# Beckmann Rearrangement in a Microstructured Chemical System for the Preparation of ε-Caprolactam

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*A microstructured chemical system, constructed with a microsieve dispersion mixer, a delay loop and a microhydrolyzer is designed to carry out the Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam. The system is operated with oleum as the dispersed phase, and cyclohexanone oxime n-octane solution as the continuous phase. The mixing performance, conversion of cyclohexanone oxime and selectivity to ϵ-caprolactam are investigated and the results show that the reaction can be very well controlled due to the formation of microdroplets ranging from 10–25 μm. Under optimized conditions, the reaction can be accomplished with a residence time less than 40 s, and the selectivity higher than 99%. A two-stage technology of low-temperature to induce reaction, and high-temperature to enhance reaction is developed, and the corresponding molar ratio of oleum to cyclohexanone oxime can be reduced to 0.8, which is much lower than the industrial value of 1.2.* © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 925–931, 2012

*Keywords: Beckmann rearrangement, ϵ-caprolactam, conversion, selectivity, microstructured chemical system*

## Introduction

The classical Beckmann rearrangement is an important step in the production of ϵ-caprolactam, the monomer for nylon-6. Nowadays, nearly 90% of caprolactam is produced by the conventional cyclohexanone process in large-scale industrial production. The conversion of cyclohexanone to cyclohexanone oxime is achieved by an oximation process and caprolactam is obtained via Beckmann rearrangement. In this process, the concentrated sulfuric acid or oleum is mainly used as catalyst. The conventional process carries several serious drawbacks, such as a high byproduction of ammonium sulfate in the following neutralization step. Nearly 2 tons of ammonium sulfate per ton of product are produced in the rearrangement step,[1,2] since high-molar ratio of oleum to cyclohexanone oxime (1.7) is applied. A three-stage rearrangement technology was described by a BASF patent,[3] lowering the acid/oxime molar-ratio to 1.2, which is the lowest value as far as we know. Process safety is also a serious issue. Since the rearrangement is very rapid and highly exothermic, an external circulation technology is applied for controlling the reaction temperature and mixing conditions, which requires quite large reactor volume and long residence time. This long residence time normally ranging from 15–180 min, leads to a negative effect on the caprolactam selectivity.[4]

As ϵ-caprolactam is an important product with growing demand, there are extensive researches ongoing for new synthesis processes. Beckmann rearrangement on solid catalysts is a promising alternative process since it would avoid the production of ammonium sulfate. Several solid acid catalysts

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have been tested for the reaction. Mao et al.[5] described the catalytic performance for the vapor-phase rearrangement over $B_2O_3$ catalysts supported on various oxides such as $SiO_2$, $Al_2O_3$, $TiO_2$ and $ZrO_2$. Among these catalysts, $B_2O_3/TiO_2$-$ZrO_2$ catalyst showed the best performance. Bordoloia and Halligudi[6] used the catalyst of WOx/SBA-15(20) under the vapor-phase reaction conditions (temperature = 350°C and 2.5 wt % oxime in MeOH), giving cyclohexanone oxime conversion of 79%, and the $\epsilon$-caprolactam selectivity of 93%. Although a serial of similar results about the vapor-phase Beckmann rearrangement processes have been reported,[7–9] low caprolactam selectivity and rapid decay of catalytic activity because of high-reaction temperatures keep the process from being widely employed in the industrial production. Meanwhile, liquid-phase Beckmann rearrangement under mild conditions in a suitable solvent would be another important research direction.[10–13] However, the conversion and selectivity are not satisfactory compared to the classic process, and the solvent such as *N*,*N*-dimethylformamide (DMF)[14] may cause new environmental problems.

Microstructured chemical system can provide another potential solution to overcome the drawbacks mentioned previously in the Beckmann rearrangement process. Microstructure devices can provide high heat-transfer coefficients up to 54,000 W/($m^2$·K), and high-surface area for the heat exchange.[15] Thus, the reaction heat can be removed quickly and the reaction temperature can be well controlled. Moreover, microstructure devices can provide efficient mixing conditions,[16] which is helpful for improving the selectivity[17] and reducing the consumption of oleum. Fast mass-transfer rate between microdroplets and their surrounding solutions can significantly increase the apparent reaction rate and even finish the fast reactions within milliseconds to seconds.[18] Zuidhof et al.[19] carried out the Beckmann rearrangement of cyclohexanone oxime with oleum (containing caprolactam) in three microreactors: Y-junction, interdigital and split and recombine mixers. The split and recombine mixers perform better than the other two, achieving high selectivity (>99%) in the M-ratios (M-ratio = ($[H_2SO_4]$ + $[SO_3]$)/[$\epsilon$-caprolactam]) ranging from 2.0–2.6.

Our previous studies have shown that the microsieve dispersion mixers are effective tools for providing high-mixing efficiency[20] and fast mass-transfer rate.[21] They have been successfully used in the fast exothermic reaction between cyclohexanecarboxylic acid and oleum, a critical step in the SNIA toluene route for the preparation of caprolactam.[18,21] In this work, a new microstructured chemical system, including a micromixer, a delay loop and a microhydrolyzer, was designed to carry out the Beckmann rearrangement of cyclohexanone oxime. The objective of this microsystem is to enhance the mixing of reactants, accomplish the reaction in a short and well-controlled residence time and then reduce the byproduction of ammonium sulfate by reducing the acid/oxime molar-ratio (M-ratio). The cyclohexanone oxime was dissolved in n-octane as the continuous phase, and oleum was dispersed in the octane solutions as microdroplets in the micromixer. The rearrangement reaction proceeded in the delay loop connecting directly to the micromixer. The residence time was strictly controlled to several seconds with the quenching effect of the microhydrolyzer. The molar ratios of oleum to cyclohexanone oxime were ranged from 0.5–2.0 to test the variations of cyclohexanone oxime conversion and caprolactam selectivity at different temperatures.

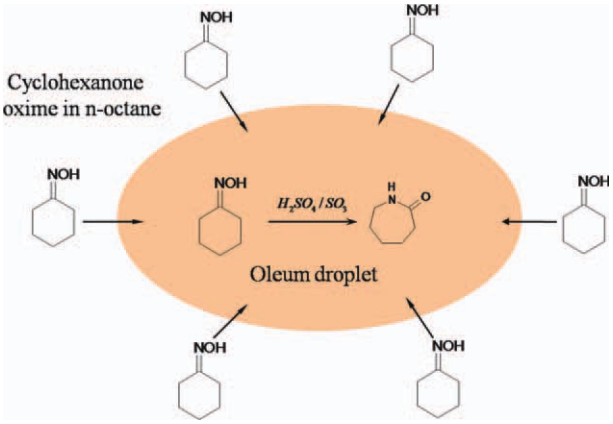


**Figure 1. Sketch view of Beckmann rearrangement in the microsystem.**

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

## Experimental

### *Beckmann rearrangement in the microsystem*

The reaction process between cyclohexanone oxime and oleum in the microsystem is shown in Figure 1. In the experiment, cyclohexanone oxime is dissolved in the n-octane, which is immiscible with oleum. The oleum is dispersed as small droplets by the n-octane solution. Cyclohexanone oxime transports from the octane phase to the oleum phase and then the reaction happens in the oleum droplets. The application of inert solvent such as octane is for heat removal as it can dilute the reactants and low-temperature gradient. Similar work is also described by Zuidhof et al.[19]

In order to control residence time accurately, we design a microhydrolyzer to quench the reaction by adding water to the reacting system. Oleum will hydrolyze quickly and forms aqueous $H_2SO_4$. Ogata et al.[22] described the kinetics of the rearrangement reaction in aqueous $H_2SO_4$ at 60°C and 90°C. The rate was found to be first-order with respect to oxime concentration, and the reaction rate constant k is about $10^{-5}$—$10^{-4}$ $s^{-1}$ at 90°C, which is rather slow. Thus, we can figure out that the reaction is stopped in the aqueous $H_2SO_4$ at room-temperature.

### *Equipment*

The microsieve dispersion mixer (316 stainless steel) with a single aperture used in this work is shown in Figure 2. It is mainly constructed with a distribution chamber and a cross-flow channel. A stainless steel sheet with a single aperture is placed in the middle as the dispersion structure. The aperture in the dispersion sheet has a square shape with 0.2 mm in side length, and the cross flow channel is 12 mm in length, 0.4 mm in width and 0.6 mm in height. In this micromixer, oleum as the dispersed phase is pressed through the aperture as small droplets and mixes with n-octane solution in the cross flow channel. The reaction takes place in the oleum

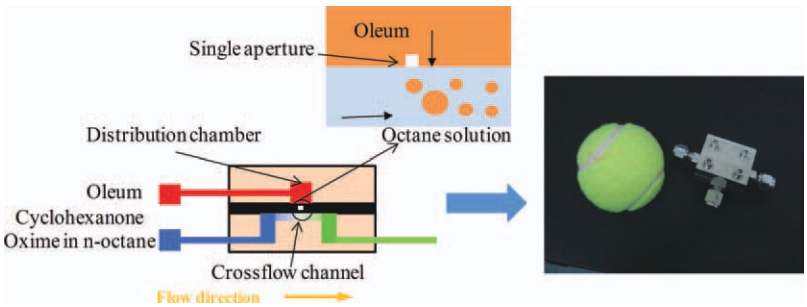


**Figure 2. The microsieve dispersion mixer.**

The left side of the picture gives a schematic view of the micromixer. The right side of the picture is the photograph of the micromixer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

droplets when cyclohexanone oxime transports from the octane phase to the oleum phase as shown in Figure 1.

A schematic overview of the microstructured system is shown in Figure 3. The cyclohexanone oxime solution and oleum were delivered by metering pumps (Beijing Satellite Co., Ltd.). Since cyclohexanone oxime has low solubility in n-octane at room-temperature, its feed pipe and the pump head were warmed by self-regulated electric heating bands (Kete electric heating Co., Ltd.) keeping the temperature at 70°C. The reactants were pumped through the pipes immersed in water bath 1 to control the feeding temperature. A delay loop (316 stainless steel) immersed in water bath 2, with an inner diameter of 2 mm and an external diameter of 3 mm was connected directly downstream to the micromixer to control the reaction time. The residence time could be controlled accurately by changing the length of the delay loop (0.2–5 m), or the flow velocity in it. Three commercial temperature sensors (PT 100, Japan, $\phi$ 2 mm $\times$ 10 mm) were integrated in the pipeline system and a data acquisition system (Beijing Riubohua Co., Ltd.) was used to record the temperature online.

The hydrolyzation step is also a fast and highly exothermic process. Thus, a microhydrolyzer was designed to achieve this process safely. The structure of microhydrolyzer is similar to the micromixer except that its inner structure is made of polytetrafluoroethylene (PTFE), and there are four microsieves (square shape and 0.4 mm in side length) for high-throughput rate of water.

During the experiment, the n-octane solution and oleum were pumped into the micromixer to induce rearrangement reaction and went on reacting in the delay loop. A large amount of water was pumped into the microhydrolyzer to quench the reaction by both cooling and dilution of oleum. After about 3 min, the system is stable (estimated from the temperature), and then the hydrolyzed samples were collected directly at the outlet after the microhydrolyzer. The sampling time was also recorded with a stopwatch.

### *Analysis*

The collected samples were separated into two phases, an organic phase and an aqueous phase. The organic phase was mainly composed of n-octane and cyclohexanone oxime. The aqueous phase was mainly composed of water, caprolactam, cyclohexanone oxime, $H_2SO_4$ and some undefined byproducts. During the analysis process, the two phases were weighed by an electronic analytical balance, respectively. Then the organic phase was diluted and measured by GC (HP 6890) with a flame ionization detector under the following conditions: nitrogen, 0.8 mL/min; the injection temperature, 260°C; the column temperature, 230°C; the detector temperature, 280°C. The sample volume for all analysis was 1 $\mu$L. The aqueous phase was diluted and neutralized with NaOH solution. Subsequently, the sample was determined by HPLC (Agilent 1100) with an ultraviolet detector under the following conditions: flow rate, 0.5 mL/min; detector wavelength, 201 nm; the column temperature, 30°C. The mobile phase was composed of acetonitrile (35%), and buffer solution (65%). The sample volume for all analysis was 20 $\mu$L. The cyclohexanone oxime conversion $C$, and

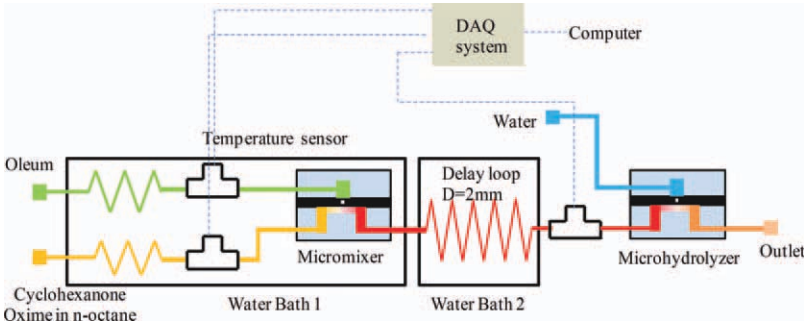


**Figure 3. The schematic overview of the experimental setup.**

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

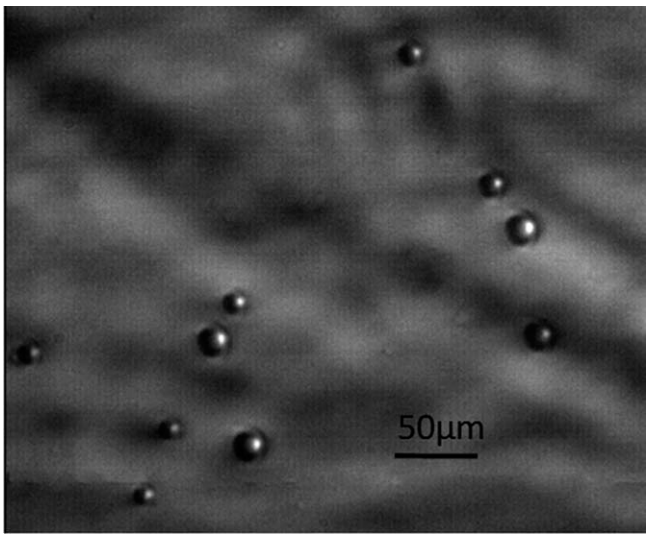


**Figure 4. The photograph of formed microdroplets.**

The flow rates of cyclohexanone oxime solution and oleum were 25 mL/min and 1.0 mL/min, respectively.

caprolactam selectivity $S$ were calculated by the following equations

$$C = 1 - \frac{W_{\text{org-ox}} \times M_{\text{org}} + W_{\text{aqu-ox}} \times M_{\text{aqu}}}{M_{\text{ox}}} \quad (1)$$

$$S = \frac{W_{\text{org-cap}} \times M_{\text{org}} + W_{\text{aqu-cap}} \times M_{\text{aqu}}}{C \times M_{\text{ox}}} \quad (2)$$

where, $W_{\text{org-ox}}$ (%) is the mass concentration of cyclohexanone oxime in the sample organic phase, $W_{\text{aqu-ox}}$ (%) is the mass concentration of cyclohexanone oxime in the sample aqueous phase, $W_{\text{org-cap}}$ (%) is the mass concentration of caprolactam in the sample organic phase, $W_{\text{aqu-cap}}$ (%) is the mass concentration of caprolactam in the sample aqueous phase, $M_{\text{org}}$ (g) is the mass of the organic phase, $M_{\text{aqu}}$ (g) is the mass of the aqueous phase, and $M_{\text{ox}}$ (g) is the feeding mass of cyclohexanone oxime calculated with the feeding rate of cyclohexanone oxime solution and the sampling time. Most of experiments are repeated for twice. The average relative errors of replication in selectivity and conversion are 2.4% and 1.3%, respectively.

To understand the dispersion and mixing performance of the microsieve dispersion mixer, the liquid-liquid reacting system before hydrolysis was collected on a piece of watch glass with a paraffin coating layer. In the experiment, octane solved in paraffin quickly, leaving the oleum droplets suspended on the glass surface. A microscope with a CCD video camera (PL-A742, PixeLINK, Canada) was used to record the formed droplets.

## Results and Discussion

### *Mixing performance of the micromixer*

In the experiment, the droplet sizes in the microstructure chemical system were recorded and is shown in Figure 4. More than 100 droplets are measured and the relative error is less than 5%. The droplet diameter ranges from 10–25 $\mu$m, indicating that a good mixing of reactants can be realized with the micromixer. Large interfacial area for mass-transport process (19300$m^2/m^3$), and short transport distance of cyclohexanone oxime (<25 $\mu$m) have been obtained in this microsystem. Therefore, fast heat and mass-transfer rates can be provided to enhance the reaction process.

### *Cyclohexanone oxime conversion*

*The Influence of Residence Time and M-ratios on the Reaction.* Figure 5 shows the conversions of cyclohexanone oxime at different residence time with the M-ratios of 1.98, 1.06 and 0.53, respectively. As shown in the figure, the reaction can be finished within 10 s at 2.0 M-ratio, and 70°C in the microstructure chemical system, which is much shorter than the residence time of 15–180 min in conventional devices. Moreover, the conversion increases quickly with the increase of residence time, and nearly 50% conversion can be obtained when the residence time is around 1 s, indicating the reaction is a quite fast process. With the decreasing of M-ratio, the reaction rate slows down. When the value of M-ratio is equal to 0.5, cyclohexanone oxime cannot be converted completely even after 40 s.

According to the kinetic rates published by Wichterle and Roček, the Beckmann rearrangement in oleum could be finished within several seconds.[23] The conventional process needs a much longer residence time due to the limitation of mass-transfer rate and the strong back-mixing operation. For comparison, microstructure devices can provide better mixing and higher transfer efficiency. Therefore, no back mixing is required in this microsystem and short reaction time can be easily achieved.

It is easy to understand that the reaction rate decreases with the reduction of M-ratio, since oleum acts as the catalyst in the working system. With the decreasing of M-ratio, less oleum droplets are formed, thus, the reaction rate

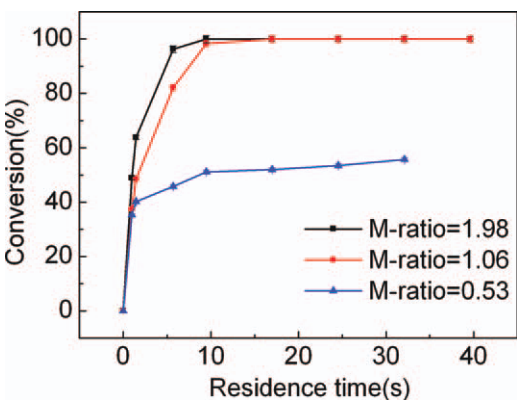


**Figure 5. The influence of M-ratio and residence time on the conversion of cyclohexanone oxime.**

The experiments were conducted at the conditions of 20 wt % $SO_3$ in oleum and 10 wt % cyclohexanone oxime in octane. The flow rate of cyclohexanone oxime solution was controlled at 25 mL/min, and the flow rates of oleum were 0.4 mL/min, 0.8 mL/min and 1.5 mL/min, respectively. The residence time was varied by changing the length of the reaction tube. The temperatures of water baths 1 and 2 were kept at 70°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

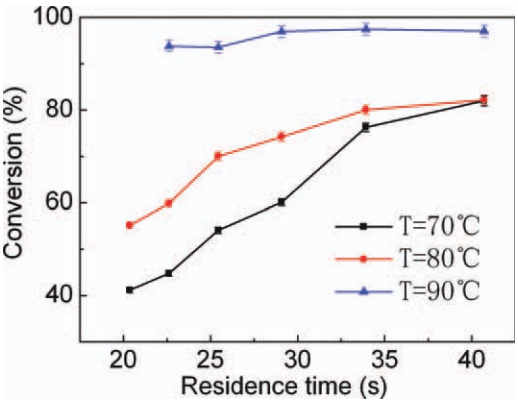


**Figure 6. The influence of temperature on the conversion of cyclohexanone oxime.**

The experimental conditions were selected as 20 wt % $SO_3$ in oleum, and 10 wt % cyclohexanone oxime in octane, respectively. The flow rates of cyclohexanone oxime solution ranged from 25–50 mL/min, and the flow rates of oleum ranged from 0.5–1.0 mL/min. The M-ratio was kept at 0.7. The length of the delay loop was 5.4 m, and the residence time was varied by changing the two-phase flow rate. The reaction temperature was controlled by water baths 1 and 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreases. However, this cannot explain the reason of the low cyclohexanone oxime conversions at low M-ratio. For example, when the M-ratio is below 0.5, the conversion hardly exceeds 60%. We guess that oleum works not only as a catalyst, but also as a reactant. It has been proved that sulfuric acid can react with caprolactam to form a caprolactam hydrogen sulfate.[24] Therefore, when there is not enough oleum, the reaction rate may decrease quickly due to the consumption of oleum by the formed caprolactam. To draw any further conclusions, more work has to be done to prove the presumption.

*The Influence of Temperature on the Reaction.* Figure 6 shows the influence of temperature on the cyclohexanone oxime conversion with the variation of residence time. As shown in the figure, the conversion is low at 70°C with an M-ratio at 0.7. Although the residence time is allowed for 40 s, the conversion only reached 80%. However, the conversion higher than 90% can be achieved in a short residence time, when the temperature is 90°C. It shows that high-temperature is beneficial for acceleration of the reaction rate.

### *ε-Caprolactam selectivity*

*The Influence of M-ratio and Temperature on the Reaction.* The concentrations of $SO_3$ and cyclohexanone oxime in solutions were 20 and 10 wt %, respectively. The flow rate of cyclohexanone oxime solution was 25 mL/min. The flow rate of oleum ranged from 0.4 mL/min to 2.0 mL/min. The length of the delay loop was 5.4 m long. The residence time was 40.7 s.

The selectivity as a key parameter in the production of caprolactam can be affected by a series of factors such as M-ratio, reaction temperature, residence time and reactant concentration. Figure 7 shows the influence of M-ratio and temperature on the selectivity of ϵ-caprolactam. As shown in the figure higher than 99% selectivity is obtained with the microstructure chemical system at a temperature ranging from 70–90°C for M-ratio of about 1.0, which is much lower than the industrial value of 1.2–1.7. The selectivity becomes poor at the M-ratios beyond a limited range of around 1.0. At the M-ratio lower than 1.0, the selectivity at 90°C is much better than that at 70 °C. High selectivity larger than 99% is feasible to obtain at 90°C, even when the M-ratio is low to about 0.8, the lowest M-ratio in this experiment. Thus, the increase of reaction rate with the increase of temperature (Figure 6) is beneficial for the improvement of selectivity at the low M-ratio.

According to the previous studies, some UV-active byproducts, such as octahydrophenazine, will increase with the reduction of M-ratio.[3,25] With the increase of M-ratio, the reaction rate is so fast that temperature may become hard to control in the delay loop, which increases the risk of reactant carbonization. Hence, an optimized range of M-ratio exists for the Beckmann rearrangement in this microstructure chemical system. If the mixing of reactants is not good enough, the M-ratio may be out of control at local areas. Thus, high selectivity is difficult to be guaranteed.

The temperature of water bath 1 was 70°C and 90°C for water bath 2. The concentrations of $SO_3$ and cyclohexanone oxime in solutions were 20 and 10 wt %, respectively. The flow rate of cyclohexanone oxime solution was 25 mL/min. The flow rates of oleum ranged from 0.4– 2.0 mL/min. The residence time was 40.7 s.

Based on the aforementioned statement, we find that the low-temperature can lower the reaction rate and avoid the side reaction of carbonization at an early reaction period. Nevertheless, a higher temperature is required to enhance the main reaction rate at the following period. Therefore, we designed a new process to gain high selectivity at a range of M-ratios. The temperature of water bath 1 was set to 70°C to mix the reactant and induce the rearrangement reaction, and the temperature of water bath 2 was set to 90°C to accelerate the reaction rate. The experimental results are shown in Figure 8. High selectivity of >99% can be

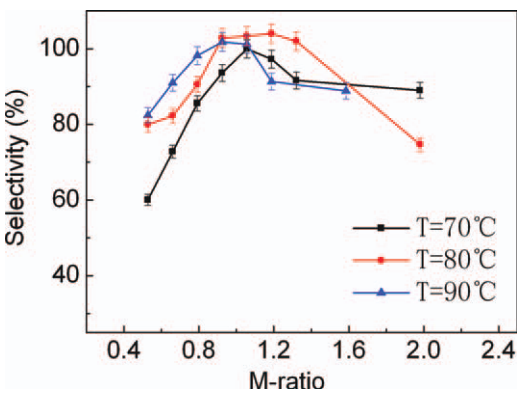


**Figure 7. The influence of M-ratio and temperature on the selectivity of ϵ-caprolactam.**

The concentrations of $SO_3$ and cyclohexanone oxime in solutions were 20 and 10 wt %, respectively. The flow rate of cyclohexanone oxime solution was 25 mL/min. The flow rates of oleum ranged from 0.4–2.0 mL/min. The length of the delay loop was 5.4 m long. The residence time was 40.7 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

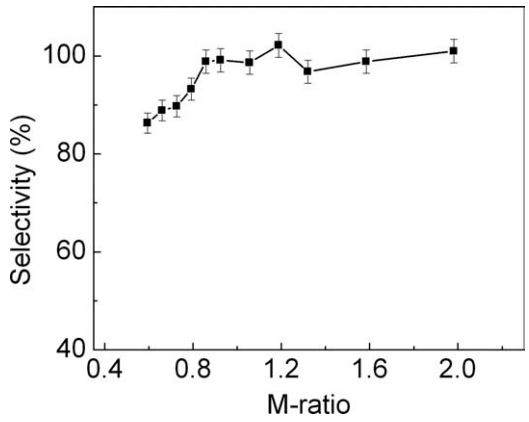


**Figure 8. Selectivity of ϵ-caprolactam at different M-ratios.**

The temperature of water bath 1 was 70°C, and 90°C for water bath 2. The concentrations of $SO_3$ and cyclohexanone oxime in solutions were 20 and 10 wt %, respectively. The flow rate of cyclohexanone oxime solution was 25 mL/min. The flow rates of oleum ranged from 0.4–2.0 mL/min. The residence time was 40.7 s.

obtained at the M-ratios ranging from 0.8–2.0. This method provides a feasible way to get a high selectivity at a range of M-ratios.

*The Influence of Residence Time on the Reaction.* Figure 9 shows the influence of residence time on the selectivity of caprolactam. Since the M-ratio is 0.7, the selectivity is not high. The results show that the selectivity reduces with an increase of the residence time. The selectivity is nearly 100% at the beginning of the reaction, and the byproducts are mainly produced with the proceeding of the process. The M-ratio is high in the oleum droplets at first as the cyclohexanone oxime cannot be transferred to the oleum droplets immediately. As the reaction process goes on, the free $SO_3$ and $H_2SO_4$ reduce in the droplets and the effective M-ratio in the oleum droplets reduce. At the low M-ratio, the side reaction may take place. Also the mixing intensity could be less with the longer residence time.

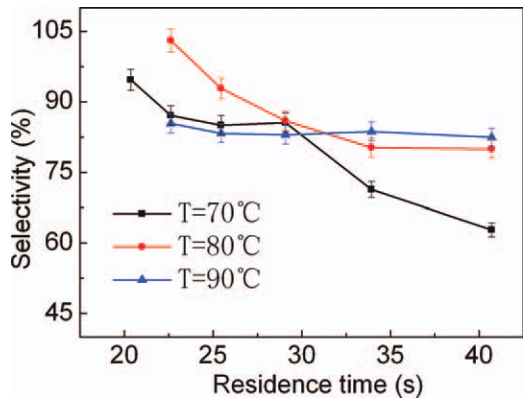


**Figure 9. The influence of residence time on the selectivity of caprolactam.**

The operating conditions are the same as in Figure 6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table 1. Comparison of the Microsystem and Conventional Reactors**

| Device | Reaction temperature(°C) | Residence time | M-ratio | Selectivity |
|---|---|---|---|---|
| Microsystem | 70 ∼ 90 | 10 ∼ 40 s | 0.8 ∼ 2.0 | 99+% |
| Conventional reactors | 70 ∼ 110 | 15 ∼ 180 min | 1.2 ∼ 1.7 | 99+% |

A performance comparison between the microsystem and conventional reactors is presented in Table 1. These data show that both two devices can achieve >99% selectivity. However, the residence time in the microsystem is less than 40 s, an obvious decrease compared to the residence time of 15–180 min in the conventional reactor. The table also shows that the M-ratio in the microreactor system can be controlled as low as 0.8, indicating decreasing in the consumption of oleum and the production of ammonium sulfate. The sizes of oleum droplets in the microsieve dispersion mixer can reach from 10–25 μm as shown in Figure 4. Comparing with those droplets at millimeter scale in the conventional reactors, good mixing performance and fast mass-transfer rate can be easily provided in the microsystem. That is the reason for the successful reducing of oleum consumption in the microstructured chemical system.

## Conclusions

In this work, a microstructure chemical system has been successfully applied to carry out the Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam. The conversion of cyclohexanone oxime and selectivity of caprolactam are investigated under various conditions: the M-ratio, temperature and residence time. 100% conversion of cyclohexanone oxime and >99% selectivity of caprolactam are gained in this microsystem with reaction time less than 40 s. Molar ratios of oleum to cyclohexanone oxime can be controlled as low as 0.8, which is much lower than the industrial value of 1.2–1.7. Furthermore, a two-stage technology of low-temperature to induce reaction- and high-temperature to enhance reaction is proposed to get a high selectivity at a range of M-ratios. This novel process has the advantage that the reaction can be safely achieved with a short residence time. It has the further advantage that this is achieved with a low M-ratio, which means that oleum consumption and the unavoidable production of ammonium sulfate can be reduced in the preparation of caprolactam.

## Acknowledgments

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