Beckmann Rearrangement of Cyclohexanone Oxime to ε-Caprolactam in Microreactors

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Selectivities are presented of the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam with oleum for various conditions in three microreactors, viz., Y-junction, interdigital, and split and recombine mixers, followed by a 50-cm long microchannel of 250 μm internal diameter. Cyclohexanone oxime is dissolved in cyclooctane, which is inert for oleum. The selectivity is measured in the temperature range of 80–132°C. The concentration range of caprolactam in the reaction mixture is 31–41 wt %, in oleum. The total volumetric flow rate is 0.4 ml/min, whereas the flow rate ratio of ε-caprolactam/oleum over cyclohexanone oxime/cyclooctane ranges from 0.3 to 3. The selectivities measured with the three microreactors are: 70–99+%, 93–99+%, and 95–99+%, respectively. High ε-caprolactam concentration (41 wt %), high temperature (110–132°C), and a ratio of free H_2SO_4 to SO_3 of unity have a negative effect on the selectivity. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 1297–1304, 2010

Keywords: microreactors, mixing, Beckmann rearrangement, selectivity

Introduction

Industrial production of ε-caprolactam by Beckmann rearrangement

The classical Beckmann rearrangement is applied for the conversion of cyclohexanone oxime to ε-caprolactam, a nylon-6 precursor. The worldwide ε-caprolactam demand is expected to grow at 2.9% per year, to reach 4.5×10^6 mt by 2010.[1] The classical bulk production used by the chemical industry is based on benzene or phenol as raw material, which is converted into cyclohexanone. The latter is converted into cyclohexanone oxime via an oximation step, and ε-caprolactam is normally produced via the Beckmann rearrangement of this oxime.[2] This reaction is catalyzed by Lewis acids and is highly exothermic and extremely fast.[3,4] In industry, fuming sulfuric acid (oleum) is generally used as a catalyst.[5] The crude ε-caprolactam reaction mixture, consisting essentially of ε-caprolactam and oleum, is then neutralized by ammonia. After this neutralization, the phase containing ε-caprolactam is separated from the phase containing ammonium sulfate. The phases are purified by extraction with benzene and water. This conventional production process has a few drawbacks. Because of the fast kinetics and exothermic behavior, the production method is limited by the heat produced during reaction. A large recycle loop (50×) in comparison with the cyclohexanone oxime feed is used to limit the temperature rise and to maintain a high selectivity of 99%.[6] This results in a large reactor volume and a long residence time for the ε-caprolactam under reaction conditions, which leads to the creation of by-products. Sumitomo, utilizes an industrial process for the production of ε-caprolactam over a heterogeneous catalyst in the gas phase, which avoids the formation of ammonium sulfate.

The Beckmann rearrangement in H_2SO_4 and oleum

The Beckmann rearrangement of cyclohexanone oxime is the conversion of this oxime to the amide ε-caprolactam, see Figure 1. The mechanism starts with the conversion of the

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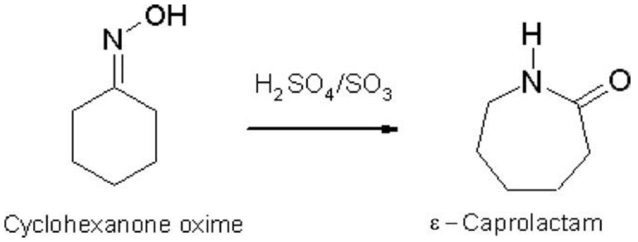

Figure 1. The Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam.

OH group of the oxime into a leaving group. This is typically accomplished by protonation with a strong acid such as sulfuric acid to give an oxonium ion, which is rearranged via the cleavage of the nitrogen-oxygen bond and the simultaneous migration of an alkyl group. This ion is a highly active complex, which reacts directly with an available oxygen group to convert to the amide complex. The kinetics of the reaction in aqueous sulfuric acid at 60 and 90°C are described by Ogata et al.[7] The rate was found to be first order with respect to oxime concentration. The kinetics are rather slow in aqueous H_2SO_4 and many by-products are formed. However, in oleum solutions the reaction rate is strongly increased, as the addition of SO_3 removes water and also increases the formation of the $OXSO_3$ compound (Figure 2). The formation of cyclohexanone oxime proceeds via a concerted mechanism by the exerted ring strain. Cavalieri d'Oro et al.[8] measured the progress of the cyclohexanone oxime rearrangement in SO_2 as a solvent at low temperature (−29 to 19°C) by NMR. They discovered that ε-caprolactam and cyclohexanone oxime are not in the free state, but exist in the form of four complexes ($CPLSO_3$, $CPLH^+$, $OXSO_3$, and OXH^+) with SO_3 and H_2SO_4 (H^+). These are shown in Figure 2. Wichterle and Roček[3,4] measured the kinetics of the final stage of the Beckmann rearrangement in various oleum/ε-caprolactam mixtures, thereby showing the major influence of SO_3 on the reaction kinetics. Their data show a region of invariable rate constant for increasing amount of SO_3, which is important for the suggestion later in this work on the role of pyrosulfuric acid ($H_2S_2O_7$) in the Beckmann rearrangement mechanism in mixtures of ε-caprolactam, sulfuric acid, and SO_3.

The Beckmann rearrangement in microreactors

The Integration of Reaction and Heat Transfer. The main industrial incentives for the integration of reaction and heat transfer equipment are a reduction of equipment size and improved heat management. However, this is only possible with equipment with high heat transfer coefficients. Reactor miniaturization, therefore, is a possible answer, as microreactor dimensions result in high heat transfer coefficients.[9] The Beckmann rearrangement to ε-caprolactam is a relatively fast and highly exothermic reaction, and the temperature rise can be as high as 150°C. To the best of our knowledge, Wichterle and Roček[3,4] are the only authors who published the kinetic rates of the Beckmann rearrangement in fuming sulfuric acid at SO_3 concentrations comparable with industrial conditions, and without additional solvent. Extrapolation of their kinetic parameters to higher temperatures indicates that under industrial conditions, the reaction is finished within seconds to milliseconds. These time scales match well with the short residence times possible in microreactors.

Mixing of Caprolactam/Oleum Mixtures. Mixtures of ε-caprolactam and oleum form an ionic liquid, in which ε-caprolactam is in its protonated form. The viscosity ranges from 300 to 50 mPa s at temperatures of 100–130°C. The physical properties of these mixtures are mainly determined by the acid over lactam ratio (M-ratio). For ratios approaching unity, the viscosity of the ionic liquid increases exponentially. This can be explained by the lattice structure of positive protonated ε-caprolactam ions and negative sulfate and HSO_4^- ions. The viscosity of these mixtures has a large influence on the mixing performance. Bourne[10] and Ottino[11] described the importance of fast mixing for the selectivity of fast reactions; improper mixing in most cases leads to inferior quality of the products. Therefore, the choice of a specific micromixer is very important and needs to be tuned to the specific process. T-mixers and Y-mixers are the most elemental micromixers and are used by many researchers.[12–14] For Reynolds numbers below 180,[13,15] a T-mixer gives a single interface between two miscible liquids, however, this generally does not provide a high mass transfer rate. To generate higher mass transfer rates, other mixing principles, therefore, need to be considered, such as: multiple injection positions, hydrodynamic focusing, splitting and recombination of the liquid layers, and internal recirculation in dispersed liquid–liquid flows. All these methods have been applied in this work.

Cycloalkanes as Inert Solvent and Mass Transfer Medium. Use of an inert solvent may lead to lower gradients of temperature and composition in the reactor, because the reactants are more diluted. The application of inert cycloalkanes as solvent for cyclohexanone oxime is already described by a BASF patent,[16] where it is used for heat removal at the boiling point. Cycloalkanes are known for their inertness toward fuming sulfuric acid, as sulfhonation of an alkane ring is less likely. Additionally water is removed from the cyclohexanone oxime feed. As cycloalkanes are immiscible with oleum/ε-caprolactam mixtures, two-phase segmented flow patterns will arise, which create increased mass transfer surface area by the formation of slugs or droplets. The mixing inside the droplets is described by Bringer et al.[17] and Taha and Cui.[18] To optimize mixing, the liquid slugs must be small but they still have to touch

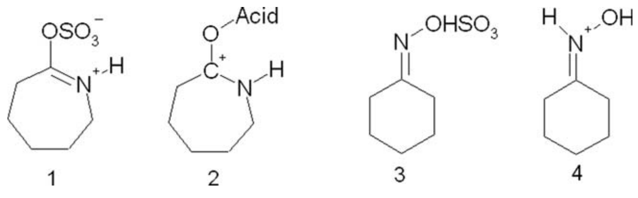

Figure 2. Four complexes of cyclohexanone oxime and ε-caprolactam with H_2SO_4 and SO_3 in SO_2 solution[8]: 1: $CPLSO_3$; 2: $CPLH^+$; 3: $OXSO_3$; and 4: OXH^+.

ε-Caprolactam is not in the free state but in the form of a complex during reaction. Cyclohexanone oxime can only be in the free state just before mixing and also forms complexes in the reaction.

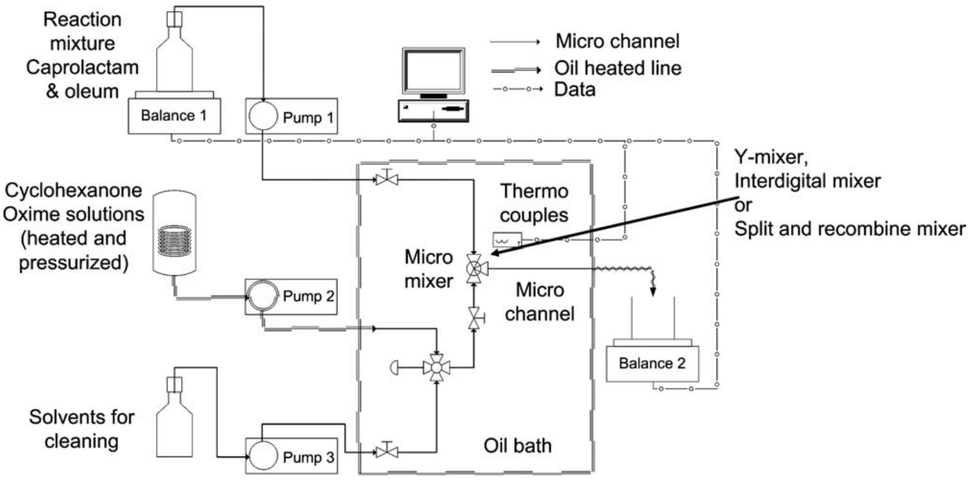

Figure 3. Schematic overview of the microreactor setup.

The microreactor is a combination of a micromixer and a microchannel. The micromixer in the setup can be interchanged between a Y-mixer, an interdigital mixer, and a split and recombine mixer. The 316 stainless steel microchannel has an internal diameter of 250 μm and a length of 50 cm. The cyclohexanone oxime feed line is completely traced to prevent solidification of the oxime.

the channel walls to create a recirculation flow within them. The Capillary number (Ca) must be less than 0.5 for internal circulations to occur, where $Ca = \mu_d u_d / \sigma$ and u_d is the velocity of the droplet.[19] These circulations increase mass transfer in the radial direction for low capillary numbers. However, the aforementioned criterion on Ca shows that there is only a narrow window of application for segmented slug flow. This window is limited mostly by the viscosity of the oleum/ε-caprolactam mixture.

Goal

In this article, selectivities toward ε-caprolactam are determined in a microreactor setup, equipped with three different micromixers: a Y-mixer, an interdigital mixer, and a split and recombine mixer. The microreactor is seen as a combination of a mixer and a microchannel for added residence time. The aforementioned mixers comprise a series of increasing mixing intensity, the highest by means of the split and recombine mixer. Selectivity is chosen as the parameter to evaluate reactor performance.

Experimental

Equipment

A schematic of the microreactor setup is shown in Figure 3. In this work, the microreactor is considered as the combination of a micromixer and a 316 stainless steel microchannel with an internal diameter of 250 μm, a length of 50 cm, and an external diameter of 1.6 mm. The liquid flow is controlled by two Gilson 305 HPLC pumps and the mass flow is recorded by two Sartorius balances with an accuracy of 0.01 g. An additional HPLC pump for pure cyclooctane (thermoseparation-spectra P200) is used prior and after the experiments for cleaning of the microchannel. The cyclohexanone oxime in cyclooctane mixture feed line including the HPLC pump head is temperature traced (>90°C) by a Lauda ecoline thermostat. The cyclohexanone oxime supply vessel is slightly pressurized by inert nitrogen atmosphere and heated by an internal heat coil fed by the same Lauda ecoline thermostat. The oleum/ε-caprolactam HPLC pump is equipped with high viscosity spring loaded, PTFE sealed, check valves. The microreactor, valves, and preheater channels are immersed into another Lauda ecoline thermostat, where the temperature is measured by two thermocouples. The 316 stainless steel feed lines are sufficiently long to guarantee the same inlet temperature of both reactants. The ratio of oleum over ε-caprolactam (M-ratio: ([H_2SO_4] + [SO_3])/[ε-caprolactam]) is chosen close to unity (≈1.3), to reduce the production of ammonium sulfate coproduct. Three different micromixers were tested, viz., a Y-mixer, an interdigital mixer, and a split and recombine mixer.

Three different micromixers were tested, viz., a Y-mixer, an interdigital mixer, and a split and recombine mixer.

Y-mixer. The stainless steel Y-junction element has a 90° angle between the inlet channels. The channels have a diameter of 250 μm.

Interdigital Mixer. The interdigital micromixer (see Figure 4) is described in literature[20,21] and is commercially available (Institut für Mikrotechnik Mainz GmbH).

Split and Recombine Mixer. The design of the stainless steel split and recombine mixer (Figure 5) is adapted from the glass split and recombine mixer of Micronit (Enschede,

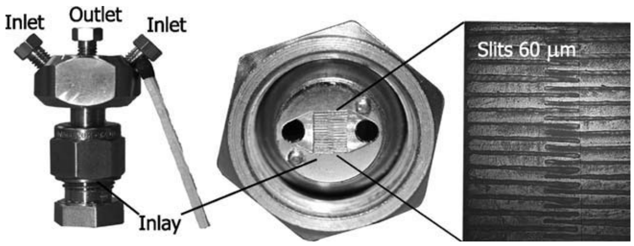

Figure 4. The HPIMM slit interdigital micromixer (left) with Valco® connectors.

A Swagelok® nut with an inserted micro interdigital element (middle). Detail of the microinterdigital inlay of the mixer (right). The slits have a width of 60 μm.

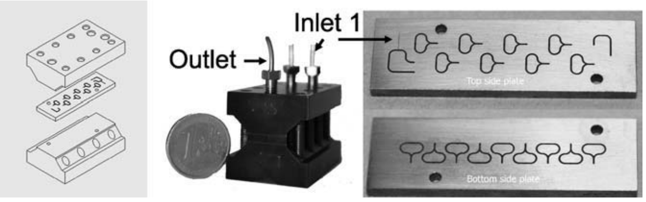

Figure 5. The split and recombine micromixer with a protective coating of diamond-like-carbon (DIARC®).

The left picture shows a schematic view of the assembly. The middle picture shows the assembled mixer. The right picture shows the top and bottom sides of the lasered plate. The large channel has a width of 312 μm, the small channel has a width of 122 μm. The top and bottom sides are interconnected by lasered holes with a diameter of 250 μm.

The Netherlands). Inlet 1 has a smaller hydraulic diameter compared with the main channels to increase the velocity of the low-viscosity dispersed cyclooctane phase. The channels are manufactured by laser ablation with tolerances of 2 μm. The channels have the shape of a triangle, rounded at the bottom, where the cross-sectional surface area available for flow is equal to the surface area of a round channel with a diameter of 250 μm (Figure 6). The small channel has a parabolic shape with 1/10th of the cross-sectional surface area of the main channel. The mixer is coated with a 1 μm Diarc® diamond-like-carbon layer to prevent corrosion. The reactants are combined in the T-section where the cyclooctane solution is fed by the smaller channel (Inlet 1).

Microchannel. One mixer is connected to a microchannel as described earlier. Pressure tightness of connections is guaranteed by 1/16 inch HPLC Valco® connections. The outlet of the microchannel is in a beaker in open air, where the product sample is collected on a Sartorius balance.

Measurement procedures

Synthetic reaction mixtures were prepared by carefully admixing of known quantities of known concentrations of oleum, sulfuric acid, and ε-caprolactam. The resulting synthetic mixtures (Syn-CL-A) were measured by HPLC, titration, and NMR for verification of the chosen composition. Cyclohexanone oxime/cyclooctane solutions (Ox-COc) were prepared according to the desired mass fractions and heated if necessary to completely solvate all cyclohexanone oxime.

Selectivity. The cyclohexanone oxime solution supply vessel was filled with the desired solution and maintained at a temperature >90°C under slightly pressurized nitrogen atmosphere (~0.2 bar). The mixer and microchannel were flushed with pure cylooctane until the thermostatic bath was stationary at the desired temperature. Then the synthetic ε-caprolactam/oleum mixture was introduced in the micromixer and subsequent microchannel and contacted with the cyclohexanone oxime/cyclooctane solution. The reactor and feed channels were flushed for at least 30 min. The sample was collected over a period of 45–60 min and the weight gain of the sample as well as the weight loss of the synthetic oleum/ε-caprolactam mixture were recorded, the difference accounts for the amount of cyclohexanone oxime/cyclooctane solution. This results in an accuracy of 0.7% for the quantity of ε-caprolactam and cyclohexanone oxime. The resulting product reaction mixture and cyclooctane phases were separated. The ε-caprolactam/oleum phase samples were measured by HPLC, titration, and NMR and the cyclooctane samples by GC to determine the total composition.

The selectivity S_{proc} was calculated by the following equation:

$$S_{\mathrm{proc}} = \frac{P_{\mathrm{prod}} \times F_{\mathrm{cap}} - P_{\mathrm{syn}} \times F_{\mathrm{capsyn}}}{F_{\mathrm{oxime}}} \qquad (1)$$

where P_{prod} [%] is the purity of ε-caprolactam in the product mixture, P_{syn} (%) is the purity of ε-caprolactam of the synthetic mixture, F_{cap} (g) is the total amount of ε-caprolactam and converted oxime in the product reaction mixture, F_{capsyn} (g) is the amount of ε-caprolactam in the synthetic mixture, and F_{oxime} (g) is the amount of converted cyclohexanone oxime in the product mixture. The purity is determined by NMR measurement. By this method, the selectivity (measured in percentage) is determined within a measurement error of 1%.

Conversion. The conversion of cyclohexanone oxime was determined by quenching the reaction mixture in a small bottle, which was cooled by liquid nitrogen to stop the reaction. Subsequently, the sample was diluted by D_2O for NMR analysis or by water for HPLC analysis. The quantities of cyclohexanone oxime, of ε-caprolactam, of cyclohexanone, and of aminocaproic acid were used to determine the total conversion of cyclohexanone oxime within a measurement error of 0.3%.

Results

Conversion

Table 1 shows the conversion of cyclohexanone oxime versus temperature in the reactor setup equipped with the Y-mixer and the interdigital mixer, respectively. The initial composition and the flow rate of the synthetic oleum/ε-caprolactam solution are constant at an M-ratio of 2.0 (Table 2) and a flow rate of 0.2 ml/min. The flow rate of the 10 wt % solution of cyclohexanone oxime in cyclooctane is 0.2 ml/min. The residence time of the reactants in the mixer and

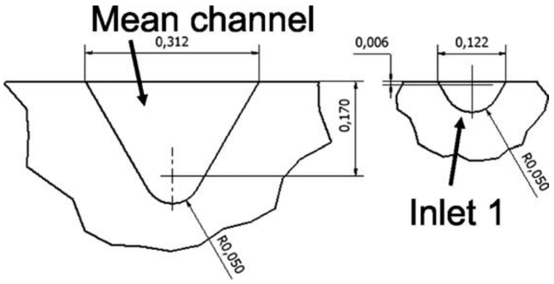

Figure 6. Cross-section of the large main microchannel and the small side inlet in the split and recombine mixer.

The dimensions are in millimeter (mm). The cross-section of the large channel has the same cross-sectional surface area as a round channel with a diameter of 250 μm, the small channel has a surface area of 10% that of the large channel.

Table 1. Conversion of Oxime in the Y–Mixer and the Interdigital Mixer

	50°C	60°C	70°C	80°C	90°C	100°C
Y–Mixer	63%	68%	79%	93%	–	–
Interdigital mixer	–	–	–	94%	99%	100%

The error in the measurement is ± 0.3%.

the subsequent microchannel is ≈4 seconds. The conversion is incomplete at low temperature (<90°C), which shows that the time needed for mixing and reaction is insufficient. The Y-mixer and the interdigital mixer both have a similar conversion at 80°C. The reaction is completed within a few seconds at temperatures above 90°C, and cyclohexanone oxime is completely converted at 100°C in case of the interdigital mixer. The apparent activation energy of the reaction in these experiments is close to 45 kJ/mol, both for the Y-mixer as well as for the interdigital mixer, where Wichterle and Roček[3] report 104 kJ/mol for experiments with oleum at lower temperatures. This means the reaction is in a different kinetic regime or, as the activation energy is approximately half of the value found by Wichterle and Roček, more likely is under mass transfer limited conditions. However, the amount of data is too limited to draw any further conclusions.

Selectivity

Cyclohexanone Oxime Concentration. Figures 7a–c show selectivities toward ε-caprolactam as a function of temperature for different cyclohexanone oxime concentrations. The composition of the oleum/ε-caprolactam solution is kept constant (Table 2, M-ratio = 2.0). Constant flows of Syn-CL-A mixture (0.2 ml/min) and cyclohexanone oxime solution (0.2 ml/min) were fed to the reactor. With increasing cyclohexanone oxime concentration, the percentage of oxime in the total feed of oxime and lactam increases and more lactam is produced. For the experiments with 20 and 30 wt % solutions of oxime in cyclooctane, the cyclooctane phase still contained cyclohexanone oxime at the outlet of the reactor, which means that the conversion was not complete. This may explain the lower selectivities, as the reaction continued in the collection beaker under uncontrolled circumstances. The highest selectivities for all mixers are found for a solution of 10 wt % of cyclohexanone oxime. At conversions of 93–100% for the Y-mixer, selectivities of 99% and higher are reached for temperatures between 80 and 96°C. The interdigital mixer shows a maximum selectivity of 99% at 90°C. A comparison between Figures 7a,b shows higher selectivities for the interdigital mixer also at high temperatures, compared with the Y-mixer. This can be attributed to the additional surface area for mass transfer, created in the interdigital micromixer by the multilamination inlet section.[20,21] The selectivities for the 5 wt % solution of cyclohexanone oxime in cycloctane are remarkably lower, even compared with the 20 wt % solution. Use of the split and recombine mixer also leads to decreased selectivities for the 5 wt % solution of cyclohexanone oxime in cyclooctane. As 10 wt % solutions yielded the highest selectivities at 100% conversion, this concentration is used in later experiments. It should be noted that for a 10 wt % solution of cyclohexanone oxime in cyclooctane, the ratio of cyclohexanone oxime to ε-caprolactam in the feed section is a factor 7 higher than for an industrial reactor.

Figure 8 shows selectivities measured for the Y-mixer at a constant flow rate of Syn-CL-A mixture (M-ratio = 2.0) of 0.2 ml/min and an increasing flow rate of cyclohexanone oxime solution from 0.08 to 0.4 ml/min at a constant temperature of 111°C. 5 wt % solutions of cyclohexanone oxime in cyclooctane have a considerable lower selectivity when compared with 10 wt % solutions. This lower selectivity and variation can be attributed to the role of the pyrosulfuric acid ($H_2S_2O_7$) equilibrium in the mixture of oleum and ε-caprolactam, as discussed in the next section.

Pyrosulfuric Acid. Fuming sulfuric acid or oleum can be represented by $H_2SO_4 \times x \times SO_3$. If x equals 1, oleum forms pure pyrosulfuric acid with the chemical formula $H_2S_2O_7$:

$$H_2SO_4 + SO_3 \rightleftharpoons H_2S_2O_7 \tag{2}$$

Pure pyrosulfuric acid, which corresponds to oleum with 44.9 wt % free SO_3, crystallizes at about 35°C, the maximum of the freezing-point curve in the oleum range. In addition to oleum, the Beckmann rearrangement mixture contains mainly ε-caprolactam and cyclohexanone oxime, which, however, do not exist in the free state in the reaction system. The most prominent complex that can be found[8] is $CPLH^+$, the product of capture of H_2SO_4 by ε-caprolactam, see Figure 2. It forms an ionic liquid. The capture of H_2SO_4 diminishes the total amount of H_2SO_4 in the mixture, which can bring the ratio of the concentrations of SO_3 and H_2SO_4 close to one. Because of the equilibrium with pyrosulfuric acid (Eq. 2), the sum of the concentrations of SO_3 and H_2SO_4 then is at a minimum. In studies on the mechanism of the Beckmann rearrangement, the role of SO_3 as catalyst as well as dehydration agent is acknowledged. Wichterle and Roček[4] determined reaction rate constants in oleum/ε-caprolactam mixtures as a function of SO_3 concentration. As mentioned earlier, they found a region between 5 and 12 wt % of SO_3 where the rate constant is constant. This region corresponds to the region where the remaining H_2SO_4 and SO_3 have a ratio close to 1. We show a number of experiments (Figures 7b,c,h, and 8) where the selectivities for 5 wt % cyclohexanone oxime solutions are lower than for 10 wt % solutions. As in the case of 5 wt % solution for 100% conversion a lower amount of cyclohexanone oxime is converted, less heat is generated and therefore a lower amount of by-products and thus a higher selectivity is expected. However, if we compare free H_2SO_4 over SO_3 concentration ratios of the 5 wt % cyclohexanone oxime experiments, they have a ratio close to 1, whereas the other experiments have

Table 2. Composition of the Synthetic Caprolactam Mixtures

M-Ratio	Caprolactam (wt %)	H_2SO_4 (wt %)	SO_3 (wt %)
2.6	31	58	11
2.3	34	56	11
2.0	37	52	11
1.7	41	48	11

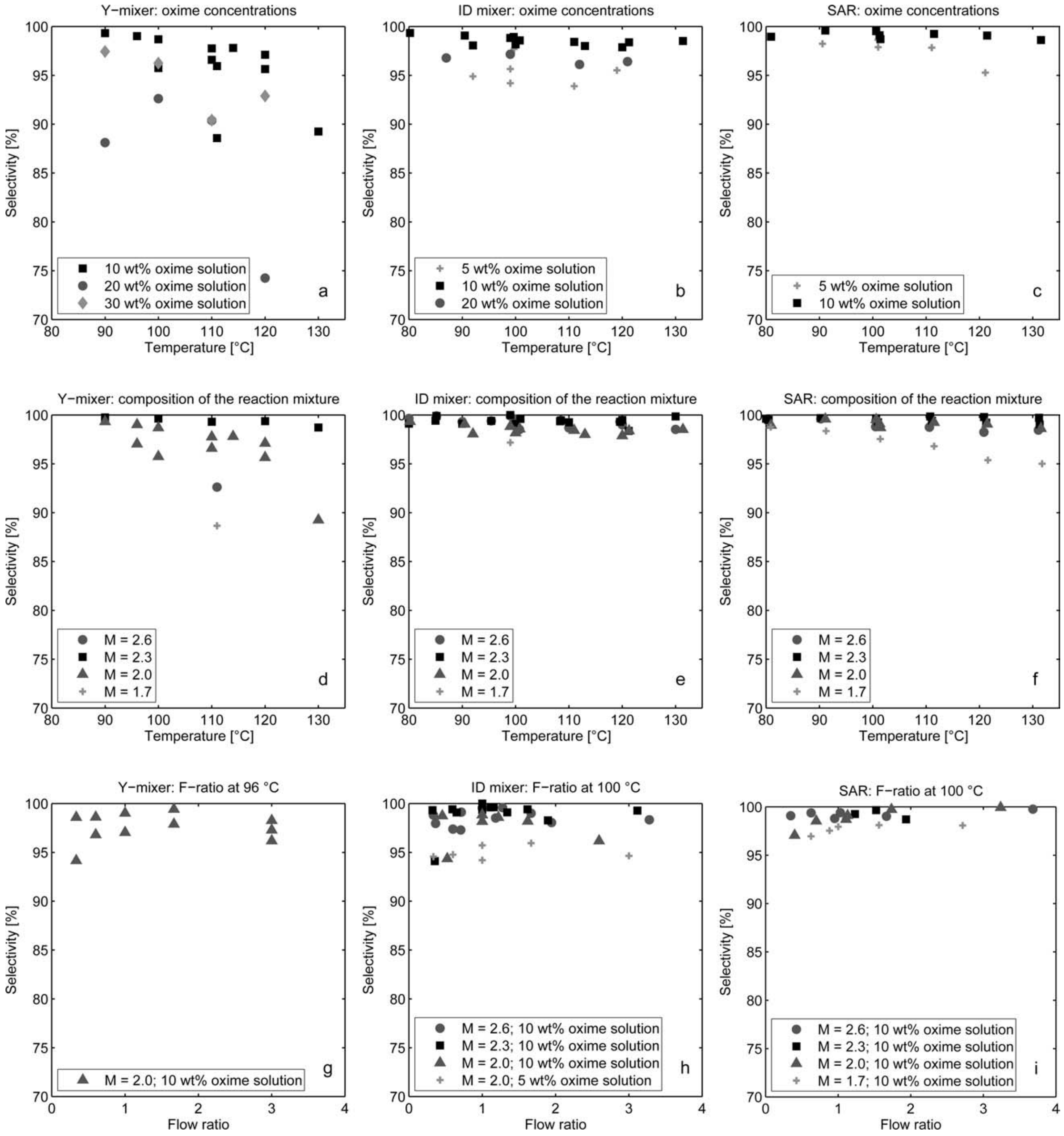

Figure 7. (a–i) The selectivities to ε-caprolactam measured for the Y-mixer, the interdigital (ID) mixer, and the split and recombine (SAR) mixer for temperatures from 80 to 132°C in a 3 × 3 matrix for easy comparison between the mixers.

(a–c) Oxime concentrations of 5, 10, 20, and 30 wt % for an M-ratio of 2.0; (d–f) The selectivities for four compositions (M-ratio of 2.6, 2.3, 2.0, and 1.7) measured at a flow rate of 0.2 ml/min of Syn-Cl-A and 0.2 ml/min of cyclohexanone oxime in cyclooctane; and (g–h) the selectivities for various flow ratios of Syn-Cl-A over cyclohexanone oxime in cyclooctane at constant temperature.

either higher or lower values. This suggests that the pyrosulfuric acid equilibrium can also influence the route of reaction, and therefore selectivity.

Composition of the Reaction Mixture. Figures 7d–f show the influence of the composition of the Syn-CL-A mixtures and reaction temperature on the selectivity. Four compositions are used with increasing amount of ε-caprolactam at constant SO_3 concentration (Table 2). Constant flows of Syn-CL-A (0.2 ml/min) and 10 wt % cyclohexanone oxime in cyclooctane (0.2 ml/min) are fed to the reactor. The Y-mixer shows a low selectivity for an M-ratio of 2.6. The interdigital and split and recombine mixers show high selectivities around 99%. The temperature has a small effect on the selectivity (1–2% with a measurement error of 1%). An

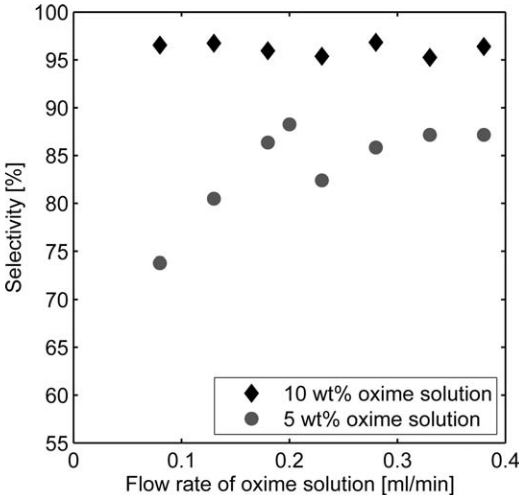

Figure 8. Selectivities to ε-caprolactam using the Y-mixer with 5 and 10 wt % solutions of cyclohexanone oxime at a temperature of 111°C.

The flow rate of cyclohexanone oxime in cyclooctane is increased, whereas the flow rate of Syn-CL-A (M-ratio = 2.0) is kept constant at 0.2 ml/min.

M-ratio of 2.3 shows the highest selectivities for all three mixers; all are above or only slightly below 99%. At an M-ratio of 2.0, the selectivity in the Y-mixer drops below 98%. The selectivities of the interdigital mixer remain around 98%, whereas the selectivities in the split and recombine mixer remain at about 99%. At an M-ratio of 1.7, the composition is approaching 40 wt % of ε-caprolactam, which comes close to industrial conditions. In this case, the selectivity decreases strongly for the Y-mixer and moderately for the interdigital mixer. For the split and recombine mixer the selectivity of the process decreases as well; only at low temperatures of 80°C the selectivity reaches toward 99%.

Flow Ratio. Figures 7g–i show the influence of the flow ratio of the Syn-CL-A mixtures over a cyclohexanone oxime in cyclooctane solution. The temperature was kept constant at 96°C for the Y-mixer and at 100°C for the interdigital and split and recombine mixers. The total flow rate is kept constant by varying both flows of ε-caprolactam/oleum and cyclohexanone oxime in cyclooctane between 0.1 and 0.3 ml/min to a total of 0.4 ml/min. The highest selectivities are reached for a flow ratio between 1 and 1.7. At lower flow rates, the selectivity drops, which can be attributed to either the decreased mixing in the larger Syn-CL-A mixture slugs or to the role of the SO_3 to H_2SO_4 ratio mentioned earlier. The decrease in selectivity with increasing cyclohexanone oxime flow rate is explained by the larger amount of the oxime that is converted in the reaction. For the interdigital mixer, the flow ratio only has a minor effect on selectivity in this range of flows, and is high for the tested range of conditions. The selectivity at 5 wt % solution of cyclohexanone oxime in cyclooctane is again remarkably lower compared with that of the 10 wt % solution. This can be attributed to the role of pyrosulfuric acid and the SO_3 to H_2SO_4 ratio, as mentioned earlier. For an M-ratio of 2.6, the split and recombine mixer shows selectivities above or only slightly below 99%. Increasing the amount of ε-caprolactam slightly decreases the selectivity. Also for an M-ratio of 2.0 the selectivity varies around 99%. An M-ratio of 1.7, with the highest concentration of ε-caprolactam and the highest viscosity, comes close to industrial compositions as the M-ratio decreases to 1.4 along the reactor by the additionally formed ε-caprolactam. However, in this case all selectivities are below 99%. Smeets et al.[6] show that at this composition selectivities higher than 99% are possible in the turbulent regime, with high *Re* numbers, therefore even more intense mixing is needed for this composition. This means that a mixer with an even higher mixing intensity than the split and recombine mixer is needed for this temperature and compositions, for example, less distance between the split and recombine steps, feed of the reactant by an interdigital design with multiple injections, and/or more split and recombine steps.

Discussion

For M-ratios of about 2.3 selectivities of 99% are found for all micromixers. Furthermore, the chosen amounts of cyclohexanone oxime, ε-caprolactam, and oleum fed to the microreactor in this work increase the ratio of cyclohexanone oxime over ε-caprolactam that is introduced into the mixing section of the reactor when compared with the industrial mixer. This implies that the industrial recycle ratio thus can be decreased from 50 to 7 by means of microtechnology. However, for industrial application, the M-ratio in the mixture must decrease to a lower value of about 1.4.

Higher concentrations of ε-caprolactam lead to a clear distinction between the mixers and only the split and recombine micromixer is able to reach 99% selectivity. However, this can only be achieved at low temperature, whereas for heat management and liquid conveying reasons the reaction should be operated at a temperature as high as possible, while maintaining 99% selectivity. For these high concentrations of ε-caprolactam, the capillary number is ≈0.5, the critical limit above which no internal circulation occurs in the slugs. In general, the selectivities of all micromixers show a decrease in this region, which can be attributed to less intensified radial mass transfer. This can be circumvented by reduction of the flow rate. However, this will increase the amount of microchannels needed for production. Apparently, the micromixers used in this study are reaching their limit at high ε-caprolactam concentrations. The radial mass transfer should be enhanced by other micromixer designs, for example, multiple inlets and smaller and shorter split and recombine steps. For even smaller channels, clogging of the micromixer by highly viscous by-products created during the Beckmann rearrangement is likely to occur. This was also experienced by the authors during experiments under too extreme conditions.

Concluding Remarks

Selectivities are presented of the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam for various conditions in three micromixers, viz., Y- junction, interdigital, and split and recombine micromixers, followed by a 50-cm long and 250 μm inner diameter microchannel. All micromixers yield selectivities of over 99% for certain operating conditions.

Y–mixer

Selectivities as high as 99% are reached for M-ratios of 2.3. However, the selectivity decreases below 99% for lower M-ratios. Selectivities determined for the Y-mixer have a broad range (74–99%), implying that mass transfer conditions in the microchannel are not ideal.

Interdigital mixer

The mass transfer and reaction performance is increased in this micromixer. This is shown by a 100% conversion with 100% selectivity, within experimental error, for M-ratios of 2.3. However, at lower M-ratios, the selectivity decreases below 99%.

Split and recombine mixer

The application of the split and recombine mixer provides a range of conditions (M-ratio of 2.6–2.0) for which the selectivity is above 99%, compared with the other two mixers. However, for reaction mixtures with 41 wt % of ε-caprolactam (M-ratio of 1.7) in the mixture, the selectivity is below 99%.

High ε-caprolactam concentration (41 wt %, M-ratio of 1.7) and high temperature (110–132°C) have a negative effect on the selectivity of the Beckmann rearrangement and all three micromixers used are not capable of performing the conversion of cyclohexanone oxime toward ε-caprolactam at selectivities of 99%. As the *Ca* number is ≈ 0.5 for this higher ε-caprolactam concentration, the lower selectivities are attributed to a decrease in recirculation, and therefore less mass transfer, in the liquid slugs.

Pyrosulfuric acid

Experiments where the composition of the reaction mixture, a mixture of mostly $CPLH^+$, SO_3, and H_2SO_4, has a molar ratio of unity for SO_3 and H_2SO_4, show remarkably lower selectivities. Y-mixer, interdigital mixer, and split and recombine mixer lead to selectivities decreased by 2–5%, when compared with experiments with a double amount of cyclohexanone oxime. The pyrosulfuric acid equilibrium is suggested to influence selectivity because less SO_3 or H_2SO_4 is available as catalyst and/or dehydration agent if the molar ratio is unity.

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