Introduction

Phase transfer catalysis is used widely in the synthesis of many different organic chemicals in liquid–liquid systems enabling fast reactions between otherwise non-reacting components. Conversion and selectivity of phase transfer catalyzed reactions in stirred reactors depend, among other things, on the rate of catalyst transfer across the interface between the liquid drops of both phases in the reactor. The liquid drops in a liquid-liquid stirred reactor system have a wide size distribution as the result of an inhomogeneous energy dissipation induced by the mechanical stirring of the suspension [1]. Consequently, the conversion and selectivity vary from drop to drop. These synthesis reactions can be carried out in capillary microreactors with typical channel diameters of 150 to 250 µm to enlarge the liquid-liquid interfacial surface area beyond the limit which can be achieved using conventional stirred reactors.

The combination of phase transfer catalysis and microchannel reactor technology reduces mass transfer limitations and can increase the selectivity and the reaction rate per unit reactor volume. The alkylation of benzyl cyanide (1) by butyl bromide (2) was chosen as a test reaction to demonstrate this influence of hydrodynamics on conversion and selectivity (Scheme 1). The reaction can yield multiple products and therefore is suitable for the study of reaction selectivity towards the monoalkylated product (3). The phase transfer catalyzed alkylation was investigated under solvent free conditions. The reaction is mass transfer limited, and its rate increases with increasing liquid-liquid interfacial surface-to-volume ratio [2].

Scheme 1: Two phase alkylation of benzyl cyanide

 Slug flow as a tool for reaction control

Summary

Precise control over the segmented flow in a microchannel reactor offers an important tool for the optimization of reaction yield and productivity. The fluidic control over the reaction was demonstrated on the selective alkylation of benzyl cyanide to the monoalkylated product in a 250 µm microchannel reactor. The conversion of benzyl cyanide increased from 39.9% to 99.7% as a result of a 97% larger slug surface-to-volume ratio when the volumetric aqueous-to-organic phase flow ratio was raised from 1.0 to 6.1 at the same residence time. Conversion and selectivity in the microchannel reactor are both significantly larger than in a stirred reactor.

Keywords

Micro-reactors, Complex reacting flows, Process intensification
Precise control over the interfacial area of aqueous and organic slugs in segmented flow in a microchannel reactor provides an attractive means to optimize yield and productivity of a liquid-liquid reaction system. A Y-mixer microchannel system provides a reproducible slug flow, which allows a high degree of control over the slug size distribution and the liquid-liquid interfacial surface-to-volume ratio [3]. By varying the flow ratios of the aqueous (KOH, quaternary ammonium salt as a catalyst) and organic (benzyl cyanide, butyl bromide) phases, the size of the liquid slugs changes (Figure 1). The conversion of benzyl cyanide increases from 39.9% to 99.7% as a result of a 97% larger organic slug surface-to-volume ratio when the volumetric aqueous-to-organic phase flow ratio (AO) is raised from 1.0 to 6.1 at the same residence time of 10 minutes. The larger surface-to-volume ratio significantly promotes catalyst phase transfer and increases the conversion but decreases the selectivity due to the simultaneous increase of the rate of the consecutive reaction to the dialkylation product. Therefore an optimum flow ratio was found with a maximal productivity (Figure 2). The conversions in the microchannel are significantly larger than in a stirred reactor which had a maximal conversion of 25%. Furthermore, the maximal selectivity in the microchannel reactor was 98%, while the batch reactor had 87% for the same residence time.

**Conclusions**

In conclusion, we have demonstrated the potential of using a continuous flow microchannel reactor in solvent-free and selective phase transfer alkylation where the interface between the segmented liquid phases can be precisely controlled to optimize the productivity. This provides a clear advantage over traditional stirred reactors.

**References**

