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Reducing Side Product by Enhancing Mass-Transfer Rate

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Fast mass transfer rate and short reaction time are required to reduce side product of the premixing reaction, in the SNIA Viscosa process, as a liquid-liquid competitive consecutive system. In order to obtain high selectivity, a microstructure device, named a membrane dispersion mini-reactor, was designed and tested at several operation conditions. The mass transfer rate of cyclohexanecarboxylic acid (CCA) was significantly increased by membrane dispersion in this mini-reactor compared with a traditional batch reactor and a membrane free one, just with a residence time less than 80 ms. The results showed that the nominal yield of side product was lower than 10% in the reaction products and about 5% lower than the traditional stirring method. Additionally, a theoretical model was developed to eliminate the mass transfer flux in this mini-reactor, and the calculation results fit well with the experimental data. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 4207–4213, 2006

Keywords: microstructure reactor, mass transfer, selectivity, cyclohexanecarboxylic acid

Introduction

Selectivity and microstructure device

In the 21st century, the demand is for chemical engineering to achieve chemicals synthesis in highly efficient and environmentally benign ways.[1] In order to meet such demand, the enhancement of reaction selectivity is strongly called for. In general, the selectivity is determined by kinetics and thermodynamics. But, considering the diversity of the reaction process, many factors can affect this important property, for example, mass transfer rate,[2,3] temperature,[4,5] reaction time,[6] and so forth. In some situations, some of them will become the key constraints to improve selectivity. In a multiphase reaction system, mixing condition plays an important role, and sometimes well mixing is needed to reduce side products.

Microstructure reactors have triggered an explosion of scientific and industrial interest during recent years,[7–11] which exhibit numerous practical advantages in reactor design and production process, including easy magnification and safety. However, most of the chemical reactions are still taken place in macro-scale batch reactors or tubular reactors now. These reactions are usually slow (reaction time min-h), since fast reactions are difficult to control.[1] With the help of the microstructures, extremely fast reactions (reaction time ms-s) are possible to proceed in micro-reactors, which can provide efficient mixing, fast mass transfer rate, and easily controlled reaction time. Many studies have shown that not only the reaction rate but also the selectivity is remarkably increased by the development of a micro-reactor system.[12–14] For homogeneous systems, the selectivity can be improved by enhancing mixing conditions, especially for competitive parallel reactions[2] and competitive consecutive reactions.[3] For heterogeneous systems, the advantage of microstructure devices is that they can provide well dispersion to reduce mass transfer scale, thus solving some of the problems confining the enhancement of selectivity as well.

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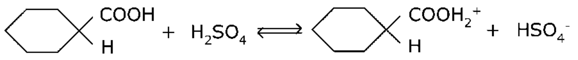
In our laboratory a microstructure reactor, a membrane dispersion mini-reactor, with a micro-filtration membrane as the dispersion medium was developed.[15–18] By using the micro porous membrane, droplet dispersion and efficient mixing are easily achieved in this mini-reactor with low equipment cost. Chen et al.[18] tested the micro-mixing performance in this mini-reactor with the Dushman reaction, and found that the segregation index was less than 0.002. When used in extraction, the membrane dispersion mini-reactor can produce well-dispersed droplets, with the diameter ranging from 10 μm to 200 μm.[17] Xu et al. evaluated the mass transfer characteristics in this mini-reactor with six different liquid–liquid phase systems, and indicated that the extract Murphee efficiency had reached to nearly 100% with a contact time barely from 0.15 s to 0.45 s.

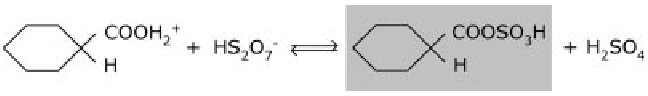
Premixing reaction

In our research, the reaction between cyclohexanecarboxylic acid (CCA) and oleum, a crucial reaction in the SNIA Viscosa process,[19,20] was introduced to this mini-reactor. As a multiphase reaction, the n-hexane solution of CCA was used as the continuous phase and oleum as the disperse phase. The reaction takes place in the aqueous phase, and the details are shown below.[21–23]

It begins with a proton exchange reaction between CCA and sulfuric acid:



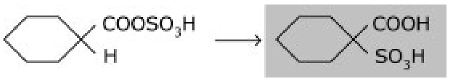
Then the protonated CCA interacts with the pyrosulfuric acid ion, forming the mixed anhydride of cyclohexanecarboxylic acid with sulphuric acid, the precursor of caprolactam, immediately. The mixed anhydride is shown with a gray background:



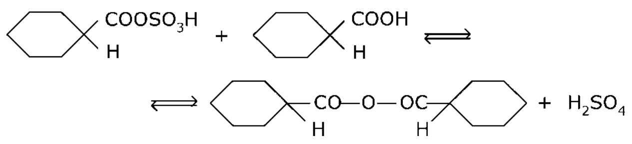
Pyrosulfuric acid ion is obtained from the following reaction:

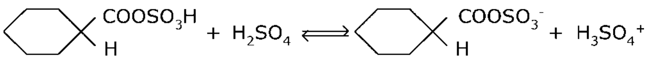
$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^-$$

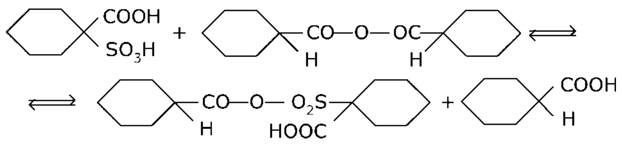
An irreversible side reaction takes place when the mixed anhydride is produced, which is changed to sulphocarboxylic acid, as shown in the scheme below:



In addition, six other equilibriums exist in the aqueous phase:







$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^-$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$$

Mass transfer process is the key to enhance the selectivity

The formation of mixed anhydride from CCA is a reversibly ultra fast process, and the side reaction is a less fast one, under experiment conditions.[24,25] Equilibrium constants of the above reactions were given by Giuffre and Sioli in their early work.[26] According to their analysis, when the oleum is excessive in the aqueous phase, the same as in our experiment, the concentration of CCA and carboxylic anhydride (the production of the reaction between mixed anhydride and CCA) can be assumed to be zero in the aqueous phase, because CCA is transformed rapidly. Considering the low concentrations, the last six equilibriums are not important in this process. The whole process, including mass transfer of CCA and the crucial reactions, can be simply shown in Figure 1.

As a competitive consecutive reaction system, it is a nice way to enhance selectivity based on the differences of reaction rates between the main and the side reaction. In order to get more mixed anhydride in the reaction chain, a short reaction time is called for, since the mixed anhydride will be transformed to side product irreversibly as time passes. However, only a short reaction time is not enough. Though the transformation from CCA to mixed anhydride is ultra fast, the reaction rate is restricted by the mass transfer of CCA. In other words, the selectivity must be enhanced without decreasing CCA conversion. So, a fast mass transfer rate is the key factor to enhance selectivity.

Based on the previous work in our group, the membrane dispersion mini-reactor has been proved to perform good mixing competence, fast mass transfer rate, and easily controlled prosperities. It has been used well in miscible liquid reactions[15,16] and multiphase extraction processes.[17] In this work, the premixing reaction was introduced into this mini-reactor, and the side product was effectively reduced. With the enhancement of mass transfer by the small droplet, the formation of mixed anhydride was increased. The residence time was well controlled to the micro second level through reasonable design of the mixing room and adjusting the flux of the reactants. In addition, the phase ratio of the disperse phase and continuous phase in the premixing reaction is very low, as shown in the experiments below. Mixing under extreme phase ratios can be easily achieved in this mini-reactor by the shear of the continuous phase. The influences of several operation conditions have been considered in this work, including feed ratio, CCA concentration, and flow rate. A batch stir reactor and a membrane free reactor were tested for comparison.

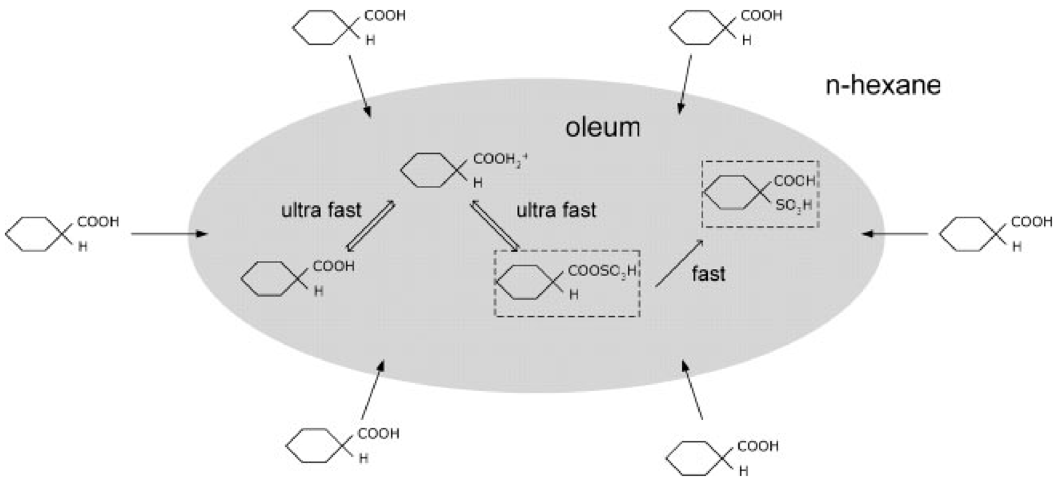


Figure 1. Mass transfer and reaction mechanism of premixing reaction.

Experimental

The membrane dispersion mini-reactor used in this experiment is shown in Figure 2a, and the principle of membrane dispersion is illustrated. A stainless steel micro-filtration membrane with average pore size 5.0 μm (0.3 mm thick) was placed in the middle of the reactor. The active membrane area was 0.1 cm^2, and the volume of the mixing chamber was 0.038 mL. The n-hexane solution of CCA was prepared before the experiment, and the concentration of CCA was determined by gas chromatography (HP 6890). The oleum (63% wt SO_3) was pressed though the membrane first at the beginning of each experiment. Then the CCA hexane solution was pumped directly into the mixing chamber. The reaction temperature was kept constant at 30°C. An ice bath was placed at the outlet to quench the reaction. As a comparison, the premixing reaction was introduced into a batch stir reactor, too, as shown in Figure 2b.

The reaction product was collected into a beaker in the ice bath and split phase quickly. The CCA concentrations in the continuous phase were measured by gas chromatography. Considering that the CCA concentration is not high enough to affect the volume of the hexane solution, we assume that the volumes of the continuous phase remain constant. So the mass transfer flux can be calculated from Eq. 1:

$$M = (C_0 - C_1) \times Q_c \qquad (1)$$

where M is the mass transfer flux of CCA (mol/min), C_0 is the original concentration of CCA (mol/L), C_1 is the concentration of CCA after reaction (mol/L), and Q_C is the volume flow rate of the organic phase. The conversion of CCA can be calculated by the change of CCA concentration:

$$\Phi = \frac{C_0 - C_1}{C_0} \times 100\% \qquad (2)$$

To measure the mixed anhydride and the side product, 1 ml aqueous phase was taken out and hydrolyzed by NaOH solution (20% wt) in the ice bath. Then the pH of the hydrolysis

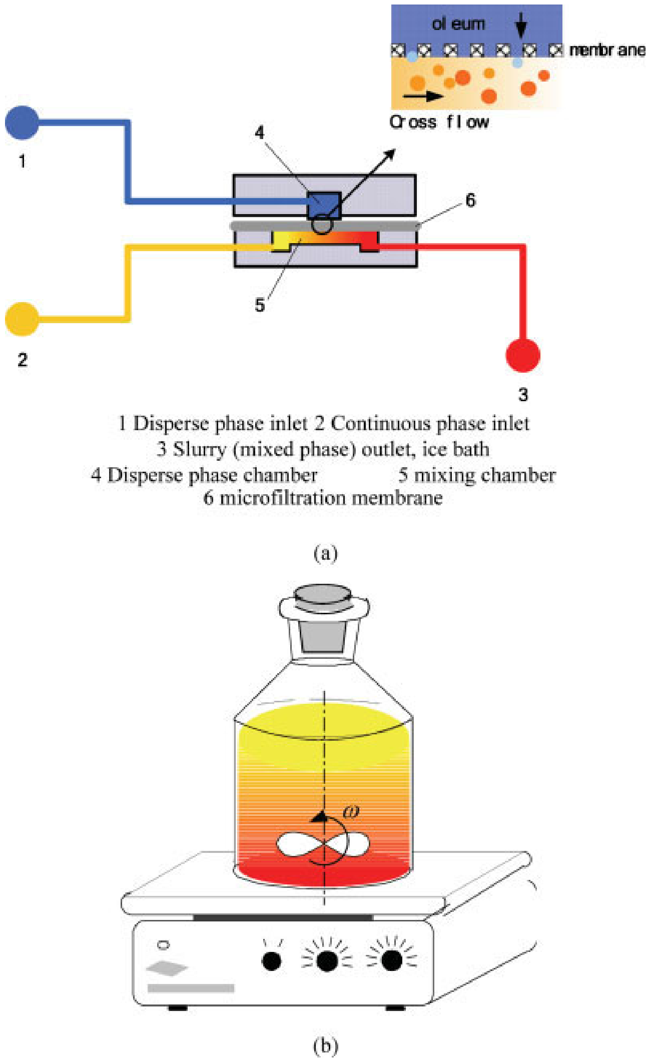


Figure 2. Reaction setups: (a) membrane dispersion mini-reactor, and (b) Batch reactor.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

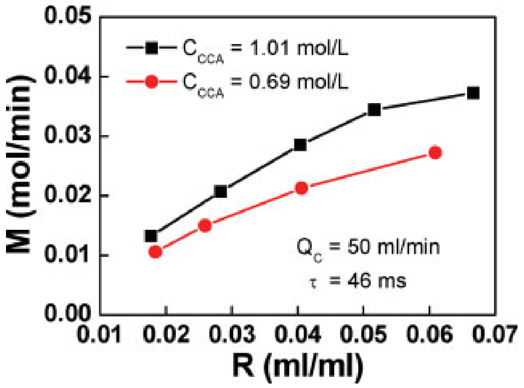


Figure 3. The influence of CCA concentration and feed ratio on mass transfer flux.

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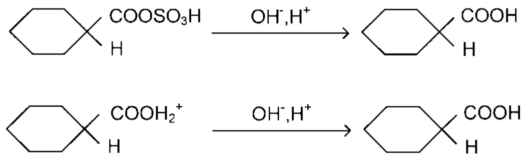
product was adjusted to 2.0, transforming the mixed anhydride and protonated CCA back to CCA feedstock, as shown in the schemes below:



After that, the hydrolysis product was turned to 20 mL by adding water, and mixed with 20 mL n-hexane. After 30 min extraction, the CCA concentration in hexane (C_2) was measured. With a partition coefficient of 9.48 (C_{CCA} organic phase/C_{CCA} aqueous phase, pH = 2), the concentrations of side product in the aqueous phase could be calculated in terms of Eq. 3:

$$C_p = \frac{M}{Q_d} - \frac{C_2 \times (1 + 1/K) \times 20\,\text{ml}}{1\,\text{ml}} \tag{3}$$

where M is the mass transfer flux (mol/min), Q_d is the volume flow rate of the aqueous phase (L/min), C_2 is the CCA concentration in hexane (mol/L), and K is the partition coefficient. Then the nominal yield of side product in the outcomes, including the mixed anhydride, protonated CCA, and side product, could be calculated with dividing the concentration of the side product by the concentration of the whole outcomes, as shown in Eq. 4:

$$S = \frac{C_p}{M/Q_d} \times 100\% \tag{4}$$

Results and Discussion

The influence of operation conditions on mass transfer and side product nominal yield

The Influence of CCA Concentration and Feed Ratio. Figure 3 shows the values of mass transfer fluxes at different CCA concentrations in the continuous phase and feed ratios of oleum to hexane solution. Increasing the CCA concentration not only increased reactant CCA but also accelerated the mass transfer rate, by enhancing the concentration driving force between the two phases. The results showed that the mass transfer flux of CCA increased with the increasing of the feed ratio. As more oleum pumped in, more dispersion phase droplets were produced by the shear of the continuous phase, so the mass transfer rate increased with the increasing of the mass transfer area.

Chen et al. indicated that the flow performance in this mini-reactor was approximately plug flow from the RTD results.[18] Thus, the reaction time (residence time) can be calculated with dividing the volume of the mixing chamber by the flow rate of the two phases. The residence time in this experiment was 46 ms. Figure 4 shows the nominal yields of side product, which are rather small, owing to the extremely short reaction time. Little side product was produced at high CCA concentration, due to fast consumption of SO_3 by the large amount of CCA. According to Wu's result,[27] excessive oleum will promote the side reaction, so the yield of side product increases with the increasing of the feed ratio too.

The Influence of the Continuous Phase Flow Rate. Xu et al. indicated that one of the main factors to affect the droplet size in this mini-reactor is the continuous phase flow rate,[17] since the high flow rate can provide strong cross-flow drag force to produce small droplets, which can shorten the mass transfer distance, provide large mass transfer area, and enhance the mixing process. In addition, it is necessary to make the continuous phase flux high enough in this mini-reactor, since it not only produces small droplets, but also enhances the flow disturbance in the mixing chamber. Figure 5 shows that the mass transfer flux of CCA increases with the increasing of the continuous phase flow rate, even though the residence time (τ) decreases.

The decreasing of residence time with an increase of the continuous phase flow rate reduced the side product as well, as shown in Figure 6. The nominal yield of side product decreased with the increase of the flow rate, since high mass transfer flux of CCA made the product of mixed anhydride form quickly, and less reaction time reduced the opportunity to create side product.

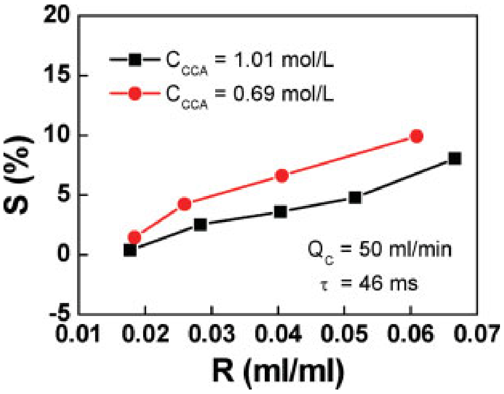


Figure 4. The influence of CCA concentration and feed ratio on the nominal yield of side product.

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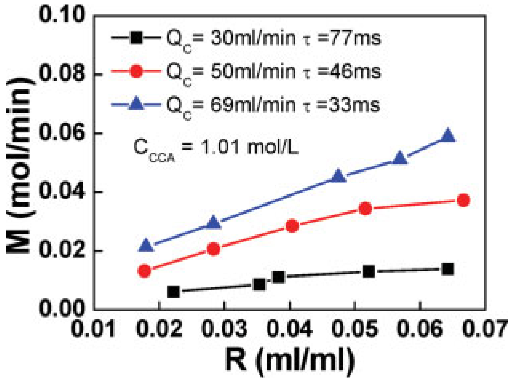

Figure 5. The influence of continuous phase flow rate and feed ratio on the mass transfer flux of CCA.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The comparison with a batch reactor and a membrane free reactor

As is well known, the mass transfer process is strongly dependent on mixing conditions in chemical reactions. Compared with the continuous process in the mini-reactor, a batch one, shown in Figure 2b, was introduced. The mass transfer rate was significantly enhanced in the mini-reactor by comparing the CCA conversion with the reaction time, as shown in Figure 7. In experiments, 50 ml (note V_C in figure) CCA hexane solutions (1.01 mol/L) were used to react with different volumes of oleum at a rotational speed of 1000 r/min. After 5 min reaction, the samples from the two phases were measured.

The mass-transfer fluxes of CCA in different reactors are given in Figure 8, from which we can see that the average mass fluxes of CCA in the batch reactor are much less than the mini-reactor and the membrane free one. The mass transfer fluxes in the mini-reactor are about 80% higher than the membrane free one, owing to the dispersion effect of the membrane.

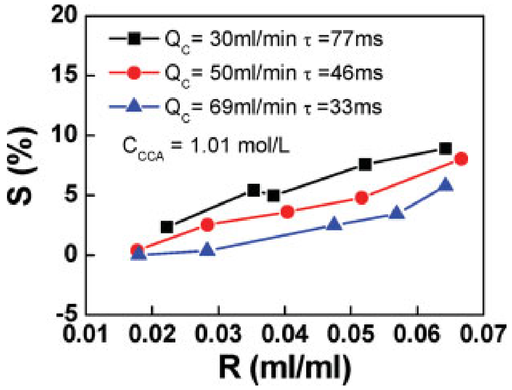

Figure 6. The influence of flow rate and feed ratio on the nominal yield of side product.

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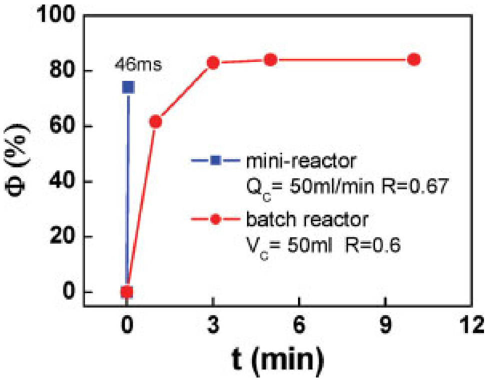

Figure 7. The change of CCA conversion with the reaction time in the mini-reactor and the batch reactor.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figures 9 and 10 indicate the results of CCA conversion and the side product produced in the mini-reactor, the membrane free reactor, and the batch one at different feed ratios. Because of the long contact time in the batch reactor, the CCA conversion is a little higher than that in the mini-reactor at the same feed ratio, but the side product is 5% higher, as shown in Figure 10, owing to the slow mass transfer rate and long reaction time. Without the membrane, the droplet sizes in the mini-reactor become large, so the mass transfer amount is much lower than the membrane one at the same residence time. The nominal yields of side product in the mini-reactor and the membrane free reactor are at the same level due to the same short reaction time.

Dependence of the selectivity on the conversion

Actually, high selectivity and high conversion usually cannot be achieved at the same time. Though we cannot give an exact definition of selectivity for the premixing reaction, we can use the side product nominal yield instead. Figure 11 gives the nominal yields of side product with the CCA con-

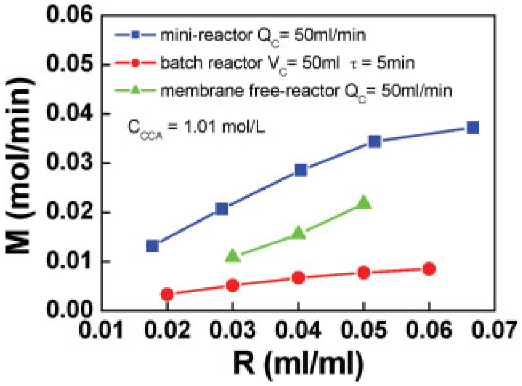

Figure 8. The mass-transfer flux of CCA at different feed ratios in three different reactors.

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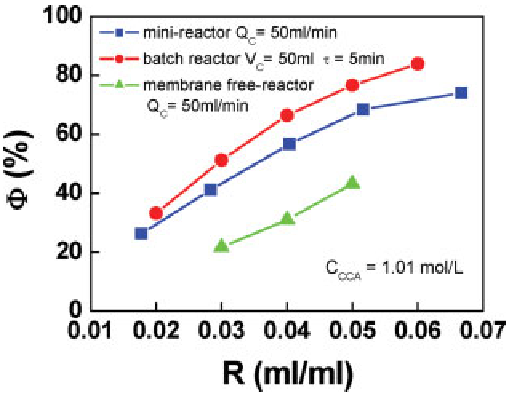

Figure 9. The CCA conversions at different feed ratios in three different reactors.

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versions in those three reactors mentioned above, and shows that the yield of side product increases with the increasing of the CCA conversion. The amounts of side product produced by the mini-reactor are nearly 5% lower than the batch one at high CCA conversion (1.01 mol/L) and high continuous phase flow rates (50 mL/min and 69 ml/min). From the figure we can see that the membrane free reactor can produce less side product than the batch one, but the CCA conversions are much smaller than those in the mini-reactor.

A model to predict mass-transfer flux in the mini-reactor

In this mini-reactor, the violent mixing occurs in the mixing chamber. With the model given by Xu's work,[28] the size of disperse phase droplets can be estimated. Thus, if the mass-transfer coefficient is given, the mass transfer flux in the mini-reactor can be predicted.

The overall mass-transfer coefficient can be described as:

$$\frac{1}{K_{\mathrm{OC}}} = \frac{1}{k_c} + \frac{1}{mk_d} \tag{5}$$

where k_c refers to the continuous phase mass transfer coefficient (m/s), k_d refers to the disperse phase mass transfer coefficient (m/s), and m refers to the participation coefficient. Since the participation coefficient of CCA is much greater than one, the second item in Eq. 5 can be neglected, and the overall mass-transfer coefficient is simplified as:

$$K_{\mathrm{OC}} = k_c \tag{6}$$

which can be calculated by the correlation given by Brauer.[29]

$$Sh_c = 2 + 0.0511\mathrm{Re}^{0.724}Sc_c{}^{0.70}$$
$$4 < \mathrm{Re} < 1000,\ 130 < Sc_c < 23600 \tag{7}$$

$$Sc_c = \frac{\mu_c}{(\rho_c D_c)},\ \mathrm{Re} = \frac{d_d u \rho_c}{\mu_c},\ Sh_c = k_c d_d \rho_c$$

where μ_c refers to the viscosity of the continuous phase (Pa·s), ρ_c refers to the density of the continuous phase (kg/m^3), Dc refers to the mass-transfer coefficient of CCA (m^2/s), d_d refers to droplet diameter (m), and u refers to the velocity of the continuous phase (m/s).

There is cross flow in the mixing chamber. As the concentration of CCA in the aqueous phase is assumed to be zero, the mass-transfer flux can be expressed by Eq. 8:

$$M = K_{\mathrm{OC}} A \Delta C_M \tag{8}$$

Where A is the total surface area of the disperse phase (m^2) and ΔC_M is defined as:

$$\Delta C_M = \frac{\Delta C_0 - \Delta C_1}{\ln(\Delta C_0/\Delta C_1)} = \frac{C_0 - C_1}{\ln(C_0/C_1)} \tag{9}$$

The total area A required to complete the equation can be calculated in terms of the phase ratio (R) and the droplet size (d_d):

$$A = \frac{R}{1+R} \cdot V \cdot \frac{6}{d_d} \tag{10}$$

The calculated results and the experimental data of the mass transfer flux are shown in Figure 12. The calculated data fit

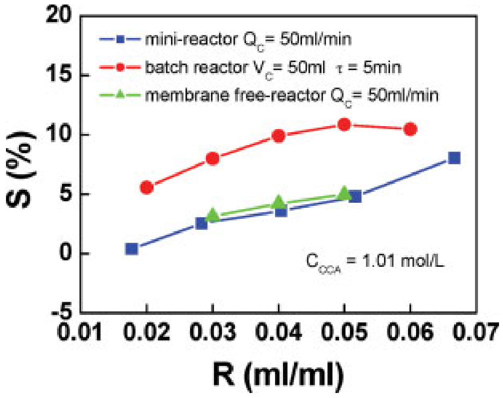

Figure 10. The nominal yield of side product at different feed ratios in three different reactors.

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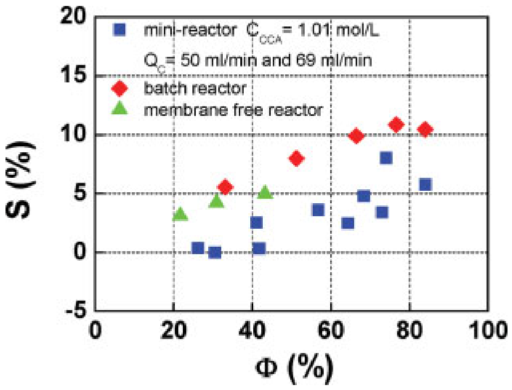

Figure 11. Dependence of the selectivity on the conversion in different reactors.

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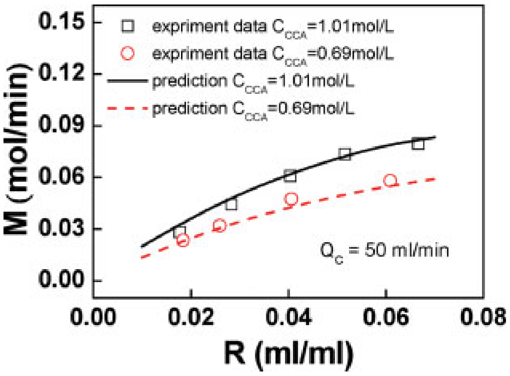

Figure 12. Calculated results and the experiment data of mass-transfer flux.

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well with the experimental results, with a relative deviation of less than 2.0% at high flow rate ($Q_C = 50$ mL/min).

Conclusion

The selectivity of the premixing reaction was enhanced by increasing the mass transfer rate in the membrane dispersion mini-reactor. The results showed that both CCA concentration and flow rate of the continuous phase had significant effects on the mass transfer flux and the residence time in this mini-reactor. Increasing CCA concentration increased the mass transfer driving force, and increasing continuous phase flow rate reduced the disperse phase droplet size with the reaction time, which intensified the mixing process and reduced the side product. Compared with a common batch reactor and a membrane free reactor, the mini-reactor has been proved to enhance the mass transfer process and provide quite a bit less side product at any conversion. Additionally, a cross flow mass transfer model was established to estimate the mass transfer flux, and the calculated results fit well with the experiment data.

Acknowledgments

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