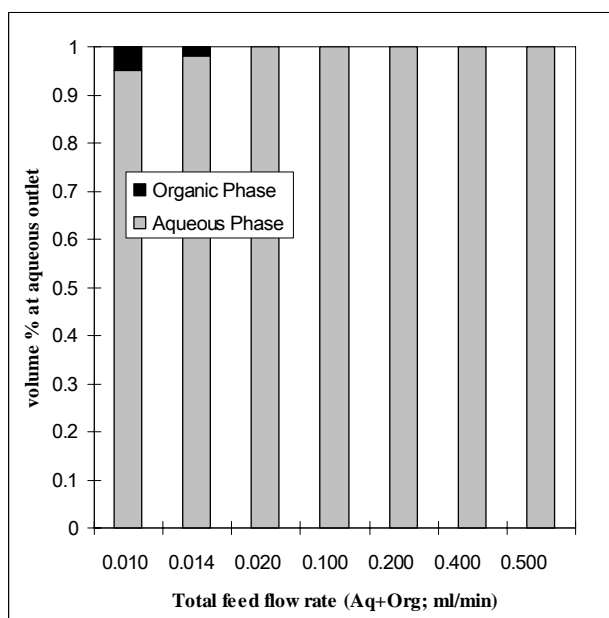


Fig. 4 Contents of the collected liquid from the aqueous outlet

Since the microchannel is made of glass, its hydrophilic properties will make the aqueous phase wets the microchannel wall. Thus, it was not possible to separate the whole aqueous phase from the aqueous phase outlet. On the other hand, when the total feed flow rate (= sum of the organic feed flow and the aqueous feed flow) is higher than 0.02 ml/min, the organic phase was separated completely without being detected at the aqueous outlet within experimental errors. When the total feed flow rate is less than 0.02 ml/min, the aqueous phase was contaminated by the presence of organic phase as the organic phase was unequally distributed between the aqueous and organic outlets.

B. Phase Transfer Catalysis in the Microchannel

The catalytic phase transfer reaction of RCl was studied at different volume flow rates using fresh aqueous phase feed

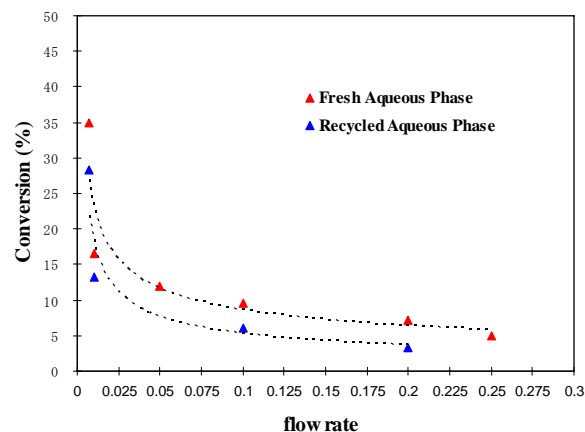


Fig. 5 Conversion vs. organic phase flow rate

The data in Fig. 5 was presented in terms of the organic phase flow rate since it is not reliable to relate the conversion to the residence time in the microchannel only. The organic phase was surrounded by the aqueous phase not only in the microchannel (10 cm) but also in the organic outlet channel (3 cm) and the outlet capillary tubing (10 cm). Thus the actual conversion is governed by the development of the reaction in these three sections. Typically, higher conversion was obtained at lower organic phase flow rate.

It is obvious from Fig. 5 that operating the reaction with recycled aqueous feed has slightly affected the conversion. It is noteworthy that the recycled aqueous phase feed was collected from the aqueous outlet while operating the reaction continuously at 0.05 ml/min (fresh organic feed) and 0.05 ml/min (fresh aqueous feed). At this flow rate around 12% conversion was obtained. That means that the reactivity of the aqueous phase has been slightly influenced by the developed reaction under this flow rate. Therefore, when it was reused, the conversion profile was as discussed above.

In a real processing, microreactors are operated continuously at fixed flow rates. The reaction product is sent to another operation unit (typically for further separation). Thus it is important to evaluate the performance of the reactor under continuous condition. Fig. 6 shows the conversion as function of time when operating the microreactor under .05 ml/min (fresh organic feed) and 0.05 ml/min (fresh aqueous feed).

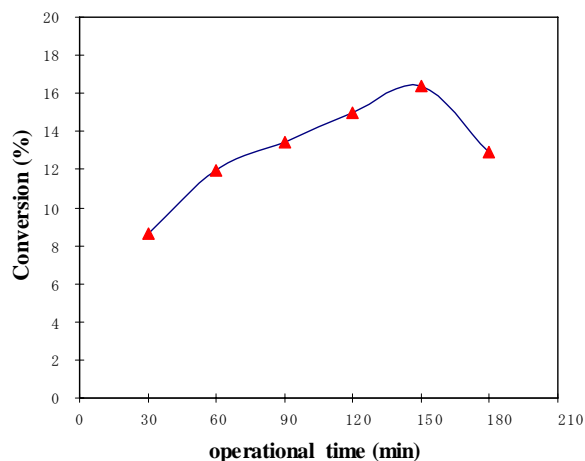


Fig. 6 Effect of the continuous mode of operation on the conversion

An inspection of Fig. 6 shows that there is a slight increase in conversion with time. According to the reaction scheme, salts (NaCl, NaBr) are expected to be produced as byproducts. With time, these salts are accumulated in the microchannel and hardly can be removed from the microchannel by the flow of the organic phase (see Fig. 7).

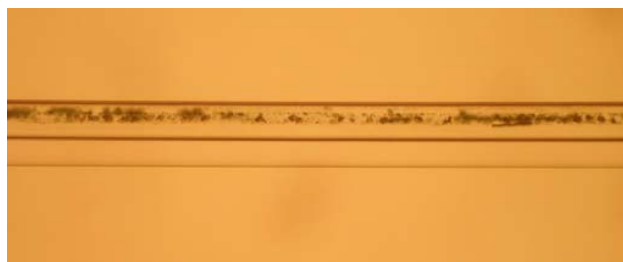


Fig. 7 Salts accumulation inside the microchannel reactor

The presence of these salts has affected the stability of the multiphase flow. It was obvious through optical observation that the multiphase flow was unstably switching from parallel flow to slug flow. The development of the slug-type flow in the microchannel has speeded up the reaction through the extended interfacial area and the internal circulation associated with the formed slugs [10]. However, the excess presence of these salts with time has retarded the reaction.

Fresh water as well as strong alkali solution (concentrated NaOH solution) were pumped through the microchannel inlets to clean the microchannel reactor. However, these salts could not be removed. On the other hand, when sulphuric acid (pH =3) was pumped through the inlets of the microchannel, the salts were removed completely (see Fig. 8).

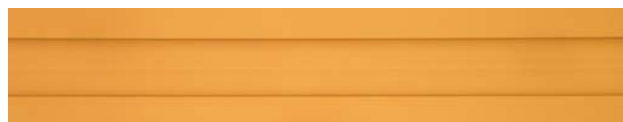


Fig. 8 Salts removal from the microchannel reactor

IV. CONCLUSION

The catalytic phase transfer reaction between benzyl

chloride and sodium sulfide has been studied in a microchannel reactor under two-phase parallel flow conditions. Utilizing a guideline structure ensured the parallel flow pattern inside the microchannel. Phase separation has been examined at different feed flow rates. The wettability property of the microchannel reactor has affected the separation performance of the two phase system. The aqueous phase has been split between the two exits, whereas the organic phase could be separated completely from the organic outlet. The collected aqueous phase has been reused with slightly affecting the performance of the phase transfer catalysis system.

ACKNOWLEDGMENT

Mr. Hajime Ito from Nagoya University is highly acknowledged for his valuable technical assistance and advice.

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