The Beckmann rearrangement of cyclohexanone oxime to (epsilon)-caprolactam in micromixers and microchannels

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Summary

The Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam in micromixers and microchannels

Chemistry is the symphony of molecules and chemical reactors are the engineering instruments to orchestrate chemistry. The chemical engineer is seeking for the most selective, most efficient, most compact, safest, and economical chemical reactor. Microreactors are seen as promising production instruments for small scale production in the life science and pharmaceutical industry. By the scaling up by scaling out principle microreactors are able to increase production rate for these industries. Although, economy of scale is a general accepted rule for bulk processes, the application of microreactors for bulk chemical processes can be beneficial as well. Some of these processes are limited by mass and/or heat transfer, which can put technological limitations to the process design. This can lead to far from ideal solutions for bulk processes. Scaling down to microreactor dimensions (50 - 500 μm) can increase mass and/or heat transfer in such cases tremendously to allow a much improved process design with respect to conversion, selectivity, purification, energy consumption, and safety. The safety aspect is especially important in case of strongly poisonous and dangerous chemicals and run-away reactions. When a number of these conditions apply to the bulk process, a strong impulse for the application of micro technology for this process exists. Of course, lining-up millions of microchannels is not a viable way to go, but one can find certainly many examples where an existing reactor can be replaced economically by a number of microreactor units. Several bulk chemical processes meet the requirements for downscaling, thereby improving the heat management, selectivity, and decreasing risks.

In this thesis the investigation of one of these, viz. the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam in fuming sulphuric acid as catalyst and solvent, is the central chemical process. With this bulk chemical process a number of the benefits and limitations of microreactor systems can be demonstrated: use of hazardous chemicals and/or safety, heat management, and selectivity. The Beckmann rearrangement has a high selectivity in the bulk process by the application of very intensive mixing, however, a reduction of the rate of mass transfer in the reactor leads

to many side reactions, decreasing the selectivity. When the Beckmann rearrangement shows a high selectivity with microreactor technology this would be an excellent demonstration of the potential of microreactor systems. Furthermore, the side reaction products are very likely to cause plugging and blockage of the microchannels, which necessitates excellent control of the process conditions. This will lead to improved engineering of microreactor systems, for better performance in chemical processes.

A thorough knowledge of the material properties is needed for a full and comprehensive understanding of the Beckmann rearrangement in a microreactor (**Chapter 2**). Therefore the material properties of the ε-caprolactam/oleum mixtures, cyclooctane, cyclooctane with cyclohexanone oxime solutions, molten cyclohexanone oxime and glycerol/water, which are all liquids that are used in this thesis, are presented. The density of ε-caprolactam/oleum mixtures shows a linear relationship with temperature and composition. The viscosity shows a major increase with the amount of ε-caprolactam in the ε-caprolactam/oleum mixtures, and the viscosity decreases with temperature. Viscosity of cyclooctane with cyclohexanone oxime solutions shows a decrease with temperature and only a small influence of composition. The solubility of cyclohexanone oxime in cyclooctane is approximately 11 wt% at room temperature and increases with temperature. The surface tensions of the liquids decrease with temperature as well. The composition of the ε-caprolactam/oleum mixtures has a large influence (order of magnitude) on the surface tension at low temperatures, at temperatures between 90 and 120 °C the influence is small. The influence of the composition on the surface tension of cyclooctane with cyclohexanone oxime solutions is negligible. The surface tension of glycerol/water mixtures at room temperature is comparable with surface tensions measured for ε-caprolactam/oleum mixtures at 90–120 °C (which are temperatures normally used for production of ε-caprolactam). Therefore, glycerol/water mixtures can replace the oleum/ε-caprolactam mixtures in a study of the liquid-liquid flow behavior in micromixers, this is simplifying the investigations in Chapter 4 tremendously.

Chapter 3 describes the Beckmann rearrangement of molten cyclohexanone oxime in a microchannel. First the reaction in the microchannel is modelled mathematically by one dimensional and (pseudo) two dimensional models of a micro T-mixer. The T-mixer is designed as a small side inlet (10 μm) slit for molten cyclohexanone oxime into a main channel (width 200 μm) containing a mixture of oleum and

ε-caprolactam. The Beckmann reaction is shown to be very fast when mass transfer is not limiting with a one dimensional model (model 1). The two dimensional models (model 2 and model 3) both show that mixing, by diffusion of a 20 μm layer of molten cyclohexanone oxime into the main stream (180 μm) of a mixture of oleum and ε-caprolactam, is not fast enough to completely convert all cyclohexanone oxime within a microchannel of 20 cm length and a width of 200 μm. A liquid-liquid layer mathematical model (model 4) shows that a layer of cyclohexanone oxime between 2 and 5 μm combined with a 20 to 50 μm layer of oleum and ε-caprolactam is small enough to completely convert cyclohexanone oxime for the above mentioned microchannel, with a flow ratio of 1:10 (cyclohexanone oxime : oleum/ε-caprolactam). The Beckmann rearrangement reaction is therefore performed in a split-and-recombine micromixer, which can experimentally create these size of liquid layers. For an M-ratio $(([H_2SO_4] + [SO_3])/[\varepsilon\text{-caprolactam}])$ of 2.6 to 2.2, the Beckmann rearrangement shows selectivities ranging from 99.6 to 96.7%. An M-ratio of 2.0 to 1.7 shows a selectivity of 97.6% at 100 °C. A higher temperature (110 °C) leads repeatedly to complete blockage of the micromixer and channel. The small side inlet for cyclohexanone oxime and the main microchannel are completely filled with particle like by-products, which are caused by the rapid reaction and insufficient mixing of the liquid layers. However, this is the first time this reaction is accomplished successfully in a microreactor with molten cyclohexanone oxime, ε-caprolactam and oleum with concentrations comparable with industrial conditions. However, the application of lower M-ratios seems to be complicated in a microreactor system, therefore other solutions are needed.

Flow patterns, flow regime maps, liquid hold up, slug velocity and slug size are determined in three micromixers, viz. a Y–junction, an interdigital, and a split-and-recombine mixer (**Chapter 4**). A total of nine flow pattern maps are defined for three viscosities of glycerol/water. Glycerol/water mixtures are used as the primary phase, whereas cyclooctane is used as the secondary phase. This particular liquid-liquid system is used because the viscosity and surface tension at ambient conditions are comparable with the liquid-liquid system of oleum/caprolactam mixtures and cyclohexanone oxime in cyclooctane mixtures at reaction conditions of the Beckmann rearrangement ($\sim$ 100 °C). Correlations for the liquid hold up as a function of flow quality are obtained, as well as slug length and slug velocity. The liquid hold up to flow quality ratio is given at 0.49, 0.45, and 0.58, at 65 mPa·s viscosity and 0.44,

0.52, and 0.52 at 100 mPa·s viscosity of the glycerol/water mixture for the Y-type, the interdigital, and the split-and-recombine micromixers, respectively. The slug velocity was found to be twice that of the overall superficial velocity, which decreases the residence time of the cyclooctane phase considerably. The cyclooctane slug length is also observed to increase with increasing cyclooctane velocity or volumetric flow rate. The interfacial area between the glycerol/water mixture and cyclooctane using the split-and-recombine mixer with Taylor slug flow with small droplets is larger by a factor of 2-3 than for Taylor slug flow in the interdigital and the Y-type micromixers for flow velocities of both phases of 0.04 m/s. The Beckmann rearrangement of cyclohexanone oxime at 100 °C is completed in approximately 4 seconds or less, furthermore enough residence time for the mixing of the reactants is needed, which means for a reasonable length and pressure of the microreactor the flow regimes drop flow, Taylor flow, Taylor slug flow with droplets, and slug flow with overlapping droplets are the most interesting regimes for this thesis.

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 (**Chapter 5**). 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 ε-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 to 99+%, 93 to 99+%, and 95 to 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.

The selectivity of the Beckmann rearrangement of cyclohexanone oxime, dissolved in cyclooctane, into ε-caprolactam is determined for conditions with a high concentration of ε-caprolactam, meaning that the M-ratio $(([H_2SO_4] + [SO_3])/[\varepsilon\text{-caprolactam}])$ is as low as 1.7 to 1.4 (**Chapter 6**). The microreactor consists of one low temperature mixing zone followed by a high temperature reaction zone. The mixing is conducted at 65 °C in a split-and-recombine micromixer followed immediately by a second zone at high temperature (100 - 127 °C) for complete conversion of cyclohexanone oxime. Selectivities of 99% are found for these con-

ditions, almost independent on the temperature of the high temperature zone. The selectivity of the Beckmann rearrangement for the same mixer, reactants, and flow velocities at a single temperature for mixing and reaction at 130 °C was found to be 95%, as discussed in Chapter 5. This means that by decreasing the mixing temperature, and therefore suppressing the reaction during mixing the selectivity is increased by 4% at industrial relevant oleum and ε-caprolactam concentrations.

The flow distribution in a circular symmetrical 10 channel microreactor is examined for relevant flow rates (**Chapter 7**). This microreactor is designed for its capability of upscaling; circular symmetrical microchannels around a larger cooling tube is a concept where crossover and leakage is less likely as there is no need for bonding of microstructured stacks of plates, as is needed for non circular symmetrical concepts. Moreover, the tube needed for cooling can have a larger diameter e.g. centimeter range, which makes the requirements for the purity of the cooling liquid less stringent. An equal flow distribution over the microchannels is a first requirement for a regular operation, and is therefore investigated with the most straightforward flow distributor: a "large" liquid chamber (0.5 ml) in front of all microchannels. The flow distribution is tested with a series of liquids varying in viscosity and flow rate. Furthermore, the behavior of liquid mixing of liquids with varying viscosities is investigated in this straightforward flow distributor. Glycerol/water mixtures with viscosities above 50 mPa·s provide a regular flow distribution, with standard deviation of 3% over the 10 channels of the microreactor. Water, with a lower viscosity, provides a decreased flow distribution with a standard deviation of 5%, which can be understood by the lower pressure drop over the microchannels. Simultaneous operation of two liquids with different viscosities significantly reduces the quality of the flow distribution. This is due to the viscosity changes and the pressure fluctuations caused by these changes. Therefore multiple steady states for the liquid distribution over the microchannels are possible, which leads to a maldistribution over the channels. Although this makes the 10 channel microreactor less adequate for mixing of the reactants, the distributor of the 10 channel microreactor is very well capable of distributing premixed viscous liquids. This is in agreement with the conclusion of Chapter 6 where a low temperature premixer is suggested as a method to gain high selectivity for the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam.

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Introduction

1

1.1 Introduction

Chemistry is the symphony of molecules and chemical reactors are the engineering instruments to orchestrate chemistry. The chemical engineer is seeking for the most selective, most efficient, most compact, safest, and economical chemical reactor. Microreactors are seen as promising production tools for small scale production in the life science and pharmaceutical industry (Sahoo et al., 2007). By the scaling up by scaling out principle microreactors are able to increase production rate for these industries. Although, economy of scale is a general accepted rule for bulk processes, the application of microreactors for bulk chemical processes can be beneficial as well (Tonkovich et al., 2005). Some of these processes are limited by mass and/or heat transfer, which can put technological limitations to the process design. This can lead to far from ideal solutions for bulk processes. Scaling down to microreactor dimensions (50 - 500 μm) can increase mass and/or heat transfer in such cases tremendously to allow a much improved process design with respect to conversion, selectivity, purification, energy consumption, and safety. The safety aspect is especially important in case of strongly poisonous and dangerous chemicals and run-away reactions. When a number of these conditions apply to the bulk process, a strong impulse for the application of micro technology for this process exists. Of course, lining-up millions of microchannels is not a viable way to go, but one can find certainly many examples where an existing reactor can be replaced economically by a number of microreactor units (e.g. Forschungszentrum Karlsruhe and DSM Linz, 2005). Several bulk chemical processes meet the requirements for downscaling, thereby improving the heat

management, selectivity, and decreasing risks. The goal of this thesis is the investigation of a microreactor system for one of these, viz. the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam in fuming sulphuric acid as catalyst and solvent (Figure 1.1) (Ritz et al. (2002); Dahlhoff et al. (2001)). With this bulk chemical process a number of the benefits and limitations of microreactor systems can be demonstrated: use of hazardous chemicals and/or safety, heat management, and selectivity. The used chemicals, fuming sulphuric acid and cyclohexanone oxime, in the process are considered hazardous (corrosion, reaction with any organic material, hazardous fumes, instability, explosion, etc.) (Kapias and Griffiths (1998a); Kapias and Griffiths (1998b); Kapias and Griffiths (1999); Kapias et al. (2001)). Many examples exists where run-away reactions and explosions or other disasters have occurred with these chemicals (Grint and Grant, 1990). The bulk chemical process is limited by heat transfer, and therefore the temperature of the cooling medium must remain low (70 °C), which is economically less interesting. By increasing the reaction temperature an improved heat management is possible, which necessitates a better heat transfer. The Beckmann rearrangement has a high selectivity in the bulk process by the application of very intensive mixing, however, a reduction of mass transfer in the reactor leads to many side reactions, decreasing the selectivity (Jodra et al., 1981). When the Beckmann rearrangement shows a high selectivity with microreactor technology this would be an excellent demonstration of the potential of microreactor systems. Furthermore, the side reaction products are very likely to cause plugging and blockage of the microchannels, which necessitates excellent control of the process conditions. This will lead to improved engineering of microreactor systems, for better performance in chemical processes, which is needed as still 20–50% of the incidents and accidents can be attributed to erroneous design (Taylor, 2007).

1.2   The Beckmann rearrangement in microreactors

The classical Beckmann rearrangement is applied for the conversion of cyclohexanone oxime to ε-caprolactam, a nylon-6 precursor. Its kinetics under industrial conditions, however, is fairly unknown, mostly because of the high reaction rate at relevant temperatures, and the rather large heat of reaction. Mixing of reactants proves to be very important to obtain a high selectivity (Hlidkova-Kadlecova et al., 1986), as inadequate mixing leads to uneven heat distribution in the reaction mixture, and
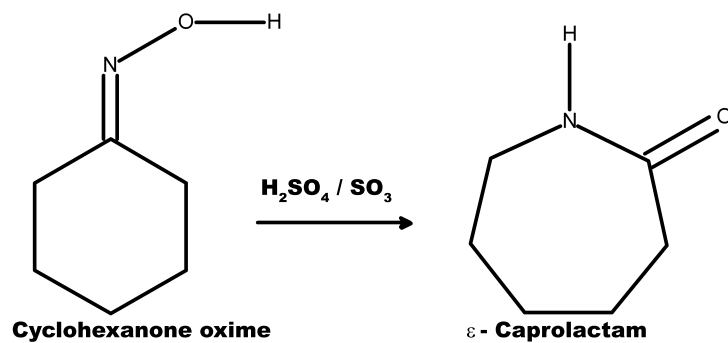
Figure 1.1: The Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam.
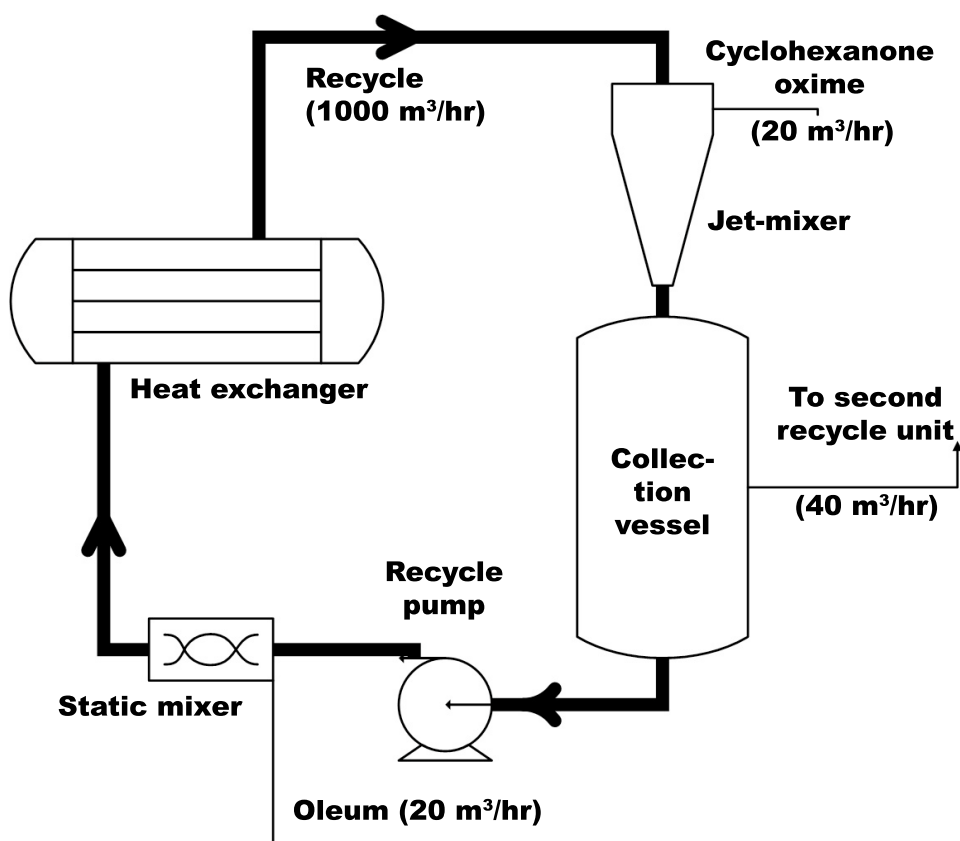
Figure 1.2: Schematic of one of the three recycle reactors in series for the Beckmann rearrangement

to undesirable secondary reactions (Schaffler and Ziegenbein, 1955). This reaction is catalyzed by Lewis acids and is highly exothermic and extremely fast (Wichterle and Roček (1951a,b); Ogata et al. (1955); Nguyen et al. (1997); Yamabe et al. (2005)). In industry, fuming sulphuric acid (oleum) is generally used as a catalyst (Fisher and Crescentini, 2000). This conventional production process has a few drawbacks. Due to the fast kinetics and exothermic behavior, the production method is limited by the heat produced during reaction. Almost all commercial processes for the production of ε-caprolactam are based on the Beckmann rearrangement of cyclohexanone oxime in oleum, which is of sufficient strength to consume the several percent of water in the molten oxime (Smeets et al. (2004); Fisher and Crescentini (2000); Ritz et al. (2002)). Although extrapolation of available kinetic data may be unreliable, it is clear that the reaction occurs in the time frame of seconds to milliseconds, i.e. almost mixing time equals reaction time. However, the reaction is quite exothermic, so that, for reasons of temperature control, a large external recycle is used to cool down the reaction mixture (Figure 1.2). This leads to long overall residence times in the order of 20 minutes. The long residence time causes side and consecutive reactions, so that in the end a large purification section is needed. A mixer design used for the industrial production of ε-caprolactam is shown in Figure 1.3. The molten cyclohexanone oxime is injected by 24 inlets (3 mm) into the main stream with a velocity of ca. 30 m/s. The main stream, which is a mixture of oleum and ε-caprolactam, has a velocity of ca. 30 m/s as well. The diameter of the main tube is ca. 10 cm. The mixing of the reactant occurs in the turbulent regime. Higher velocity of the liquid flow provides the highest selectivity (more than 99%) (Smeets et al., 2004).

Microreactors are nowadays regarded as a separate class of chemical reactors, characterized by small dimensions, i.e. reactors with a channel diameter of 50 - 500 μm and a channel length of 1 - 1000 mm. Microreactor technology can also lead to significant reductions of the environmental impact resulting from chemical production processes (Kralisch and Kreisel, 2007). Microreactors exhibit an extremely large surface-area-to-volume ratio in the order of 10^4 to 10^5 m^2/m^3 that leads to significantly different reaction conditions as compared to large scale reactors. Every chemical reactor has to perform up to three tasks simultaneously, viz. (i) allowing necessary reaction time, (ii) transporting reaction heat, and, in case of multiphase systems, (iii) providing interface between the various phases. In all three tasks, the above-mentioned microreactors offer advantages above conventional reactors (Hessel et al., 2005). The small

structures allow for very precise contact times, whereas, because of their inherently large surface-area-to-volume ratio, heat management and mass transfer can be optimized easily, to avoid secondary reactions. With respect to the third task, mixing is, of course, more an item for liquid-liquid, liquid-gas, and triple phase reactions than for pure gas phase reactions, as mass transfer in small scale systems mainly is caused by diffusion. However, in micro systems a very large interfacial area can be obtained as, e.g. in static mixers, the dimensions of multi-laminated lamellae are fixed by the dimensions of the micro structure (Kashid and Agar, 2007, Kashid et al., 2005). The generation of these thin mixing lamellae or other small shapes in micromixers, nowadays, is based on division of a main stream into many small sub streams, on reduction of the channel width along the flow axis, on hydrodynamic focussing, or on biphasic flow patterns (e.g. Werner et al. (2005); Schönfeld et al. (2004); Nguyen and Wu (2005)). Additionally, one may rely on assisting streaming phenomena to improve mixing, as for example a split-and-recombine mixer. These convection type of micromixers change the shape of the liquid in that matter that eventually diffusion can finally mix all reactants. The combination of precise reaction time, small temperature gradients, and avoidance of large mass transfer paths can lead to the achievement of higher selectivity in these type of reactors as compared to bulk-scale reaction systems, as was shown by Hessel et al. (2004) and Watts and Haswell (2005) for various organic syntheses, by Rebrov et al. (2001) in case of a highly exothermic reaction with an integrated heat-exchanger, by Pennemann et al. (2005) for the hydrolysis of benzal chloride, by Schwalbe et al. (2002) for large number of organic synthesis, and Renken et al. (2007) for ionic liquids.

1.3   The project

The research presented in this thesis was part of and funded by the NWO ACTS Aspect project (nr 053.62.010) under the name "Improving liquid phase reactions in bulk chemical processes by application of micro reaction technology". The research was performed at the Eindhoven University of Technology. The project's objective was to demonstrate the feasibility and performance of a microreactor system for the Beckmann rearrangement. The research was performed in close cooperation with DSM and other industrial partners.
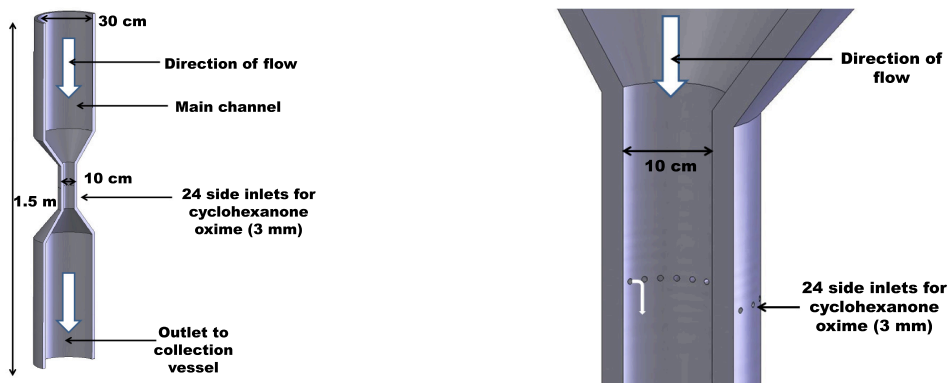
Figure 1.3: The figures show an artistic impression of a mixer tube used in chemical industry for the production of ε-caprolactam (Smeets et al., 2004). The molten cyclohexanone oxime is injected by 24 side inlets (with diameters of 3 mm) into the main stream (large tube) with a velocity of ca. 30 m/s. The main stream, which is a mixture of oleum and ε-caprolactam, has a velocity of ca. 30 m/s as well. The diameter of the main tube is ca. 10 cm. The mixing of the reactant occurs in the turbulent regime.

1.4 Scope and outline

The goal of the project was the development of a microreactor system for the Beckmann rearrangement of cyclohexanone oxime into ε-caprolactam. The project described in this thesis shows the performance of the Beckmann rearrangement in microreactor systems. This thesis focusses on the mixer design, with selectivity enhancement of the Beckmann rearrangement as the main selection parameter. The following research questions need an answer: to what extent do the properties of the chemicals influence the pressure drop and the mixing in the microchannels; what is the critical size of the liquid packages needed for complete mixing; is a single phase Beckmann rearrangement possible in a microchannel; what kind of micromixer provides the highest interfacial surface areas for mass transfer for biphasic microchannel operation; which kind of micromixer provides the highest selectivities; is it possible to reach high selectivities at industrial relevant conditions; what considerations are needed for scaling out the microchannel reactor. In the following chapters these research question are answered to a certain extent. Although most research questions have a satisfactory answer, the question on scale out is still open, as more research is needed to answer this question. Each chapter is prepared to be read on a stand-alone

basis, creating some redundancy of information over different chapters.

Chapter 2 presents the material properties of the ε-caprolactam/oleum mixtures, cyclooctane, cyclooctane with cyclohexanone oxime solutions, molten cyclohexanone oxime and glycerol/water, which are all liquids that are used in this thesis. Material properties as viscosity, solubility, density and surface tensions are presented. The material in this chapter provides a comprehensive and compact overview of the properties of the liquids needed in this thesis and has a more assisting function for the following chapters.

In **Chapter 3** the Beckmann rearrangement with an ε-caprolactam/oleum mixture with molten cyclohexanone oxime is tested in a split-and-recombine microreactor, which is specially designed for the addition of a small quantity of molten cyclohexanone oxime directly to a main stream with a mixture of ε-caprolactam and oleum in a stable manner. This is the most straightforward method for replacing an industrial reactor by microreactor technology, as the same reactants are used, which would only necessitate the replacement of the reactor/heat-exchanger. The reaction is modelled to estimate the conversion of cyclohexanone oxime in a microchannel, with a straightforward one dimensional model and by models where radial diffusion is taken into account. The effect of ε-caprolactam concentration (composition) and temperature is discussed. Also, the M-ratio ($([H_2SO_4] + [SO_3])/[\varepsilon$-caprolactam]), for which repetitive blockage of the microreactor channels occurs, is presented, which shows the severity of the reaction.

Flow patterns, flow regime maps, liquid hold up, slug velocity and slug size are determined in three micromixers, viz. a Y–junction, an interdigital, and a split-and-recombine micromixer in **Chapter 4**. A total of nine flow pattern maps are defined for three viscosities of glycerol/water. Glycerol/water mixtures are used as the primary phase, whereas cyclooctane is used as the secondary phase. This particular liquid-liquid system is used because the viscosity and surface tension at ambient conditions are comparable with the liquid-liquid system of oleum/ε-caprolactam mixtures and cyclohexanone oxime in cyclooctane mixtures at reaction conditions of the Beckmann rearrangement ($\sim 100\,^{\circ}$C).

The selectivity of the Beckmann rearrangement in a Y-mixer, interdigital and split-and-recombine mixer with dispersed liquid-liquid flow of oleum/ε-caprolactam mixtures with cyclohexanone oxime solution in cyclooctane is studied in **Chapter 5**. The effect of temperature, composition, flow rate, flow ratio on selectivity are

provided for three micromixers with an increasing degree of micromixing.

In **Chapter 6** the best performing micromixer, the split-and-recombine mixer, is used for experiments with two temperature zones. The lower temperature is used for the mixing section, whereas the subsequently higher temperature zone is used for complete conversion of cyclohexanone oxime. This effectively decreases the second Damköhler number in the mixing section, which makes mixing less critical. In the high temperature zone the reaction rate is high and therefore reactor volumes can be small, whereas the reaction heat can be removed at higher temperature, which makes better energy management possible. Selectivities of the Beckmann rearrangement via this approach are presented and show the potential of this method for industrial application of the Beckmann rearrangement with micro technology.

A circular symmetrical 10 channel microreactor design is used to study the flow distribution in **Chapter 7**. The microreactor was designed for use with molten cyclohexanone oxime via a small side inlet. The flow distribution for the two inlets of the microreactor is studied separately as well as during simultaneous operation. The resulting flow distributions are presented.

Chapter 8 shows a summary of the main conclusions of this thesis and suggestions for further research are given.

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Material properties - viscosity, solubility, density and surface tension

2

Abstract

A thorough knowledge of material properties is needed for a full and comprehensive understanding of the Beckmann rearrangement in a microreactor. Therefore, this chapter presents the material properties of the ε-caprolactam/oleum mixtures, cyclooctane, cyclooctane with cyclohexanone oxime solutions, molten cyclohexanone oxime and glycerol/water, which are all liquids that are used in this thesis. The density of ε-caprolactam/oleum mixtures shows a linear relationship with temperature and composition. The viscosity shows a major increase with the amount of ε-caprolactam in the ε-caprolactam/oleum mixtures; it decreases with temperature. Viscosity of cyclooctane with cyclohexanone oxime solutions also show a decrease with temperature and only a small influence of composition. The solubility of cyclohexanone oxime in cyclooctane is approximately 11 wt% at room temperature and increases with temperature. The surface tension of the liquids decreases with temperature as well. The composition of the ε-caprolactam/oleum mixtures has a large influence (order of magnitude) on surface tension at low temperatures; at temperatures between 90–120 °C the influence is small. The influence of the composition on the surface tension of cyclooctane with cyclohexanone oxime solutions is negligible. The surface tension of glycerol/water mixtures at room temperature is comparable to the surface tension measured for ε-caprolactam/oleum mixtures at 90–120 °C (which are temperatures normally used for production of ε-caprolactam). Therefore, glycerol/water mixtures can replace the oleum/ε-caprolactam mixtures in a study of the

liquid-liquid flow behavior in micromixers, this is simplifying the investigations in Chapter 4 tremendously.

2.1   Introduction

A thorough and basic knowledge of the material properties is needed for a full and comprehensive understanding of the Beckmann rearrangement in a microreactor. The published data on the properties of oleum/ε-caprolactam mixtures is very limited, and only sparse data on the composition and corresponding properties is provided, for example by Fábos et al. (2008), Fisher and Crescentini (2000), Hlidkova-Kadlecova et al. (1986). The specific compositions that are used in this work are therefore more thoroughly investigated. The linear velocities and pressure drops in microchannels can only be calculated if the properties as density and viscosity are known. The surface tension is needed as this property determines biphasic behavior. Furthermore, it is needed to be able to compare the liquids used in Chapter 4 with the actual Beckmann rearrangement reactants. The solubility of cyclohexanone oxime in cyclooctane is needed to determine the minimal temperature in the cyclohexanone oxime feedline without solidification of the feedstock. Therefore the material properties that are investigated are the density, the viscosity, the solubility of cyclohexanone oxime in cyclooctane, and the surface tension of liquids used in this thesis.

The density is a function of temperature and composition and provides in most cases a linear relationship. The viscosity determines the pressures that are needed to convey the liquid in the microchannel and especially the mixture of fuming sulphuric acid and ε-caprolactam shows large differences in viscosity as a function of temperature and, more importantly, composition of the mixture. In Chapter 3 it is shown that the direct mixing of molten cyclohexanone oxime provides difficulties for mixtures containing more ε-caprolactam (M-ratio ($([H_2SO_4] + [SO_3])/[\varepsilon\text{-caprolactam}]$) of 2.0 to 1.7). Therefore, cyclooctane is used as a solvent for cyclohexanone oxime; as cyclooctane is inert for oleum. However, besides inertness for oleum the solvent should also dissolve a substantial amount of cyclohexanone oxime, if this amount would be too small a practical application would be impossible. Also the viscosity of this cyclooctane/cyclohexanone oxime solutions is determined. Cyclooctane and mixtures of oleum/ε-caprolactam form a biphasic system, where ε-caprolactam

is almost completely segregated in the oleum phase and forms an ionic liquid. Ionic liquids are currently under investigation in microreactor systems for their potential in process intensification (e.g Renken et al. (2007)). The surface tension between ionic liquids and nonionic liquids is investigated by Aerov et al. (2007), where they found that the interface comprises an electric double layer. The presence of this layer stabilizes the interface and increases the surface tension. On the other hand, the short-range volume interactions promote the segregation and decrease the surface tension. This makes the surface tension of ionic liquids as the oleum/ε-caprolactam mixture different than other liquids. The surface tension of cyclooctane and mixtures of oleum/ε-caprolactam is determined in order to determine the difficulty of creating a liquid-liquid interphase, which is needed for the mass transfer of cyclohexanone oxime to the oleum/ε-caprolactam phase. The surface tension of glycerol-water mixtures is determined as these mixtures are used to model the oleum/ε-caprolactam mixtures at room temperature in a microscopic study of liquid-liquid mixing in Chapter 4. This study of material properties offers the parameters that are needed to calculate volumetric flow rates, velocities, pressure drops and relevant dimensionless numbers for the Beckmann rearrangement in a microreactor. Furthermore, it provides practical information on the amount of cyclohexanone oxime in cyclooctane solutions that can be used without the formation of solid cyclohexanone oxime particles. This is needed to prevent blockage of the microchannels. Finally, interfacial surface tensions provide information on the amount of energy that is needed to create liquid-liquid surface area for mass transport of the reactants.

2.2 Experimental

The synthetic oleum/ε-caprolactam mixtures are manufactured by mixing oleum, ε-caprolactam and sulphuric acid of known concentrations to form the compositions shown in Table 2.1. The density was determined by means of a standard calibrated pycnometer. The viscosity was determined by a standard viscosimeter with rotating spindles at various speeds. The surface tension was determined by a SensaDyne 6000 Surface tensiometer by the maximum bubble pressure method, and was calibrated by de-mineralized water (72.8 mN/m) and ethanol (22.3 mN/m). The temperature of the liquids during the measurements of density, viscosity, and surface tension was maintained by a Lauda thermostatic bath. The solubility of cyclohexanone oxime in

cyclooctane was determined by the preparation of saturated samples, which where subsequently diluted for GC analysis, according to Dahlhoff et al. (2001).

Table 2.1: Composition of the synthetic ε-caprolactam mixtures with H_2SO_4 and SO_3 used for the measurements of the physical parameters.

M-ratio	wt% caprolactam	wt% H_2SO_4	wt% SO_3
2.6	31	58	11
2.3	34	55	11
2.0	37	52	11
1.7	42	47	11
1.4	47	42	11

2.3   Results and discussion

2.3.1   Density of oleum/ε-caprolactam mixtures

Table 2.2: Density of the synthetic ε-caprolactam mixtures with H_2SO_4 and SO_3 (Table 2.1) as a function of M-ratio and temperature. The error on the measured density is approximately 0.0002 (g/cm^3).

M-ratio:	2.6	2.3	2.0	1.7	1.4
Temperature (°C)	Density (g/cm^3)				
room temperature	1.5433	1.5210	1.5012	1.4738	1.4396
50	1.5232				1.4201
60	1.5153				
70	1.5090	1.4875		1.4381	1.4060
73			1.4621		
80	1.5013				
90	1.4928				
100	1.4873	1.4737	1.4440	1.4175	1.3860
110	1.4786		1.4363	1.4101	1.3791

The density of oleum/ε-caprolactam mixtures for various M-ratios is shown in Table 2.2 and Figure 2.1 as a function of temperature. The M-ratio is defined as
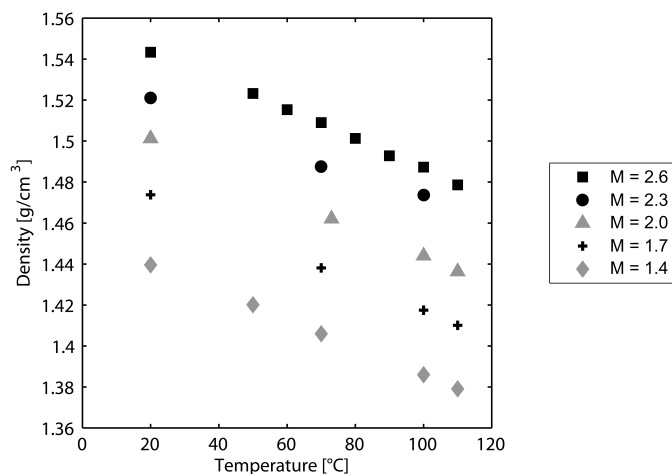
Figure 2.1: Density of the synthetic ε-caprolactam mixtures with H_2SO_4 and SO_3 (Table 2.1) as a function of temperature for various M-ratios.

$([H_2SO_4] + [SO_3])/[\varepsilon\text{-caprolactam}]$ and is actually the molar ratio between acid and ε-caprolactam; it is an important parameter for the properties of oleum/ε-caprolactam mixtures (also named ε-caprolactamium hydrogen sulphate). The highest density is measured for the highest M-ratio, and it decreases with M-ratio. The density of oleum/ε-caprolactam mixtures show a linear relationship with temperature, with R^2 values of 0.992 or higher. The thermal expansion coefficient (α) of the liquid can be calculated to be in the order of 5×10^{-4} K^{-1}, which is larger than for most liquids. The density shows a linear behavior with composition as well (Table 2.2). Extrapolation of the linear relationship with composition shows that ε-caprolactam occupies a volume in the mixture, which at 20 °C is close to 1 g/cm^3, whereas extrapolation to a weight fraction of 1 for the density of oleum in the mixture shows densities of about 1.7 g/cm^3 at room temperature. The density of ε-caprolactam is very close to the reported literature value of 1.01 g/cm^3 (Lide, 1999). The density of oleum reported by Bright et al. (1946) is higher (1.8 g/cm^3) and therefore oleum occupies less volume. This can be expected in an ionic liquid and can be explained by the strong interaction or complexing behavior of ε-caprolactam and SO_3. This strong interaction is also described by Fábos et al. (2008) in their work on ε-caprolactamium hydrogen sulphate.

2.3.2   Viscosity of oleum/ε-caprolactam mixtures, cyclohexanone oxime and cyclohexanone oxime/cyclooctane mixtures
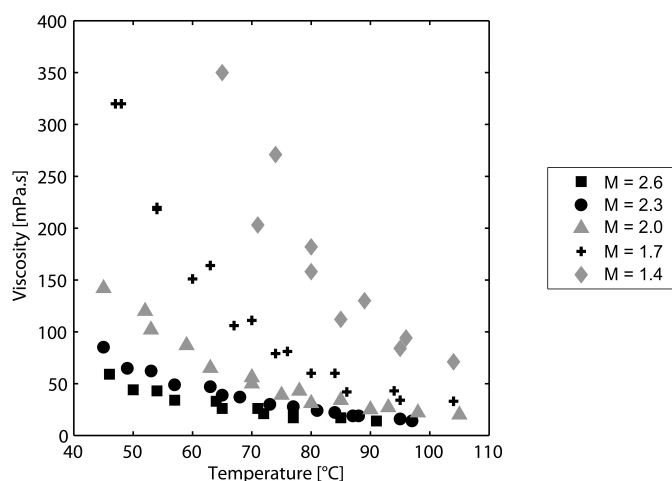
Figure 2.2: Viscosity of the synthetic ε-caprolactam mixtures with H_2SO_4 and SO_3 (Table 2.1) as a function of temperature for several M-ratios.

The viscosity of synthetic ε-caprolactam mixtures with H_2SO_4 and SO_3 (Table 2.1) is shown in Figure 2.2. The viscosity decreases with temperature for all mixtures. The viscosity shows a change over an order of magnitude with composition, for example at a temperature of 90 °C the viscosity ranges from 14 to 130 mPa·s. The influence of SO_3 concentration is reported by Fábos et al. (2008); they report a decrease in viscosity for higher SO_3 concentration. The M-ratio in their work is close to 1 and is clearly lower than 1.4, which is shown as well by their reported density of 1.372 to 1.353 at 50 and 80 °C, respectively. They report a solid at room temperature for their mixture of oleum and ε-caprolactam, which was not found in this work for M-ratios of 1.4 and higher. The variation in viscosity has a major impact on the flow behavior of the liquid in a microchannel, especially as during reaction the amount of ε-caprolactam is increasing in the mixture by conversion of cyclohexanone oxime, which will change the viscosity and that changes the pressure in the microchannel. As the pressure has an influence on droplet formation (Jovanovic et al., 2010), this will influence the flow regime, which influences mass transfer. Therefore, a stable (steady-state) operation of a microreactor for the Beckmann rearrangement can only

be guaranteed for microreactors with a properly designed pre-(micro)mixer, which is shown in Chapter 4.
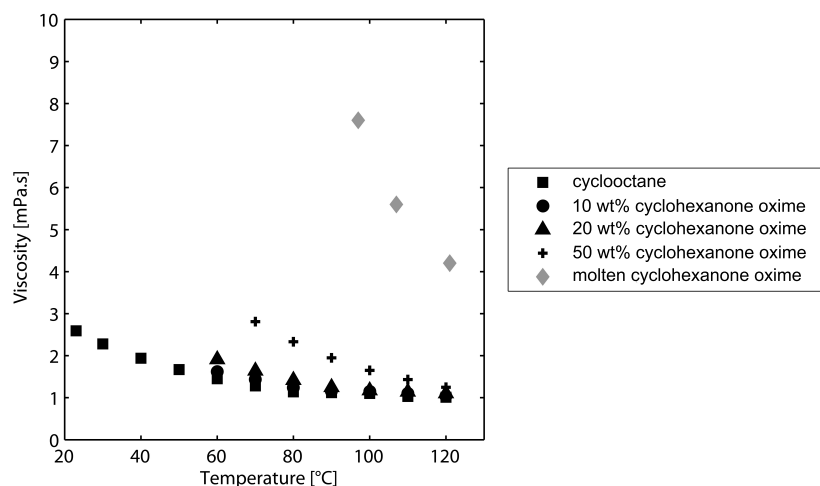
Figure 2.3: Viscosity of cyclooctane, of cyclooctane solutions with cyclohexanone oxime (10, 20, and 50 wt%), and of molten cyclohexanone oxime as a function of temperature.

The viscosity of cyclooctane, of cyclooctane solutions with cyclohexanone oxime (10, 20, and 50 wt%), and of molten cyclohexanone oxime as a function of temperature are shown in Figure 2.3. The viscosity of molten cyclohexanone oxime is between 4 and 8 mPa·s and shows the major difference in viscosity between mixtures of oleum/ε-caprolactam and cyclohexanone oxime. Mixing liquids with different viscosities can provide difficulties in the inlet section, especially as the volumetric flow rates are not the same in most cases. The viscosity of cyclooctane, and of cyclooctane solutions with cyclohexanone oxime (10, 20, and 50 wt%) all show relatively low viscosities of ca. 1–3 mPa·s. The viscosity changes slightly with increasing amount of cyclohexanone oxime. The viscosity decreases as a function of temperature, however, the amount of cyclohexanone oxime only has a minor influence. This is considered as a positive effect for reactor performance, as only small pressure fluctuations are expected by the cyclooctane flow. However, the mixing of liquids is influenced by difference in viscosity between biphasic liquids as is shown in Chapter 4.
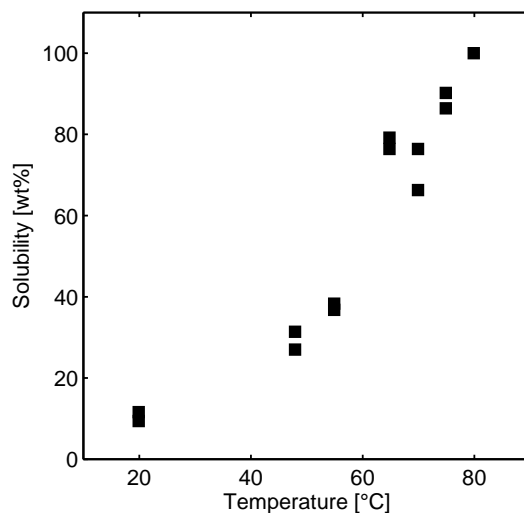
Figure 2.4: Solubility of cyclohexanone oxime in cyclooctane as a function of temperature.

2.3.3   Solubility of cyclohexanone oxime in cyclooctane

The reason for the use of an inert solvent for cyclohexanone oxime is explained in Chapter 3, as high selectivities are only possible with high M-ratios for molten cyclohexanone oxime. Furthermore, a solvent for cyclohexanone oxime has practical benefits, as clogging of the microchannels is prevented when the cyclohexanone oxime remains in solution. Furthermore, clogging can be caused by degraded cyclohexanone oxime as well; this coke-like material forms an irreversible blockage, necessitating the replacement of feed and reactor lines. Due to these advantages it is practically preferred to execute the experiments in microchannels with a solvent for cyclohexanone oxime. Cycloalkanes are inert towards oleum and immiscible with oleum and therefore a preferred solvent. The cycloalkane, cyclooctane C_8H_{16}, is utilized for the experiments. Other cycloalkanes can be utilized for this purpose as well. However, no evaporation of the cycloalkane in a microchannel is preferred. Therefore, the relatively high boiling point of cyclooctane (150 °C) makes it ideal for application at temperatures varying between 90 and 120 °C. In order to perform the Beckmann rearrangement with a solution of cyclohexanone oxime in cyclooctane it is important to know the solubility of cyclohexanone oxime in cyclooctane. Therefore, for multiple temperatures, measurements are preformed in order to determine this solubility.

Figure 2.4 shows the results obtained. Noticeable is the exponential trend of the solubility, starting at 11 wt% at room temperature and rising for elevated temperatures. At 80 °C the results show a solubility of approximately 100 wt%. However, the results obtained at elevated temperatures are more susceptible to deviations because the density of the solution is equal to the density of solid cyclohexanone oxime, hindering the formation of a clear fluid phase, which makes the collection of a saturated sample difficult. However, these high concentrations of cyclohexanone oxime are not needed in the experiments, described in this thesis.

2.3.4 Surface tension of oleum/ε-caprolactam mixtures, cyclohexanone oxime/cyclooctane mixtures, and glycerol-water mixtures

Table 2.3: Surface tension of the synthetic ε-caprolactam mixtures with H_2SO_4 and SO_3 (Table 2.1) as a function of M-ratio and temperature. Room temperature is abbreviated as RT.

M-ratio:	2.6	2.3	2.0	1.7	1.4
Temperature (°C)	Surface tension (mN/m)				
RT	67.8	80.5	91.9	118.8	134.9
40	60.9	68.1		87.8	
50	57.9	63.2		79.2	102.8
60			64.9		93.3
70	54.7	59.3	61.6	67.2	80.2
90	52.3	55.6	57.0	60.6	67.6
110	50.7	53.5	54.7	56.5	62.4
120	50.0	52.5		54.9	58.2

Table 2.3 and Figure 2.5 show the surface tension of various oleum/ε-caprolactam mixtures as a function of temperature. The surface tension is the highest for mixtures with an M-ratio of 1.4, this is expected as more ε-caprolactamium hydrogen sulphate is formed in that mixture. At room temperature the differences are the highest and range from 134.9 to 67.8 mN/m. The surface tension decreases exponentially with temperature. The surface tension shows a relatively small range (50 and 67.6 mN/m)
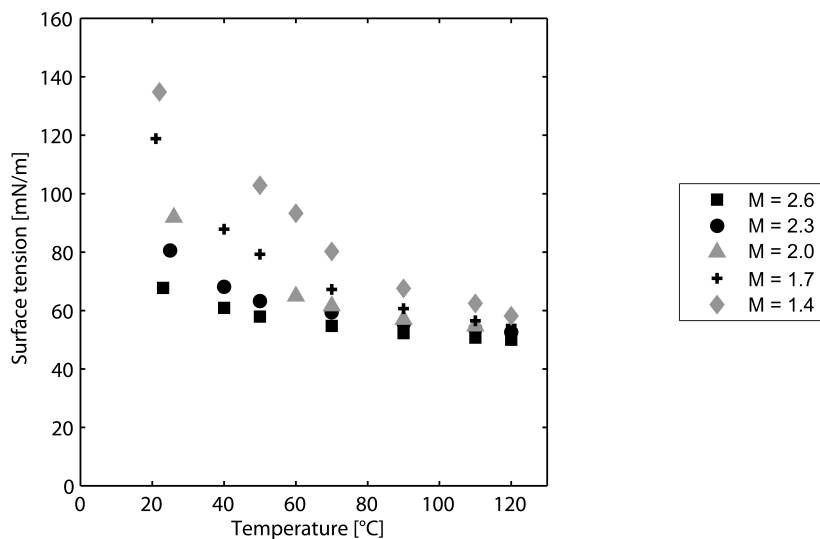
Figure 2.5: Surface tension of the synthetic ε-caprolactam mixtures with H_2SO_4 and SO_3 (Table 2.1) as a function of temperature for various compositions (M-ratios).

for temperatures that are normally used for the Beckmann rearrangement.
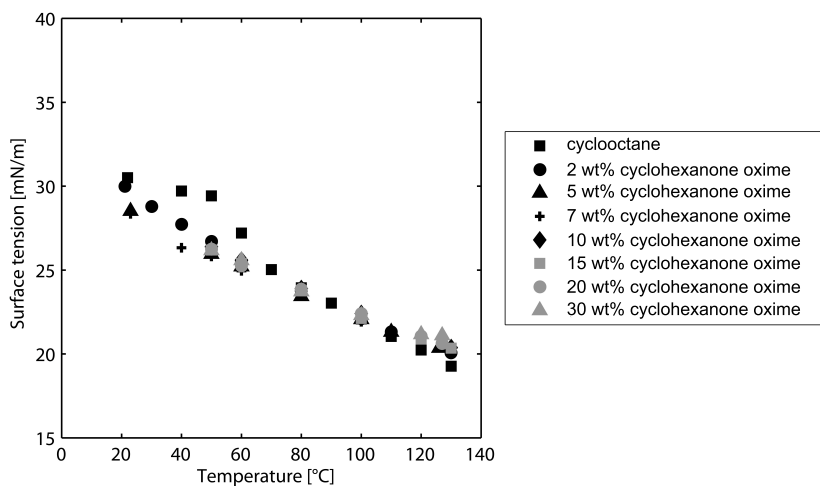
Figure 2.6: Surface tension of cyclohexanone oxime in cyclooctane as a function of temperature for various compositions.

Figure 2.6 shows the surface tension of cyclooctane and various cyclooctane–cyclohexanone oxime solutions. The differences between the mixtures is very small

and therefore cyclohexanone oxime concentration has only a small impact on the surface tension. This provides the information that cyclohexanone oxime has a small interaction with cyclooctane. This is beneficial for the use as a temporally solvent as the thermodynamic equilibrium will be a driving force for the cyclohexanone oxime towards the oleum/ε-caprolactam phase.

Table 2.4: Surface tension of the glycerol-water mixtures as a function of viscosity and temperature.

Viscosity:	66 mPa·s	100 mPa·s	150 mPa·s
Temperature (°C)	Surface tension (mN/m)		
Room temperature	65.7	65.3	64.4
40	66.5	56.2	57.5
50	65.0	55.2	55.4
60	63.3	53.6	54.0
70	61.7	52.4	51.9
80	60.4	51.5	50.9

Glycerol/water mixtures are used in Chapter 4 as model liquid to replace the ε-caprolactam/oleum mixtures for investigation of the liquid-liquid mixing by a microscope equipped with a high speed camera at room temperature. Table 2.4 shows the surface tensions of glycerol/water mixtures with the viscosities that are used in Chapter 4. The room temperature surface tensions of glycerol/water are very close to the surface tension of ε-caprolactam/oleum mixtures at high temperature conditions (90–120°C). Therefore, the model liquid (glycerol/water) is expected to provide similar liquid-liquid mixing with cyclooctane, when compared to the ε-caprolactam/oleum mixtures.

The surface tensions measured here are measured for a liquid-gas interface, this is not the interface under investigation, as this is the liquid-liquid interface between the liquids (ε-caprolactam/oleum mixtures, cyclooctane, cyclooctane with cyclohexanone oxime and glycerol/water). For the surface tension between two liquids, which have little interaction, or in other words, do not dissolve into each other, there exists a very simple correlation between the individual surface tension and the liquid-liquid

surface tension. This is described by Antonov's-rule:

$$\sigma_{liq-liq} = |\sigma_{liq1} - \sigma_{liq2}| \tag{2.1}$$

Here is $\sigma_{liq-liq}$ the surface tension between liquid 1 and 2, σ_{liq1} and σ_{liq2} the surface tensions of liquid 1 and 2 with a gas. This provides the information that the liquid-liquid surface tension of ε-caprolactam/oleum mixtures and cyclooctane with cyclohexanone oxime solutions is in the order of 25 mN/m, which is a measure for the difficulty of creating a liquid-liquid interface. Freitas et al. (1997) investigated a large number of organic liquids for their interfacial tension with water, where he found surface tension with the same order of magnitude. The surface tension is also interpreted as the energy needed to create a interface between two fluids. This is illustrated by the unit of surface tension mN/m, which can also be written as mJ/m^2. Micromixers can create liquid-liquid interfaces in the order of 20.000 m^2/m^3, therefore the amount of energy needed to create this liquid-liquid interface is 500 J/m^3, which is only a fraction of the amount of energy needed to convey the liquids in a microchannel. As a large number of liquids have surface tensions in this order of magnitude, the creation of a liquid-liquid interface between ε-caprolactam/oleum mixtures and cyclooctane with cyclohexanone oxime solutions is not seen as a major difficulty in the liquid-liquid mixing process discussed in Chapter 4.

2.4   Conclusion

- Densities of the measured ε-caprolactam/oleum mixtures vary between 1.54 and 1.38 g/cm^3 and decrease linearly with temperature with a thermal expansion coefficient of around 5×10^{-4} K^{-1}. The density also has a linear relationship with composition and the extrapolation of the data shows a correlation with the densities of ε-caprolactam and oleum.

- The viscosity of the ε-caprolactam/oleum mixture shows a decrease with temperature and it has a high dependence on the ε-caprolactam/oleum mixture's M-ratio. Lower M-ratios lead to higher viscosities. The viscosity of cyclooctane with cyclohexanone oxime solutions is much lower compared to the ε-caprolactam/oleum mixtures, however, they decrease with temperature as well.

The composition of the cyclooctane with cyclohexanone oxime solution only has a minor influence.

- The solubility of cyclohexanone oxime in cyclooctane is approximately 11 wt% at room temperature and increases to 100 wt% at temperatures of 80 °C.

- The surface tension of ε-caprolactam/oleum mixtures decreases with temperature and is the highest for low M-ratios. The surface tensions of cyclooctane with cyclohexanone oxime solutions are much lower compared to the ε-caprolactam/oleum mixtures, however, they decrease with temperature as well. The composition of the cyclooctane with cyclohexanone oxime solution only has a minor influence. The surface tension of the model liquid glycerol/water has the same magnitude as ε-caprolactam/oleum mixtures at temperatures at which the Beckmann rearrangement is normally conducted (90–120 °C). The liquid-liquid surface tension of ε-caprolactam/oleum mixtures and cyclooctane with cyclohexanone oxime solutions is approximated as 25 mN/m.

- Especially the viscosity of ε-caprolactam/oleum mixtures is important to understand the course of the reaction, by the addition of cyclohexanone oxime to the mixture the liquids becomes much more viscous during the reaction. This increases the $\partial p/\partial x$ of the end section of microchannel.

- The surface tension of glycerol/water mixtures at room temperature is comparable to the surface tension measured for ε-caprolactam/oleum mixtures at 90–120 °C (which are temperatures normally used for production of ε-caprolactam). Therefore, glycerol/water mixtures can replace the oleum/ε-caprolactam mixtures in a study of the liquid-liquid flow behavior in micromixers, this is simplifying the investigations in Chapter 4 tremendously.

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The single phase Beckmann rearrangement to ε-caprolactam in a split-and-recombine micromixer with direct injection of molten cyclohexanone oxime

3

Abstract

This chapter describes the single phase Beckmann rearrangement of molten cyclohexanone oxime in a microchannel, without any solvents. This is the most straightforward method for replacing an industrial reactor by microreactor technology, as the same reactants are used, which would only necessitate the replacement of the reactor/heat-exchanger. First the reaction in the microchannel is modelled mathematically by one dimensional and (pseudo) two dimensional models of a micro side inlet-mixer. This micro injection mixer is designed as a small side inlet (10 μm) slit for molten cyclohexanone oxime into a main channel (width 200 μm) containing a mixture of oleum and ε-caprolactam. The Beckmann reaction is shown to be very fast when mass transfer can be neglected (model 1). The two dimensional models (model 2 and model 3) both show that mixing, by diffusion of a 20 μm layer of molten cyclohexanone oxime into the main stream (180 μm) of a mixture of oleum and ε-caprolactam, is not fast enough to completely convert all cyclohexanone oxime within a microchannel of 20 cm length and a width of 200 μm. A liquid-liquid layer mathematical model (model 4) shows that a layer of cyclohexanone oxime between 2 and 5 μm combined with a 20 − 50 μm layer of oleum and ε-caprolactam is small enough to completely convert cyclohexanone oxime for the above mentioned microchannel,

with a flow ratio of 1:10 (cyclohexanone oxime : oleum/ε-caprolactam). The Beck-mann rearrangement reaction is therefore performed in a split-and-recombine mi-cromixer, which can experimentally create these size of liquid layers or packages. For an M-ratio $(([H_2SO_4] + [SO_3])/[\varepsilon\text{-caprolactam}])$ of 2.6 to 2.2, the Beckmann rearrangement shows selectivities ranging from 99.6 to 96.7%. An M-ratio of 2.0 to 1.7 shows a selectivity of 97.6% at 100 °C. A higher temperature (110 °C) leads repeatedly to complete blockage of the micromixer and channel. The small side inlet for cyclohexanone oxime and the main microchannel are completely filled with parti-cle like by-products, which are caused by the rapid reaction and insufficient mixing of the liquid layers. However, this is the first time this reaction is accomplished success-fully in a microreactor with molten cyclohexanone oxime, ε-caprolactam and oleum with concentrations comparable with industrial conditions. Furthermore, this result shows the necessity of other means to increase the mixing intensity of cyclohexanone oxime with a mixture of oleum and ε-caprolactam in a microchannel reactor.

3.1   Introduction

In industry the Beckmann rearrangement reaction is applied by the conversion of molten cyclohexanone oxime into ε-caprolactam. A commonly used industrial reac-tor consists of a vertical tube with a diameter of 10 cm and with 24 vertical positioned injectors (3 mm) of molten cyclohexanone oxime (Smeets et al., 2004). The veloc-ity in the main channel is about 30 m/s, the velocity of the molten cyclohexanone oxime is in the order of 30 m/s as well. The mixing of reactants is therefore in the extreme turbulent regime ($Re \approx 30.000$). Although mixing in the turbulent regime is possible in small scale reactors (Luo et al., 2007), the creation of turbulent conditions is nearly impossible in micromixers and microreactors for the mixing and reaction of molten cyclohexanone oxime and oleum (or a mixture with ε-caprolactam) as the mixture is very viscous (50 - 300 mPa·s, see Chapter 2), which means a laminar flow regime and low Reynolds numbers apply to this system. Common by-products in ε-caprolactam are for example investigated by Eppert et al. (1990) and originate from almost all steps in the process, however, contact between pure oleum and pure molten cyclohexanone oxime leads to very vigorous reactions, and forms black tar-like vis-cous by-products, which will immediately block the micromixer and microchannel. In industry this is prevented by the injection of cyclohexanone oxime into a mixture

of ε-caprolactam and oleum, where the main stream of ε-caprolactam and oleum is recycled. The volumetric flow rate of this main stream is a factor of 50 higher compared to the volumetric flow rate of cyclohexanone oxime to decrease the reaction rate of the Beckmann rearrangement.

In this chapter the direct single phase reaction of molten cyclohexanone oxime with a mixture of ε-caprolactam and oleum is investigated in micromixers and microchannels. The influence of fast and slow reactions on the diffusion and mixing behavior is mathematically modelled by e.g. Ou and Ranz (1983), where they show the effect of fluid mixing on chemical reactions by means of a model which treats reactants as adjacent sheets of fluid with single-step irreversible reactions. This model shows much similarities with the Beckmann rearrangement of cyclohexanone oxime with oleum/ε-caprolactam mixtures. They show the limits of reaction control by mixing, including diffusion, and by chemical kinetics in terms of the second Damköhler number (Da_{II}). First the liquid Beckmann rearrangement reaction is modelled in Femlab 3.0 (Comsol®) with one dimensional and two dimensional models to determine the size of the liquid layers (or other shapes) of cyclohexanone oxime and oleum/ε-caprolactam mixtures that is needed in the microchannels. Table 3.1 shows the four mathematical models used to investigate the Beckmann rearrangement in microchannels. The one dimensional model is a simple plug flow model, which accounts for the axial direction with axial dispersion, which is a basic model where the mixing of the reactants is not taken into account. The two dimensional models treat the reactants as adjacent sheets of fluid, which is similar to the mathematical model of Ou and Ranz (1983). The modelled (two dimensional) rectangular microchannel has a width of 200 μm and a length of 20 cm. The cyclohexanone oxime is injected by a small side inlet (10 μm) to account for the much smaller volumetric flow rate compared to the oleum/ε-caprolactam mixture (micro injection mixer models, Table 3.1). The cooling in the models occurs from one side of the microchannel. The reaction is modelled in a liquid-liquid layer model (model 4) as well, to determine the layer thickness of cyclohexanone oxime and the oleum/ε-caprolactam mixture. The width is 200 μm as well and the length is variable. Experimentally this liquid-liquid layer can be created by a split-and-recombine micromixer, which is used in a later section to perform the Beckmann rearrangement reaction. As the M-ratio is the main parameter determining the viscosity (see Chapter 2), the design criterion is the calculated M-ratio in the liquid, which should not be lower than 1, to prevent extremely

high viscosity of the mixture. The conversion of cyclohexanone oxime is the second
design parameter as conversion needs to be completed at the exit of the microchannel.
The amount of cyclohexanone oxime that can be converted in a microchannel is de-
pendent on parameters as e.g. the reaction rate, mass transfer and concentration of the
reactants. As a first approximation the reaction rate and mass transfer should possibly
be in the order of seconds. Furthermore, microchannels are in the order of 50 - 500
μm. As a first approximation the pressure drop over the microchannel is limited to ca.
10 bar (the same as the industrial design described by Smeets et al. (2004)). These
approximations lead to an inlet velocity of the reaction mixture of around 0.1 - 0.2
m/s. Considering a production rate of 200.000 tonnes/annum for an ε-caprolactam
production facility this leads to ca. 7–16 million microchannels with a radial dimen-
sion of 200 μm. This seems a rather large number, however a volume of $1 \times 1 \times 0.5$
m^3 can contain ca. 3 million microchannels, which puts the volume of the microre-
actor set-up in perspective. However, this large number of microchannels with this
simple mathematical extrapolation shows that techniques are needed to reduce the
number of channels as much as possible. Therefore, the approach in Chapter 6 where
mixing and reaction is physically separated is a more practical approach towards pro-
duction microchannel reactor design. In that way the number of channels can be
reduced and most probably millimeter mixer elements can be applied. In the last
section the Beckmann rearrangement of molten cyclohexanone oxime with a mixture
of ε-caprolactam and oleum in a split-and-recombine micromixer is experimentally
successfully completed. To our knowledge this is the first time the Beckmann rear-
rangement is conducted successfully in a microreactor with the single phase direct
injection of molten cyclohexanone oxime.

3.2   Modelling of the mass and heat transfer

In this section, different models are presented which were developed to gain more
insight into the heat and mass transfer during the Beckmann rearrangement inside the
microchannel of a microreactor. Table 3.1 shows the four models and their schematic
configuration and the corresponding representing micromixer. The models are used
to determine concentration and temperature profiles in the microchannel. Femlab 3.0
is used to solve the partial differential equations of the mathematical models, by a
Finite Element Method.

Table 3.1: Mathematical models and corresponding configurations for the reaction of cyclohexanone oxime to ε-caprolactam

nr	models	schematic configuration	corresponding micromixer
1	one dimensional	-	-
2	pseudo two dimensional	Figure 3.2	micro injection mixer (side inlet)
3	two dimensional	Figure 3.2	micro injection mixer (side inlet)
4	liquid-liquid layer	Figure 3.4	split-and-recombine micromixer

The conventional Navier-Stokes, convection-diffusion and energy equations are used in these mathematical models. Some simplifying assumptions are applied for the conventional Navier-Stokes, convection-diffusion and energy equations to model the fluid flow and the mass transfer process:

- The fluid is Newtonian.

- The fluid is incompressible.

- The fluid has a laminar fully developed velocity profile.

- The flow is considered laminar, since the Reynolds number is very low (Re $\sim$ 1) in microreactors, especially for the Beckmann rearrangement where the liquids have a high viscosity (Chapter 2).

- The inlet temperature of the liquids are considered similar.

- A steady-state of temperature and concentration is assumed in the microchannel.

- A no-slip boundary condition at the walls is assumed.

- For the metal cooling wall the temperature gradients in the radial direction are neglected.

- Viscous dissipation is neglected.

- A constant temperature of the cooling liquid is assumed.

The Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam is modelled by the kinetic model of Wichterle and Roček (1951a,b):

$$-r_a = k_0 \cdot c_a \cdot e^{\frac{-E_{act}}{RT_R}} \tag{3.1}$$

in which $-r_a$ is the reaction rate of cyclohexanone oxime, c_a is the concentration of cyclohexanone oxime, E_{act} is the activation energy, R is the gas constant, T_R is the temperature of the reaction mixture and k_0 is the pre-exponential factor. The pre-exponential factor is dependent on the weight fraction of oleum (w_{oleum}) in a mixture of oleum, ε-caprolactam and cyclohexanone oxime and can be estimated by the following correlation (Wichterle and Roček, 1951a):

$$\log k_0 = 9.6 + 13.5 \cdot w_{oleum} - 7.6 \cdot (w_{oleum})^2 \tag{3.2}$$

Wichterle and Roček used oleum with a sulphur trioxide content of 5 wt% for their experiments in order to obtain the pre-exponential factor. In another article Wichterle and Roček describe the dependency of the pre-exponential factor on the SO_3-content of oleum (Wichterle and Roček, 1951b). According to this article the pre-exponential factor remains constant for an SO_3-content between 5 and 12 wt%. In the developed mathematical model an SO_3-content of 14 wt% is used (Smeets et al., 2004), and therefore, the reaction rate constant is corrected by a factor 1.3, see Figure 3.1.

For all the models, a pre-set volume flow ratio of 10:1 (inlet oleum and ε-caprolactam mixture : cyclohexanone oxime) is chosen to provide a reasonable yield and concentrations of reactants in the Beckmann rearrangement mixture. The M-ratio $(([H_2SO_4] + [SO_3])/[\varepsilon\text{-caprolactam}])$ is chosen at 1.4 for comparison with industrial conditions.

The diffusion coefficient (D_{eff}) used in the models is dependent on the viscosity and temperature of the reaction mixture, according to the Stokes-Einstein equation (Perry and Green, 1999):

$$D_{eff} = D_0 \frac{\mu_0 \cdot T_R}{\mu \cdot T_{R,in}} \tag{3.3}$$

where D_0 is the diffusion coefficient at the inlet temperature ($T_{R,in}$) of 373 K and
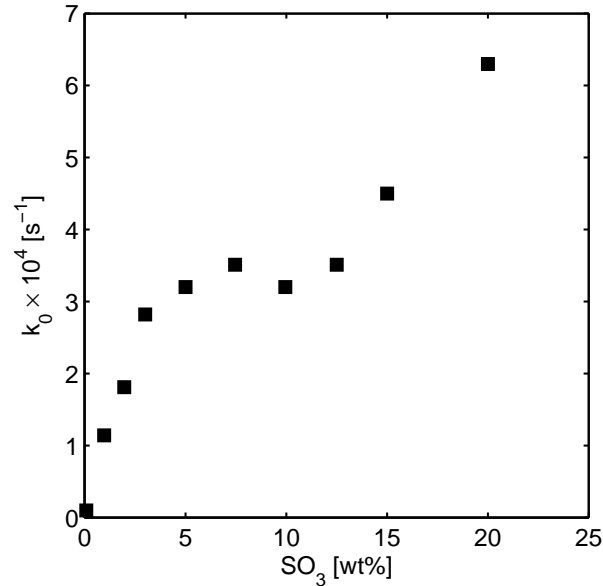
Figure 3.1: The pre-exponential factor in the kinetic rate equation (equation 3.1) of the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam as a function of SO_3-concentration (Wichterle and Roček (1951b)).

a corresponding viscosity of the inlet reaction mixture (μ_0) of 150 mPa·s. The viscosity is mainly dependent on the reaction mixture temperature, M-ratio, and the SO_3 weight percentage. These parameters will change along the channel by the diffusion of cyclohexanone oxime into the reaction mixture and the change in temperature by the reaction, which is taking place in the microchannel.

3.2.1   One dimensional model

For the one dimensional model, plug flow is assumed for both liquids. No diffusion in the radial direction has been taken into account. Therefore, the obtained results will describe the situation when both reactants are premixed before entering the reaction channel. The mass balance for the one dimensional model is given by:

$$\nabla c_a = \frac{r_a}{v} \tag{3.4}$$

in which v is the mean velocity of the reaction mixture, which is varied between 0.01 and 0.2 m/s, corresponding to experimental conditions tested in the microchan-

nel.

The heat transfer in the single microchannel is described by:

$$-\lambda_R \nabla^2 T_R = -\rho_R \cdot v \cdot C_{P,R} \nabla T_R + (-\Delta H_R)(-r_a) - U_R \cdot \frac{O_{ch}}{A_{ch}} \cdot (T_R - T_m) \quad (3.5)$$

where λ is the heat conductivity, ρ is the density, C_p is the heat capacity, ΔH is the reaction enthalpy, U is the overall heat transfer coefficient, O is the perimeter, A is the mean cross-sectional area perpendicular to the z-axis. The subscripts 'R', 'ch' and 'm' refer to the reaction mixture, the microchannel and the metal wall, respectively. For the reaction mixture there is heat transfer due to conduction, convection, reaction and heat exchange with the surroundings, which is the metal wall of the microchannel.

The energy balance of the metal microchannel wall body is given by:

$$-\lambda_m \nabla^2 T_m = U_R \cdot \frac{O_{ch}}{A_m}(T_R - T_m) - U_c \cdot \frac{O_{cool}}{A_m}(T_m - T_c) \quad (3.6)$$

where the subscripts 'c' and 'cool' refer to the cooling liquid and the cooling channel, respectively. For the metal microchannel wall body there is heat transfer due to conduction and heat exchange with the cooling liquid and the reaction mixture. The heat loss to the surroundings is neglected in this model.

3.2.2   Pseudo two dimensional model

The geometry which is used for modelling of a single microchannel in Femlab 3.0 is shown in Figure 3.2. When modelling a stationary convection-diffusion process that has negligible convective transport in one direction, in this case the radial direction, and negligible diffusive transport in the other direction, in this case the axial direction, it is possible to re-formulate the convection-diffusion equation by switching the axial derivative to a time derivative. This will change the two dimensional equation into a less demanding one dimensional time-dependent equation. This will make it a pseudo two dimensional equation. To be able to do this, a non-changing velocity profile along the axial direction is needed. The velocity profile is shown in Figure 3.3 The velocity profile is calculated with the Navier-Stokes equation for an average velocity of 0.01 m/s in a two dimensional representation of the microchannel. Cyclohexanone oxime and a mixture of oleum and ε-caprolactam are chosen as the two liquids with unequal
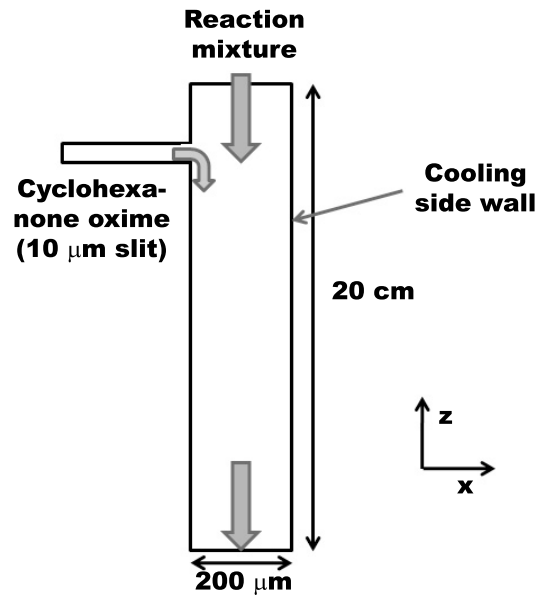
Figure 3.2: Two dimensional geometry of the single microchannel used in Femlab 3.0 to model the heat and mass transfer. The two dimensional microchannel has a width of 200 μm and a length of 20 cm.
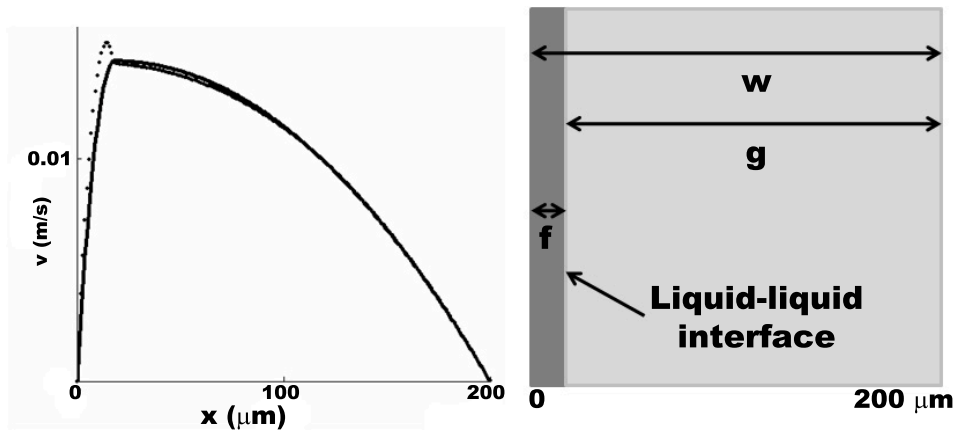
Figure 3.3: Velocity profile (left graph) of the low viscous and high viscous liquid. The right schematic shows the positions of the indicated letters f and g in the equations 3.7 and 3.8. The liquid–liquid interface is indicated. The w indicates the total width of the channel (200 μm).

viscosity. With this result a parabolic function is obtained for the velocity profile with a maximum near the interface between the two liquids (see Figure 3.3 on the right):

$$v = -5.75 \cdot v_{avg} \cdot (\frac{x}{2f})^2 + 5.75 \cdot v_{avg} \cdot (\frac{x}{2f}) \tag{3.7}$$

For $0 \leq x < f$ (see Figure 3.3)

$$v = -5.75 \cdot v_{avg} \cdot (\frac{x + (g - f)}{2g})^2 + 5.75 \cdot v_{avg} \cdot (\frac{x + (g - f)}{2g}) \tag{3.8}$$

For $f \leq x \leq 2 \cdot 10^{-4}$ (see Figure 3.3). Here is v_{avg} the average velocity of the liquid, varied between 0.01 and 0.2 m/s, f is the location at the x-axis of the interface between the high viscous and low viscous liquid; g is the width of the channel minus f. The interface is assumed to be at $1/11$ of the total width (w) of the microchannel (200 μm), based on the volumetric flow ratio at the inlet of the ε-caprolactam and oleum mixture to the cyclohexanone oxime, which is chosen as 10 to 1. Despite the fact that the viscosity will change along the channel by the additional formed ε-caprolactam, a steady state velocity profile is assumed for the pseudo two dimensional model. The Peclet number (Pe) in the radial direction is zero except at the small inlet for cyclohexanone oxime. This means that mass transfer is mainly taking place due to diffusive transport in the radial direction:

$$Pe = \frac{d_c \cdot v}{D} \tag{3.9}$$

In this equation d_c is the characteristic length, so the width of the channel for the radial direction, v is the velocity in the radial direction, which is close to zero. D is the diffusion coefficient. In the axial direction the Peclet number is very high ($\sim 1 \times 10^6$), meaning that the mass transport is mainly taking place by convection in this direction. This means that axial dispersion is negligible and that plug flow is applicable for the reaction mixture. The equations used for the pseudo two dimensional model are the convection-diffusion equation and energy balance. The convection-diffusion equation will be one dimensional with a time-derivative instead of the z-coordinate and is given by:

$$u_{dl} \frac{\partial c_i}{\partial t} + \nabla \cdot (-D \nabla c_i) = r_i \tag{3.10}$$

in which u_{dl} is the dimensionless velocity, which is the velocity profile (Equations 3.7 and 3.8) divided by v_{avg}. Furthermore, c_i is the concentration of component i and r_i is the reaction rate of component i. The first term represents the convective transport in the axial direction, whereas the second term represents the diffusive transport in the radial direction. The energy balance for the reaction mixture is given by:

$$u_{dl} \cdot \rho_R \cdot C_{P,R} \frac{\partial T_R}{\partial t} - \lambda_R \nabla^2 T_R = \Delta H_R \cdot r_a - U_R \cdot \frac{O_{ch}}{A_{ch}}(T_R - T_m) \qquad (3.11)$$

The first term in the energy equation for the reaction mixture represents the convective heat transfer in the axial direction, the second term represents the heat transfer due to conduction through the reaction mixture in the radial direction, the third term represents the heat due to reaction and the last term represents the heat loss to the metal, surrounding the microchannel. Because this model is pseudo two dimensional, only radial heat conduction through the metal is taken into account, whereas the axial conduction is neglected. However, the assumption to neglect the axial conduction is incorrect when high temperature gradients exist within the metal, and must be verified for correct interpretation of the results. This axial conduction can be an important factor in micro technology, since the share of wall material is relatively high.

3.2.3   Two dimensional model

Since the microchannel to be modelled has a very small width compared to the length of the channel, 200 μm and 20 cm, respectively, the equation is scaled in order to avoid excessive amount of elements and nodes. Therefore a new scaled z-coordinate is introduced, and a new differential for the mass balances, according to the equations below:

$$\hat{z} = \frac{z}{S} \qquad (3.12)$$

in which $\hat{z}$ is the new scaled z-coordinate and S is the scaling factor. The Navier-Stokes equation is given by:

$$\rho(u \cdot \nabla)u = -\nabla p + \eta \nabla^2 u \qquad (3.13)$$

in which u is the velocity vector and p is the pressure. The velocity of the inlet reaction mixture is varied between 0.01 and 0.2 m/s, whereas the velocity of the cyclohexanone oxime stream is varied between 0.02 and 0.4 m/s. The convection-diffusion equation used is given by:

$$\nabla \cdot (-D\nabla c_i) = r_i - u \cdot \nabla c_i \qquad (3.14)$$

The diffusion and convection terms in this equation are both for the axial and radial direction. The energy balances for the reaction mixture and for the metal part are similar to the ones used for the one dimensional model. The convection and conduction terms in these equations again account for both the axial and radial direction.

3.2.4   Liquid-liquid layer model with variable thickness

In this section a mathematical model is shown in which liquid-liquid layers of cyclohexanone oxime (a) and oleum/ε-caprolactam mixtures (b) are modelled (Figure 3.4). This mathematical model will provide a maximum layer thickness of the cyclohexanone oxime layer. The mathematical criterion is that the M-ratio has to remain above one. This criterion is chosen for following reason: when the M-ratio is one, the ε-caprolactam will bind all of the oleum (SO_3 and H_2SO_4) in the reaction mixture, therefore the reaction mixture will be extremely viscous. The M-ratio is most likely to decrease at the interface of the two liquids, because of the additionally formed ε-caprolactam that will diffuse into the oleum/ε-caprolactam mixture. Another design criterion that has to be accounted for in the model is the conversion of all cyclohexanone oxime within a set length of a microchannel. The length of the microchannels is limited by the residence time, which should stay within the range of seconds. For an inlet velocity of 0.1 m/s the reaction should then be completed within about 50 cm of microchannel. This liquid-liquid layer model only accounts for diffusion in the radial direction in a pseudo two dimensional equation together with the energy balance for the reaction mixture and the metal part. Convective transport is neglected, as well as axial conduction. The equation for the diffusion is given by:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D\nabla c_i) = r_i \qquad (3.15)$$

The energy equations are given by equations 3.11 and 3.6 for the reaction mixture and the metal part, respectively. For the dimensionless velocity a uniform velocity profile is used, since convective transport is neglected. These small liquid-liquid layers can be experimentally created by a split-and-recombine micromixer, which is used in the next section for the Beckmann rearrangement.
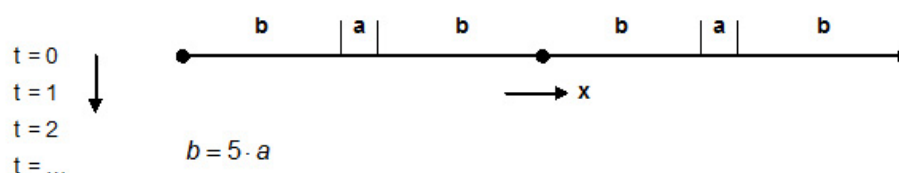
Figure 3.4: The liquid-liquid layer model, where 'a' represents the layer of the cyclohexanone oxime stream, while 'b' represents the layer of the mixture of oleum/ε-caprolactam. The layers are arranged in b-a-b-b-a-b fashion, to create symmetrical diffusion and reaction of cyclohexanone oxime into the b layer. In this way the model represents multiple layers as well.

3.3   Experimental

A schematic of the microreactor setup is shown in Figure 3.5. The experimental microreactor is considered as the combination of a split-and-recombine 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 split-and-recombine micromixer is shown in Figure 3.6 and further described in the next paragraph. 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 (Gilson 305) is used prior and after the experiments for cleaning of the split-and-recombine micromixer and the microchannel. The cyclohexanone oxime feed line including the HPLC pump head is temperature traced ($> 90\,°$C) by a Lauda ecoline thermostat to prevent solidification of the molten cyclohexanone oxime. 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,
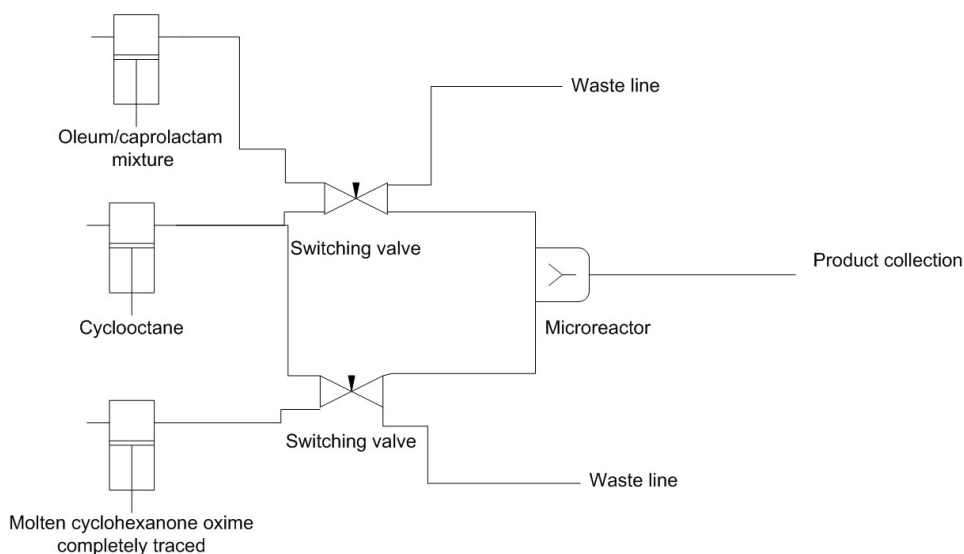
Figure 3.5: Schematic overview of the experimental microreactor setup. HPLC pumps are used for the oleum/ε-caprolactam, molten cyclohexanone oxime, and cyclooctane flow. The cyclohexanone oxime feedline is temperature traced above 90 °C, including the HPLC head, to prevent solidification of cyclohexanone oxime. The cyclooctane feedlines and the switching valves are needed to prevent unwanted contact between molten cyclohexanone oxime and the oleum/ε-caprolactam mixture during the start and end of the experiments.

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. Pressure tightness of connections is guaranteed by 1/16 inch HPLC Valco® connections. The complete setup is preheated to a temperature of at least 90 °C, while maintaining a flow of cyclooctane in all the channels.

After a steady state temperature has been reached the cyclohexanone oxime flow is initiated into a flow of cyclooctane. After a steady state cyclohexanone oxime flow has been reached the flow of cyclooctane is switched by the switching valve to a flow of a mixture of ε-caprolactam and oleum. This procedure with cyclooctane is needed to prevent unwanted side reactions to high viscous by-products during start up of the reactor. The outlet of the microchannel is into a beaker in open air, where the product sample is collected on a Sartorius balance for at least 30 minutes. The mixture is
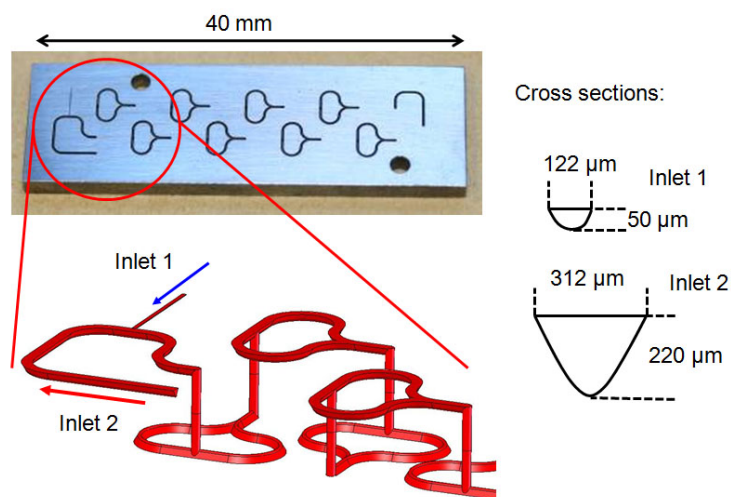
Figure 3.6: The split-and-recombine micromixer used to create multiple layers of molten cyclohexanone oxime and layers of the oleum/ε-caprolactam mixture. A total of 17 split and recombine units are fabricated in the micromixer. The upper figure shows the lasered plate (40 mm), the lower figure shows the three dimensional representation of the split-and-recombine micromixer with the small inlet channel (inlet 1) for molten cyclohexanone oxime and the larger inlet channel (inlet 2) for the oleum/ε-caprolactam mixture. The cross-sectional areas, which are shown on the right, of the inlet channels have a ratio of 10:1, which is the same as the used flow rate ratio (0.3 : 0.03 ml/min).

analyzed by NMR to determine the purity of the produced ε-caprolactam, which is used to calculate the selectivity of the process.

The design of the split-and-recombine micromixer is adapted from the glass split-and-recombine mixer of Micronit$^{\circledR}$ (Enschede, the Netherlands). Inlet 1 has a smaller cross sectional area compared to the main channel to match the fluid velocities of the incoming liquids. The channels are manufactured by laser ablation with tolerances of 2 μm. A total of 17 split and recombine units are fabricated in the microreactor. 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 (see Figure 3.6). The small channel has a parabolic shape with 1/10th of the cross sectional surface area of the main channel. The liquids are combined in the T–section where the molten cyclohexanone oxime is fed by

the smaller channel (inlet 1). The mixer is coated with a 1 μm Diarc$^{\circledR}$ diamond-like-carbon layer to prevent corrosion by the fuming sulphuric acid needed for the Beckmann rearrangement to ε-caprolactam.

3.4   Results and discussion

The mathematical models describe the single phase behavior of the Beckmann rearrangement of cyclohexanone oxime into ε-caprolactam. The reactants are completely miscible, which is also the case for the baseline industrial process. The one-dimensional model describes the limiting case where the reactants are already mixed at the entrance of the reactor. In this way the reaction kinetics are the limiting factor and shows the fast reaction rate of the Beckmann rearrangement of cyclohexanone oxime. The other models take into account that the reactant first have to diffuse before reaction can take place and shows the necessity of fast mixing for the Beckmann rearrangement. First the results of the mathematical models are provided, followed by a section on an experimental application of a split-and-recombine mixer for the single phase Beckmann rearrangement of cyclohexanone oxime.

3.4.1   Mathematical modelling of the Beckmann rearrangement in a microchannel
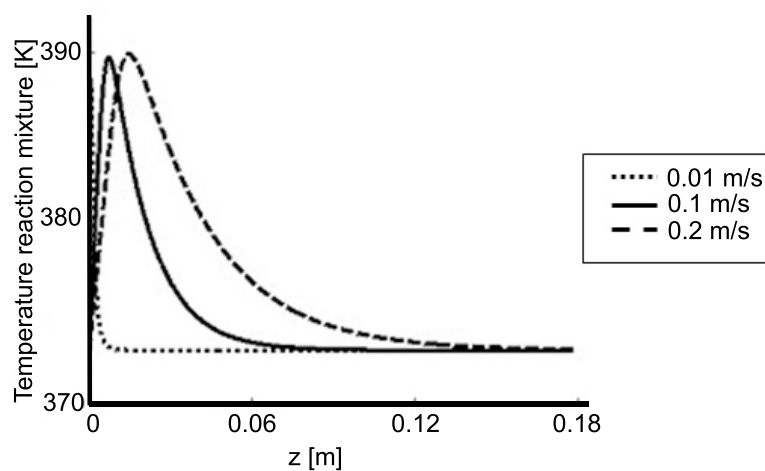
3.4.1.1   One dimensional model (model 1)

Figure 3.7: The temperature profile of the reaction mixture of the Beckmann rearrangement in a microchannel with a width of 200 μm for different velocities: 0.01 m/s (dotted line), 0.1 m/s (solid line) and 0.2 m/s (dashed line). The results are obtained with the one dimensional model.

In Figure 3.7 a plot of the temperature profile of the reaction mixture is depicted for the one dimensional model for different velocities of the reaction mixture. For low velocities the reaction mixture is heated up and cooled down in the first parts of the microchannel. The cyclohexanone oxime has completely converted in the initial part of the microchannel. This is caused by the extremely fast reaction. Diffusion in the radial direction is not taken into account for the one dimensional model, therefore this model shows the temperature increase for the limiting case where complete mixing in the radial direction has been reached.

3.4.1.2   Pseudo two dimensional model (model 2)

In Figure 3.8 a plot of the concentration profile of cyclohexanone oxime in the microchannel is depicted for the pseudo two dimensional model for different velocities of the reaction mixture. The concentration of cyclohexanone oxime is integrated over the width of the channel and then plotted against the z-coordinate. Although the reaction is extremely fast, the plot shows that for the three different inlet velocities, the reaction will not be completed within the 0.2 m length of the microchannel, because of diffusion limitations. The objective is to eventually operate at an inlet velocity of 0.1 m/s. With the current design, a microchannel length of about 5.3 m long is needed, instead of the current length of 0.2 m, in order for the reaction to be completed within the channel. The temperature profiles (not shown here) of the reaction mixture show increases in temperature in the order of 1 K above the cooling liquid, which is nearly isothermal. All of the produced reaction heat is removed from the reaction mixture by the cooling medium. This in contrast to the temperature calculated for the one dimensional model, where no radial diffusion is taken into account. The pseudo two dimensional model shows that the temperature of the reaction mixture will be highest close to the interface between the liquid cyclohexanone oxime and the liquid consisting of oleum and ε-caprolactam; at this location the heat is produced due to the reaction. Furthermore, it shows that the temperature differences are very small along the channel. This can be explained by the fact that the rate of reaction of cyclohexanone oxime is slow due to diffusion limitations. The heat exchange with the metal will therefore prevent the temperature of the reaction mixture to exceed 373.3 K. The pseudo two dimensional model shows the major impact of the radial diffusion in the microchannel, as conversion is not completed within a reasonable length of the

microchannel.
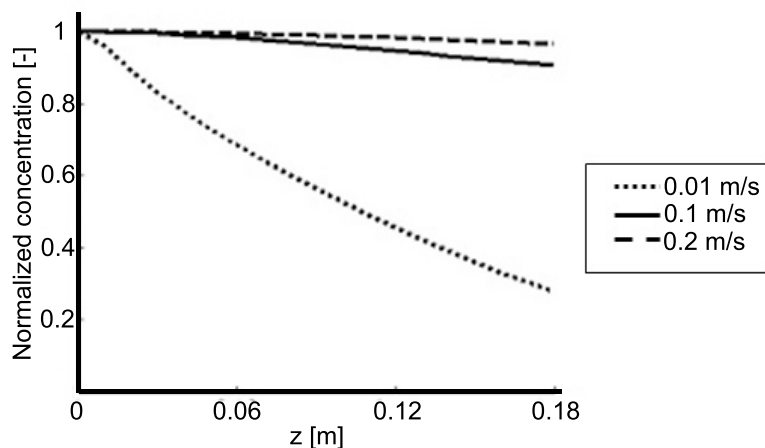
Figure 3.8: The concentration profile of cyclohexanone oxime along the microchannel for different inlet velocities: 0.01 m/s (dotted line), 0.1 m/s (solid line) and 0.2 m/s (dashed line), which is obtained by the pseudo two dimensional model.

3.4.1.3   Two dimensional model (model 3)

In Figure 3.9 a surface plot of the concentration profile of cyclohexanone oxime in the microchannel for an inlet velocity of 0.01 m/s shows a clear distinction between the low and high viscous liquids, where the low viscous liquid has a high concentration of cyclohexanone oxime and the highly viscous liquid a concentration of zero. This surface plot is calculated by the two dimensional model. The reaction is mass transfer limited and as soon as cyclohexanone oxime diffuses into the high viscous liquids, it immediately reacts to ε-caprolactam. Three crosssections of the concentration of cyclohexanone oxime were taken at different positions on the z-axis to show this phenomenon. In these plots the inlet of the reaction mixture is at z = 18 cm, whereas the outlet is at z = 0. The temperature profile of the reaction mixture does not show a major temperature increase (within 1 K). The two dimensional model does not show a major change in concentration profile compared to the results of the pseudo two dimensional model. Both the models show that the reaction is not completed within the 0.2 m length of the microchannel. With the current design of the mixer, the channel would have to be about 5.5 m long, instead of the current length of 0.2 m,

in order for the reaction to be completed within the channel, for the objected inlet velocity of 0.1 m/s. As the results obtained with the two dimensional model are very similar to the results obtained with the pseudo two dimensional model, it can be concluded that there is negligible axial conduction and diffusion and negligible radial convection in the microchannel. As can be concluded, with respect to the M-ratio in the microchannel (Figure 3.10), the small side inlet for cyclohexanone oxime is not satisfying, since the M-ratio decreases to values below one at a certain position, causing the viscosity to increase rapidly at this point. The M-ratio decreases along the channel, since the concentration of ε-caprolactam is increasing along the channel. As is expected, the M-ratio is lowest at the interface between the cyclohexanone oxime stream (low viscous liquid) and the oleum/ε-caprolactam mixture, because of the reaction of cyclohexanone oxime into ε-caprolactam.
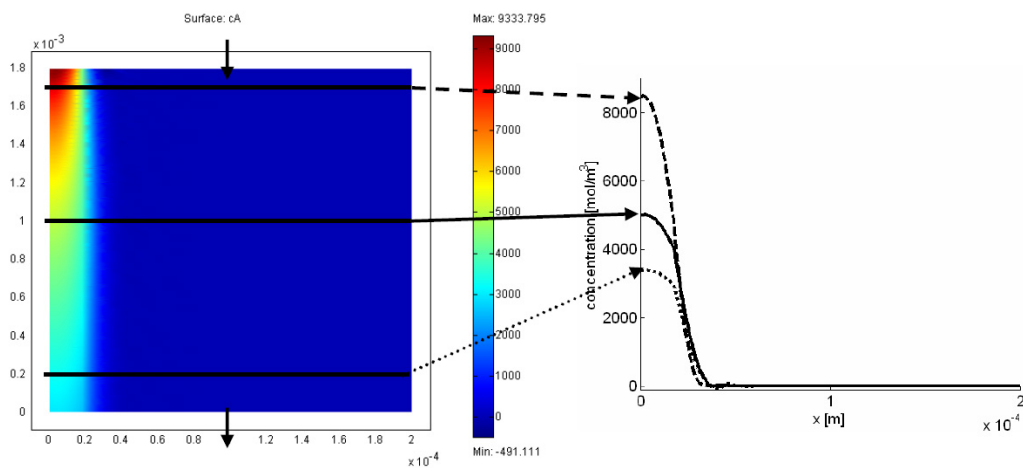
Figure 3.9: Surface plot for the concentration of cyclohexanone oxime in the microchannel (starting from the inlet of the cyclohexanone oxime) for an inlet velocity of 0.01 m/s. Scaling factor (S) is 100. Cross-sections are taken at z = 2 cm (dotted line), 10 cm (solid line) and 17 cm (dashed line). The inlet of the reaction mixture is at z = 18 cm and the outlet at z = 0. Red indicates the maximum concentration of cyclohexanone oxime (8500 mol/m^3) and blue a concentration of 0.

3.4.1.4   Liquid-liquid layer model (model 4)

To satisfy the two design criteria for the mixer, for a uniform velocity of 0.1 m/s, the maximum layer thickness of the cyclohexanone oxime stream is in the order of 2 to
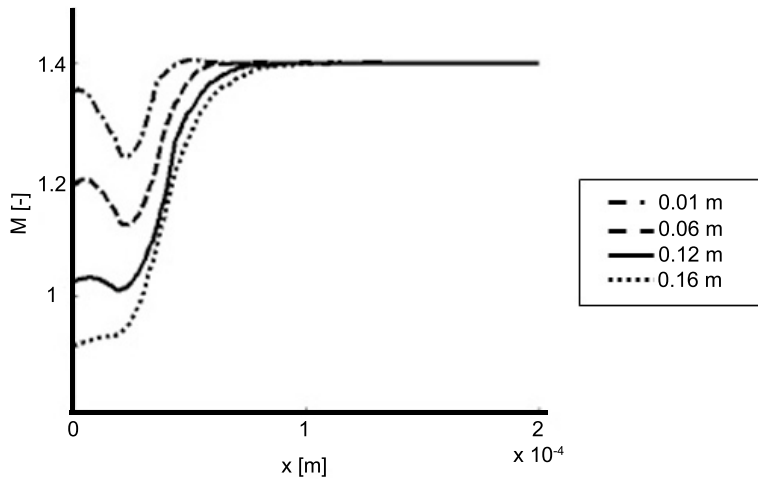
Figure 3.10: M-ratio along the width of the microchannel for an inlet velocity of 0.01 m/s at different points on the z-axis: 0.01 m (dash-dotted line), 0.06 m (dashed line), 0.12 m (solid line), 0.16 m (dotted line).

5 μm. For this layer thickness the reaction will be completed within a microchannel length of about 50 cm (Figure 3.12), which corresponds to a residence time of 5 seconds. Furthermore, for this layer thickness the M-ratio will not decrease below a value of one (Figure 3.11). The eventual value of the M-ratio at the end of the microchannel, integrated over the width of the channel, will be 1.19. This is the value of the M-ratio, when all cyclohexanone oxime is converted to ε-caprolactam. For a layer thickness of 2 μm the M-ratio will not decrease below this value, because of short diffusion times in this case. The M-ratio for every layer thickness is lowest in the region of the cyclohexanone oxime stream and at the interface between the highly and low viscous liquids, because of the reaction of cyclohexanone oxime to ε-caprolactam. With increasing mixing performance the maximum temperature of the reaction mixture will also increase, because the diffusion will be faster. With decreasing layer thickness, the temperature profile will resemble more and more the temperature profile of the one dimensional model (Figure 3.7), for which ideal mixing of the two liquids is assumed. The result of this model shows that layers of cyclohexanone oxime below 5 μm are small enough for fast mixing of the reactants. The most practical micromixer to achieve these small liquid layers is a split-and-recombine micromixer. This mixer is used in the next section to perform the mixing and reaction

of molten cyclohexanone oxime and oleum/ε-caprolactam mixtures.
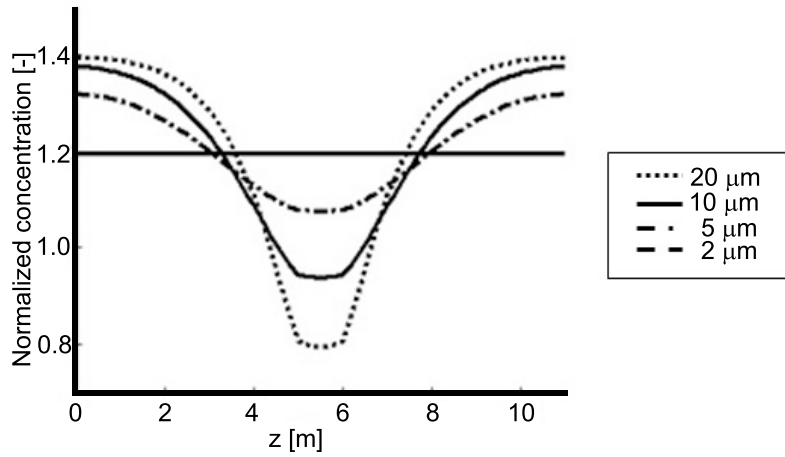
Figure 3.11: Minimum M-ratio for different layer thicknesses of the cyclohexanone oxime feed stream (d): 20 μm (dotted line), 10 μm (solid line), 5 μm (dash-dotted line) and 2 μm (dashed line). The M-ratio 1.19 line (the M-ratio after complete conversion of all cyclohexanone oxime) is indicated by a solid line as well, which completely covers the line of 2 μm, this indicates the complete mixing with layers of 2 μm. The results are obtained by model 4.
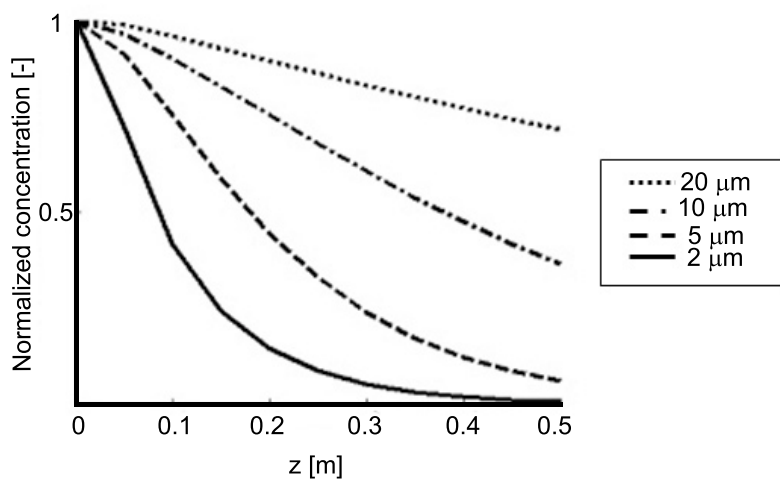
Figure 3.12: Concentration profile of cyclohexanone oxime along the microchannel for a uniform velocity of 0.1 m/s, for different diffusion path lengths: 2 μm (solid line), 5 μm (dashed line), 10 μm (dash-dotted line) and 20 μm (dotted line). The results are obtained by model 4.

3.4.2 Microreactor performance with direct injection of pure molten cyclohexanone oxime

The mathematical models illustrate that the micromixer must create liquid layers in the order of 2–5 μm or smaller, which is possible by the use of a split-and-recombine micromixer. Figure 3.13 shows the measured selectivities of the single phase Beckmann rearrangement of molten cyclohexanone oxime for M-ratios of 2.6 to 2.2 and 2.0 to 1.7 (the M-ratio changes in the microreactor by the additional formed ε-caprolactam). The flow rate of the oleum/ε-caprolactam mixture is kept constant at 0.3 ml/min and the cyclohexanone oxime flow is maintained at 0.03 ml/min (flow ratio 10:1). Figure 3.6 shows the three dimensional representation of the split-and-recombine micromixer with the small inlet channel for molten cyclohexanone oxime and the larger inlet channel for the oleum/ε-caprolactam mixture. The cross-sectional area of the inlet channels have a ratio of 10:1, which is the same as the used flow rate ratio (0.3 : 0.03 ml/min). In this way the flow of molten cyclohexanone oxime arrives at the same velocity as the oleum/ε-caprolactam mixture, which improves the stability of the mixing process. Although the conversion is not determined for this set of experiments the conversion measurements in Chapter 5 show 100% conver-

sion for temperatures of 100 °C or higher, therefore 100% conversion is assumed
for determination of the selectivity. For relatively high M-ratios of 2.6 to 2.2 the
selectivity is in the range of 99.6% – 96.7%, where higher temperatures lead to a
lower selectivity. However, by decreasing the M-ratio in the range of 2.0 to 1.7 the
selectivity decreases as well to 97.6% already at 100 °C. Furthermore, higher tem-
peratures (110 °C) for this M-ratio lead to complete blockage of the reactor. Figure
3.14 shows the micromixer and microchannel after repeated blockage by reaction
by-products at an M-ratio of 2.0 to 1.7. Afterwards the reactor is disassembled and
cleaned by ultrasonic cleaning with several solvents. The repeated blockage of the
micromixer at relatively high M-ratios shows the severeness of the Beckmann rear-
rangement with molten cyclohexanone oxime, and makes it difficult to scale up the
reaction to industrial scale, as much lower M-ratios are needed for profitable pro-
duction of ε-caprolactam. Although the split-and-recombine micromixer can create
layers that are small enough for fast diffusion, according to the mathematical mod-
els, the mixing is clearly not fast enough for this reaction. The residence time of
the reactants in the first section of the mixer should be taken into account in the de-
sign of a split-and-recombine micromixer, this residence time should apparently be
shorter. However, this would make the design of the micromixer rather complicated.
Therefore other methods to intensify the mixing between cyclohexanone oxime and
oleum/ε-caprolactam mixtures need to be considered. One of these methods is the
use of an inert solvent for cyclohexanone oxime to decrease reaction rate and con-
centration. This approach is described in the Chapters 4, 5 and 6 for the Beckmann
rearrangement with cyclooctane as additional solvent.

3.5   Concluding remarks

3.5.1   Modelling concentration and temperature profiles

The modelling work shows that a micro injection mixer approach with a single small
side inlet for cyclohexanone oxime into the microchannel is not sufficient for mix-
ing of the Beckmann rearrangement liquids (cyclohexanone oxime, oleum and ε-
caprolactam). The main consideration here is that the mass transport in the radial di-
rection in a microchannel is mainly taking place by diffusion, which is not sufficiently
fast enough for complete homogenization of the liquids in the radial direction. For
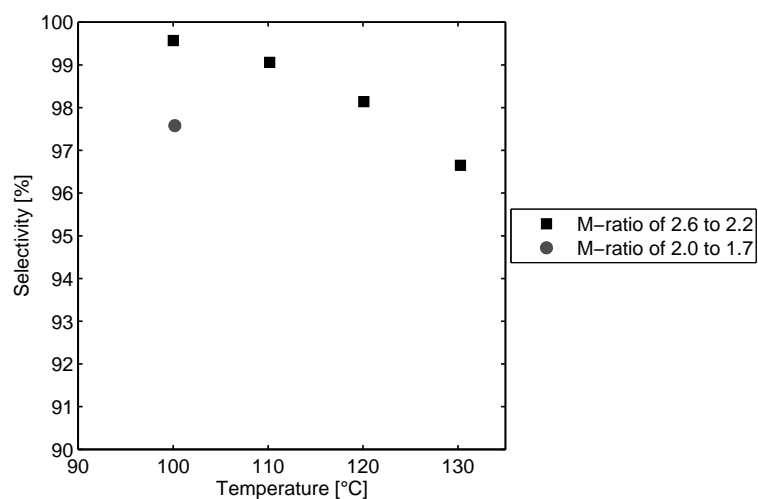
Figure 3.13: Selectivity of the Beckmann rearrangement with molten cyclohexanone oxime in the split-and-recombine micromixer for an M-ratio of 2.6 to 2.2, and 2.0 to 1.7. The error in the measured selectivity is 1%.
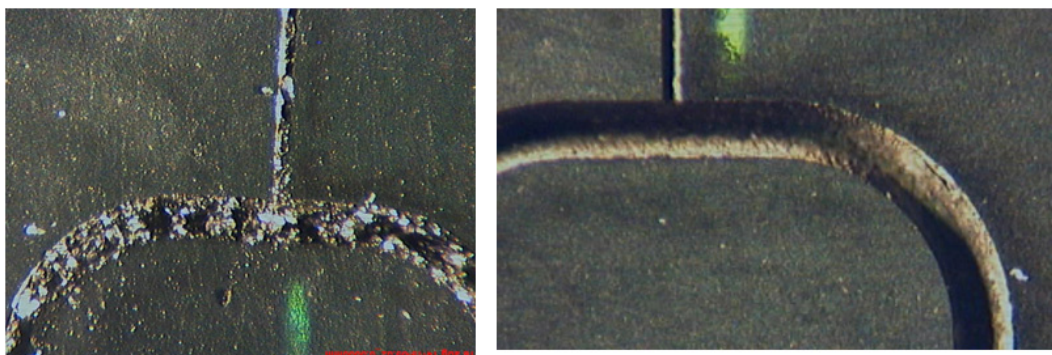
Figure 3.14: Blockage of the microreactor, which occurred repeatedly at an M-ratio of 2.0 and 110 °C. The second picture shows the channel after ultrasonic cleaning. The width of the main channel is 312 μm and the small channel width is 122 μm.

a side inlet injection mixer the microchannel needs to be about 5.4 m long in order for the reaction to be completed within the length of the channel for an inlet velocity of 0.1 m/s. For the injection mixer the M-ratio will decrease below one, which is causing the viscosity to increase rapidly locally at the interface between the liquids. The M-ratio in the microchannel is lowest in the region of the cyclohexanone oxime stream and at the interface between the high and low viscous liquid. The creation of layers of the cyclohexanone oxime stream between 2 and 5 μm is found to provide sufficient mixing of the liquids in the microchannel. For this layer thickness the reaction is completed within a length of 50 cm of the microchannel for an inlet velocity of 0.1 m/s and would still have a residence time in the range of seconds. Furthermore, the M-ratio will not decrease below one for this layer thickness, making sure the viscosity will stay within limits that are needed for the Beckmann rearrangement in a microchannel with a width of 200 μm and a length of 50 cm.

3.5.2   Reaction with molten cyclohexanone oxime

The reaction of molten cyclohexanone oxime and oleum/ε-caprolactam mixtures is possible in a split-and-recombine micromixer at relatively high M-ratio with high selectivity, without blockage of the microchannel and micromixer. However, already at M-ratios of 2.0 the split-and-recombine mixer is repeatedly blocked by viscous by-products of the Beckmann rearrangement. The decrease in channel size will make blockage even more likely, therefore, other possibilities for intensifying the mixing are needed. This makes for example the use of an inert solvent for cyclohexanone oxime necessary to reach higher selectivity and prevent blockage of the split-and-recombine micromixer. This will be shown in later chapters.

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High speed video imaging of dispersed liquid-liquid flow in Y-junction, interdigital and split-and-recombine micromixers

4

Abstract

In this chapter flow patterns, flow regime maps, liquid hold up, slug velocity and slug size are determined in three micromixers, viz. a Y–junction, an interdigital, and a split-and-recombine mixer. Nine flow pattern maps are defined for three viscosities of glycerol/water mixtures. Glycerol/water mixtures are used as the primary phase, whereas cyclooctane is used as the secondary phase. This particular liquid-liquid system is used because the viscosity and surface tension at ambient conditions are comparable with those of the liquid-liquid system of oleum/ε-caprolactam mixtures and cyclohexanone oxime in cyclooctane mixtures at reaction conditions of the Beckmann rearrangement ($\sim 100\ ^\circ$C). Comparison of the observed large differences in flow conditions in these mixers with measured selectivities in Chapter 5 shows the importance of high mass transfer and rapid mixing for the Beckmann rearrangement to ε-caprolactam. In this chapter correlations for the liquid hold up as a function of flow quality are obtained, as well as slug length and slug velocity. The liquid hold up to flow quality ratio is given by 0.49, 0.45, and 0.58, at 65 mPa·s viscosity and 0.44, 0.52, and 0.52 at 100 mPa·s viscosity of the glycerol/water mixture for the Y-type, the interdigital, and the split-and-recombine micromixers, respectively. The slug velocity was found to be twice that of the overall superficial velocity, which decreases the residence time of the cyclooctane phase considerably. The cyclooctane slug length is also observed to increase with increasing cyclooctane velocity. The interfacial area

between the glycerol/water mixture and cyclooctane using the split-and-recombine mixer with Taylor slug flow with small droplets is larger by a factor of 2-3 than for Taylor slug flow in the interdigital and the Y-type micromixers for flow velocities of both phases of 0.04 m/s. The Beckmann rearrangement of cyclohexanone oxime at reaction conditions of approximately 100 °C is completed in approximately 4 seconds, which means for a reasonable length (and pressure) of the microreactor the flow regimes drop flow, Taylor flow, Taylor slug flow with droplets, and slug flow with overlapping droplets are the most interesting regimes.

4.1 Introduction

4.1.1 Microreactor application for the bulk chemical production of ε-caprolactam

Microreactors are promising tools as internal volumes are small, which can be beneficial for handling and containment of hazardous chemicals (Hessel et al., 2005). One of the greatest benefits of microreactors is the excellent heat transfer by the small distance between the reactants and the (cooled or heated) reactor wall (and therefore the high surface area to volume ratio). Application of microreactors in bulk chemical industry is generally considered as too expensive, because economy of scale is a general accepted and universal rule in that area. However, heat transfer generally limits the chemical process design, which leads to less than optimal solutions for bulk processes. Millimeter, or micrometer scale reactors can increase the heat transfer tremendously to allow a much improved process design with respect to heat management, and therefore energy consumption, and safety. The safety aspect is especially important in case of strongly poisonous and dangerous chemicals and run-away reactions. Naturally, arranging thousands of microreactors is not a feasible process design, but certainly a number of examples exist where a reactor can be replaced profitably by microreactor module (e.g. Forschungszentrums Karlsruhe and DSM Linz, 2005). Several bulk chemical processes meet the requirements for downscaling, thereby increasing activity and selectivity, and decreasing risks. The testing of a microreactor system for one of these, viz. the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam in fuming sulphuric acid as catalyst and solvent is therefore very interesting. The product ε-caprolactam is the main intermediate in

nylon-6 production. The reaction is exothermic and fast, reaction time is in the order of seconds at a temperature of 100 °C and the industrial process is limited by the generated heat of the converted cyclohexanone oxime. Hot spots and high concentrations of the reactants can lead to run-away reactions in the process. The reaction is tested in microchannel reactors equipped with three micromixers, viz. Y-mixer, interdigital, and split-and-recombine mixer, in Chapter 5 for conversion and selectivity, with cyclooctane as inert solvent for cyclohexanone oxime. Selectivities of 99% and even more are measured in all three micromixers for certain conditions, with 100% ($\pm$ 0.3%) conversion of the cyclohexanone oxime. However, high lactam concentrations are needed for industrial application, which lead to high viscosities of the reaction mixture. For this process is found that mixing of cyclohexanone oxime and the ionic liquid of ε-caprolactam and oleum is of key importance to the conversion and selectivity of the reaction. Therefore also the shape and the size of liquid-liquid interface between the cyclooctane solvent and the ionic liquid of ε-caprolactam and oleum is of interest, as this will disclose information why a certain mixer will have better or worse performance during the reaction. Liquid-liquid mixing is investigated by a high speed camera at the downstream of the micromixers to observe flow patterns and determine flow regime maps. In this work glycerol/water mixtures are used as the primary phase, whereas cyclooctane is used as the secondary phase. This particular liquid-liquid system is used because the viscosity and surface tension at ambient conditions are comparable with the liquid-liquid system of oleum/ε-caprolactam mixtures and cyclohexanone oxime in cyclooctane mixtures at reaction conditions of the Beckmann rearrangement ($\sim$ 100 °C, M-ratio of 1.4 the viscosity is ca. 100 mPa·s for industrial conditions). This model system mimics the physical properties, and therefore simulates the resulting flow regimes, while working at ambient condition. However, the effects on viscosity and surface tension by changing reactant concentrations are not taken into account by this model system.

This chapter will disclose information on the biphasic liquid-liquid interface changes by the three micromixers and the resulting flow regimes as a function of flow rates and viscosity. Furthermore, it will provide information on the surface area available for mass transfer in these micromixers. As the residence time of both the dispersed, as well as the continuous phase are important for the microreactor, the slug velocity, slug length, and the liquid hold up are determined.

4.1.2   Mixing and interfacial surface area

Mixing of reactants is the first step of all chemical reactions and it can influence the pathway of the reaction to a great extent. Very short diffusion path lengths can be provided by decreasing the size of fluid flow channels which ultimately enhances mass transfer (Burns and Ramshaw, 2001). In microchannels mixing is most often solely taking place by molecular diffusion (Bourne, 2003). The typical residence time of the fluid in microchannels is most often considerably lower than in macroscopic systems. Due to this shorter residence time, efficient mixing can be provided by increasing the surface area, hence, by increasing the surface available for diffusion, decreasing the striation or lamellae thickness, and increasing the concentration gradient (Tanthapanichakoon et al. (2006); Ottino et al. (1979)). The diffusivity of liquids ranges from 10^{-11} m^2/s to 10^{-8} m^2/s. Therefore, channel widths should be expected to range from 10 μm to 300 μm, as the mixing is only by diffusion within the residence time in the microchannel (generally between 1 and 10 seconds).

4.1.3   Micromixers

Micromixers are categorized into two types of mixers. Active micromixers are mixers, in which external sources of energy are required to enhance the mixing in the micromixer, whereas, in case of passive mixers no external energy source is required and mixing takes place solely based on diffusion and chaotic advection. In the present study only passive micromixers are applied, as these are more suitable from an industrial approach. Furthermore, passive mixers are sub-classified by the arrangement of the mixed phases, i.e. parallel or bi-lamination of the two inlet streams, serial lamination, injection and chaotic advection (Hessel et al. (2005); Nguyen and Wu (2005); Hessel et al. (2004)). Chaotic advection manipulates the laminar flow in microchannels by introduction of flow disturbances, as changes in flow rate by for example local blockage of the flow or changes in direction, which results into improved mixing and smaller diffusion path lengths. Passive mixers create bi-lamination and multi-lamination by arrangement of the liquid feed, where the flow is forced by the microchannels to combine in a desired arrangement. Examples of bi-lamination mixers are T-mixers and Y-mixers (Christopher and Anna (2007); Thorsen et al. (2001); Bothe et al. (2006); Garstecki et al. (2006)). Interdigital mixers work by the principle of multi-lamination, and create very thin fluid layers by splitting or bifurcating of the

inlet fluid streams into many sub-streams (Haverkamp et al. (1999); Löb et al. (2006); Hessel et al. (2003)). Serial lamination micromixers are called split-and-recombine mixers (SAR), in which the inlet streams are first joined horizontally and in the next stage vertically (Hardt et al., 2006). These mixers are commonly applied for viscous liquids. As a common similarity, all methods intensify fluid-fluid contact. In the present study one mixer of each of these sub-classes is used to investigate their effect on flow regimes and liquid-liquid interfaces downstream of the micromixer.

4.1.4 Flow regimes

Günther and Jensen (2006) have reviewed previously published work on flow patterns and flow regimes for two-phase liquid-liquid immiscible flow. They discuss the following flow patterns: isolated drops, pearls necklaces, stratified flow, and pearls in various junction designs. Taylor flow or droplet flow is first observed in larger channels (Taylor, 1960) and is an important flow regime in microchannel reactors and monoliths. Anna et al. (2003) have studied monodisperse and polydisperse drop formation in a flow focusing microchannel using oil as the continuous phase and water as the dispersed phase. They also showed the effect of flow rate and flow ratio on the size of the drops. Many liquid-liquid studies in micromixers are discussed in literature (Zhao et al. (2007); Jovanovic et al. (2010); Kashid and Agar (2007), Kashid et al. (2005); Joanicot and Ajdari (2005)). Thorsen et al. (2001) demonstrated formation of an emulsion by using an oil-water two phase immiscible system in cross-flow geometry. Belder (2005) showed segmented gas-liquid-liquid three phase flow. Christopher and Anna (2007) give a topical review on droplet formation in microfluidic geometries which utilize independently controlled flows of two immiscible liquids. They distinguish the devices for droplet formation by co–flowing streams with dripping and jetting modes, by cross–flowing streams with unconfined and confined geometries, and by flow focusing with dripping and jetting modes. These devices have different sets of model equations which describe the generated droplets as a function of fluid properties, flow rate settings and the geometry of the micro device (Christopher and Anna, 2007). Important fluid properties are the viscosities, μ_d and μ_c, the densities, ρ_d and ρ_c, and the interfacial tension σ, where the subscripts 'd' and 'c' refer to the dispersed phase liquid and the continuous phase liquid, respectively. Obviously, the volumetric flow rate settings Q_d and Q_c have a large influence on the

Table 4.1: Experimental conditions and the range of superficial glycerol/water U_{gw} and cyclooctane U_{co} velocities for which the flow patterns were recorded in the Y-junction, interdigital, and split-and-recombine micro mixers at ambient conditions. The range of flow qualities used in the experiments is also provided.

viscosity of the glycerol/water mixture (mPa·s)	U_{gw} (m/s)	U_{co} (m/s)	$\frac{U_{co}}{U_{co}+U_{gw}}$ (-)
65	0.002 - 0.15	0.002 - 0.30	0.01 - 0.99
100	0.002 - 0.15	0.002 - 0.30	0.01 - 0.99
150	0.002 - 0.15	0.002 - 0.30	0.01 - 0.99

diameter of the generated droplets. Generally these devices generate droplet sizes ($\bar{d}$), which range from $0.3 < \bar{d} < 10$, where $\bar{d} = d/d_i$ is the droplet size scaled by the inner diameter of the capillary tube. Haverkamp et al. (1999) showed the formation of a large number of small droplets (smaller compared to the main microchannel) in the interdigital micromixer at high flow rates (0.3 - 12 ml/min). Flow regimes of liquid-liquid flow in the split-and-recombine micromixer are not shown in literature to the knowledge of the author. This work must be seen as an expansion of the literature for the above mentioned specific model case, where the influence of type of mixer, flow rate and viscosity on the flow regime maps is shown and compared.

4.2 Experimental

The experimental setup is used for observation of the liquid-liquid flow downstream of one of the three micromixers. The movies of the high speed camera are used to determine what flow pattern is arising downstream of the micromixer and assign the flow setting for which the flow regime is converting to another flow regime, in this way a flow regime map is prepared. For a number of selected videos, the droplet velocities, slug length, liquid hold up, and interfacial surface area are determined. An overview of the experimental conditions is provided in Table 4.1.

4.2.1   Apparatus and equipment
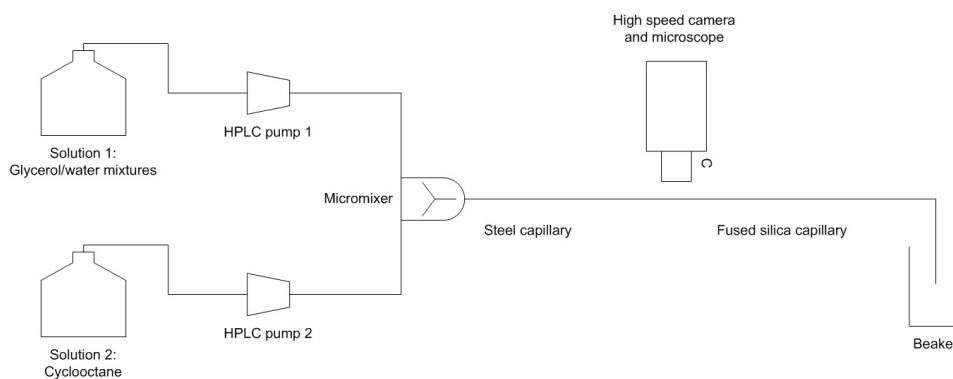
Figure 4.1: Schematic overview of the experimental setup. HPLC pumps deliver the glycerol/water solution and the cyclooctane to one of the micromixers. The micromixer is attached to a fused silica capillary, which is observed by an inverted microscope (Zeiss Axiovert 200 MAT) equipped with with a Motionpro X3 high speed camera. The micromixer in the setup can be interchanged between the Y-mixer, the interdigital mixer, and the split-and-recombine mixer.

A schematic of the experimental setup is shown in Figure 4.1. Three different micromixers, namely a Y-mixer, an interdigital mixer, and a split-and-recombine mixer are used, which are described in section 4.2.2. The liquids are delivered by two high-performance liquid chromatography pumps, a Pharmacia LKB 2150 for low viscous liquids (3 mPa·s), and a Gilson 305 for high viscous liquids (50 - 150 mPa·s). The volumetric flow rate range of the Pharmacia pump is $0.01 - 5$ ml/min (maximum pressure 200 bar). The volumetric flow rate range of the Gilson pump is $0.01 - 5$ ml/min, this pump is equipped with a high viscosity spring loaded, PTFE sealed check valves (maximum pressure 600 bar). A Zeiss Axiovert 200 M MAT D1 observer, inverted microscope and a high speed MotionPro-X3TM (Integrated Design Tools Inc., USA) CCD camera were used to observe the liquid-liquid flow inside a fused silica capillary 60 cm down flow of one of the micromixers. Two halogen light sources of 100 W were used for illumination of the capillary by transmitted and reflected light. The capillary of fused silica has an internal diameter of 320 μm. Images of the multiphase mixed flow were taken by the high speed CCD camera. The images were recorded at a resolution of 1200 x 240 pixels at a rate of 1500 frames per second (fps) for a total of 10000 frames. An exposure time of 12 - 40 μs was sufficient to eliminate blur

effects of the photographs. The length of capillary visible by the microscope and the camera is 2.27 mm. The viscosities of the glycerol/water mixture were varied from 65 mPa·s to 150 mPa·s, according to the Handbook of Chemistry and Physics (LIDE, 1999), and verified by viscometry. These viscosities are comparable to the viscosity of a mixture of ε-caprolactam and oleum, which is mentioned in the introduction. The cyclooctane flow (3 mPa·s) was varied from 0.01 ml/min to 1.5 ml/min whereas for the high viscous liquid the flow rate ranged from 0.01 to 0.7 ml/min. From a large number of combinations (125) of these two flow settings, the resulting flow patterns were recorded and analyzed, and classified in a flow regime map. In this way a flow pattern could be assigned to a regime of flow settings for which the pattern appeared. This results in a flow regime map, which is shown in the result section 4.3. All the experiments for the glycerol-water-cyclooctane system with different viscosities were carried out at room temperature.

4.2.2   Micromixers
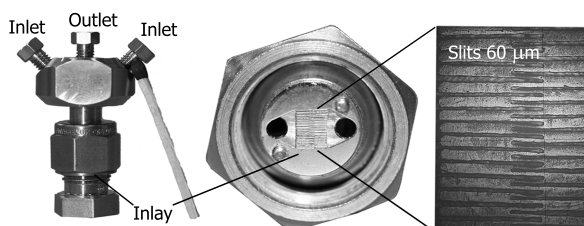
Figure 4.2: The interdigital micromixer (IMM) (left) with Valco® connectors. A Swagelok® nut with an inserted micro interdigital element (middle). Detail of the micro interdigital inlay of the mixer (right). The slits have a width of 60 μm.

Y–mixer. The 316 stainless steel Y-junction element has a 90° angle between the inlet channels and the channels have a diameter of 250 μm (Valco®).

Interdigital mixer. The interdigital micromixer (see Figure 4.2) is frequently described in literature (Hessel et al., 2003, Löb et al., 2006) and is commercially available (fabricated by the Institut für Mikrotechnik Mainz GmbH).

Split-and-recombine mixer. The third micromixer is a 316 stainless steel split-and-recombine mixer (Figure 4.3). The design is adapted from the glass split-and-recombine mixer of Micronit® (Enschede, the Netherlands). Inlet 1 has a smaller hydraulic diameter compared to the main channel to increase the velocity of the dis-
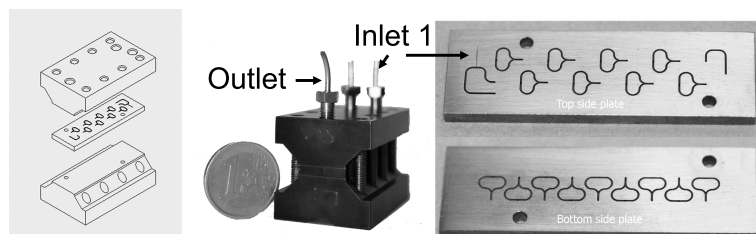
Figure 4.3: The split-and-recombine micromixer with a protective coating of diamond-like-carbon (DIARC®). The left picture shows a schematic view of the microstructured plate, clammed by a bottom and top cover. The middle picture shows the assembled mixer. The right picture shows the top and bottom sides of the lasered microstructured 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.
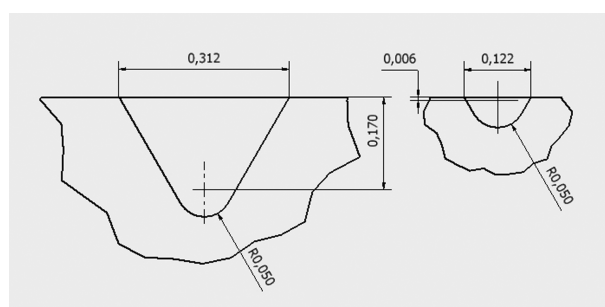
Figure 4.4: Cross section of the large main microchannel and the small side inlet in the split-and-recombine mixer. The dimensions are in mm. The cross section of the large channel has the same cross sectional surface area as a round channel with a diameter of 250 μm, the small channel has a cross sectional surface area of 10% that of the large channel.

persed 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 (see Figure 4.4). The small channel has a parabolic shape with 1/10th of the cross sectional surface area of the main channel. The liquids are combined in the T–section where the cyclooctane is fed by the smaller channel (inlet 1). The mixer is coated with a 1 μm Diarc® diamond-like-carbon layer to prevent corrosion by the fuming sulphuric acid needed for the

Beckmann rearrangement to ε-caprolactam (not presented here).
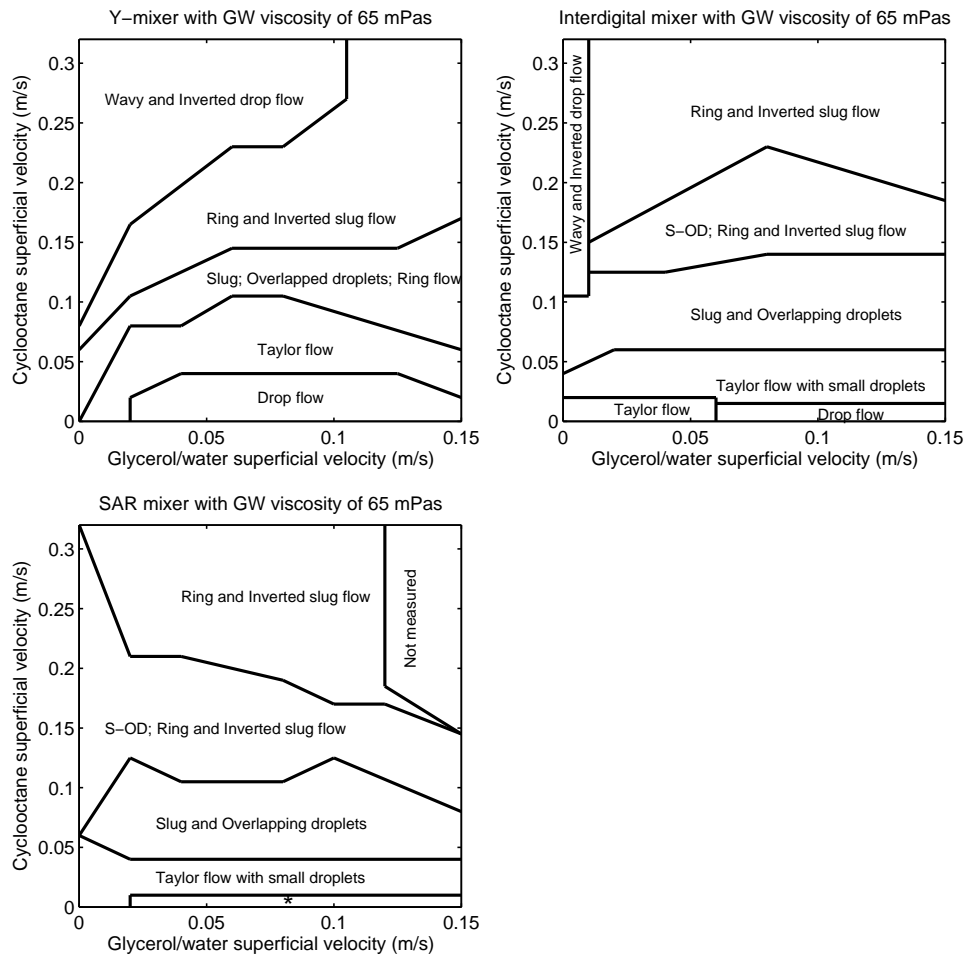
Figure 4.5: The figures show the flow regime maps of the Y-micromixer, the interdigital micromixer, and the split-and-recombine micromixer (SAR). The x-axes show the superficial velocity of the glycerol/water mixtures and the y-axes show the superficial velocity of cyclooctane. The viscosity of the glycerol/water mixtures was 65 mPa·s. For clarity the flow regime slugs and overlapping droplets is abbreviated as S-OD and glycerol/water as GW in the figures. The * indicates drop flow in the flow map of the split-and-recombine mixer.
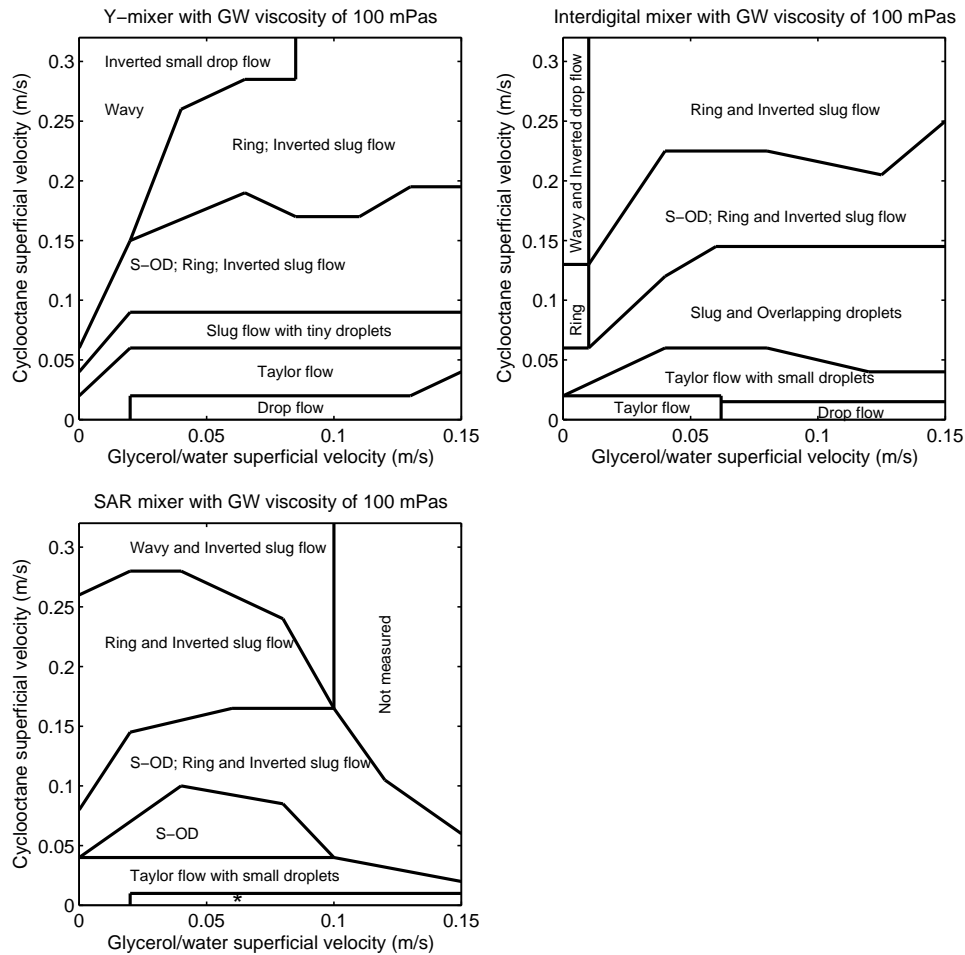
Figure 4.6: The figures show the flow regime maps of the Y-micromixer, the inter-digital micromixer, and the split-and-recombine micromixer (SAR). The x-axes show the superficial velocity of the glycerol/water mixtures and the y-axes show the superficial velocity of cyclooctane. The viscosity of the glycerol/water mixtures was 100 mPa·s. For clarity the flow regime slugs and overlapping droplets is abbreviated as S-OD and glycerol/water as GW in the figures. The * indicates drop flow in the flow map of the split-and-recombine mixer.
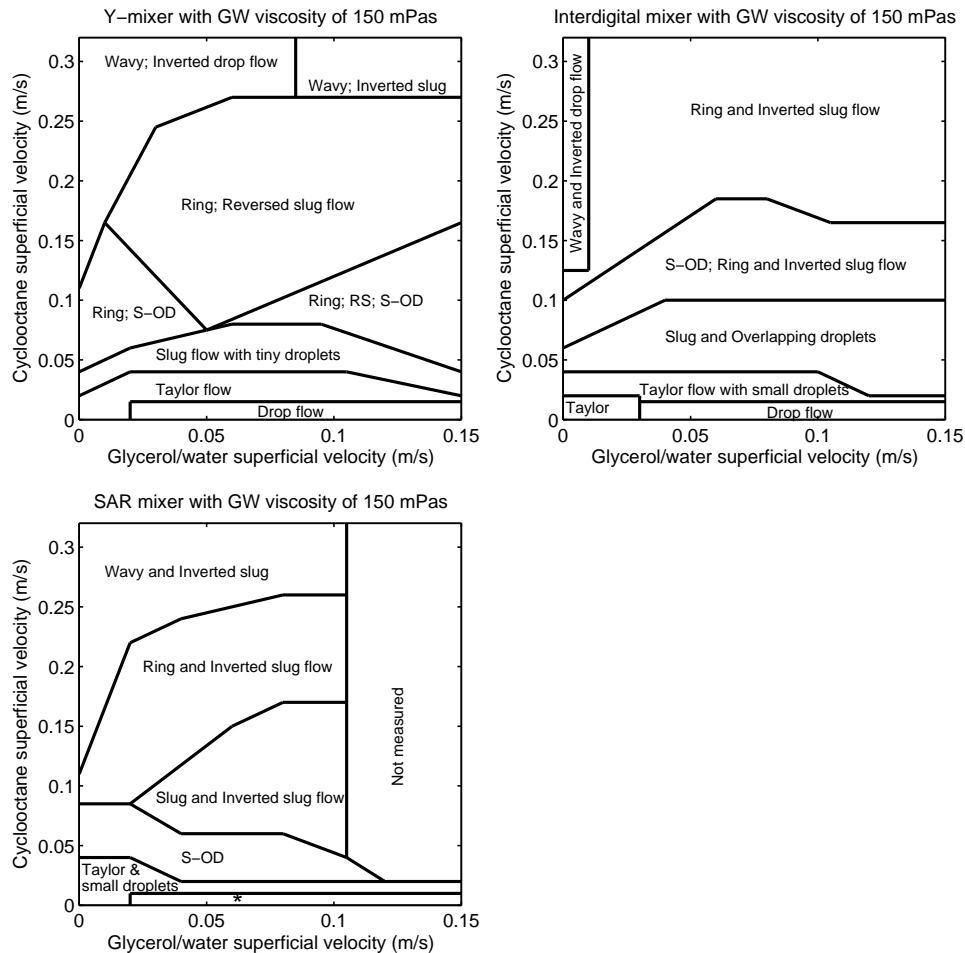
Figure 4.7: The figures show the flow regime maps of the Y-micromixer, the inter-digital micromixer, and the split-and-recombine micromixer (SAR). The x-axes show the superficial velocity of the glycerol/water mixtures and the y-axes show the superficial velocity of cyclooctane. The viscosity of the glycerol/water mixtures was 150 mPa·s. For clarity the flow regime slugs and overlapping droplets is abbreviated as S-OD and glycerol/water as GW in the figures. The * indicates drop flow in the flow map of the split-and-recombine mixer.
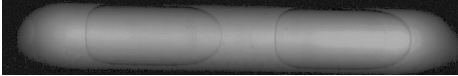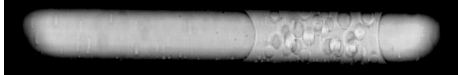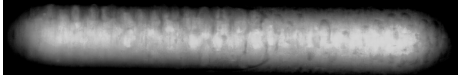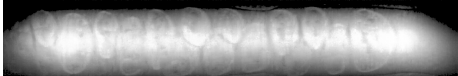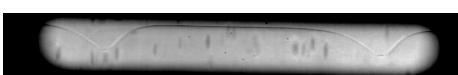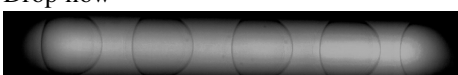
4.3   Results and discussion

4.3.1   Flow regime maps

Figures 4.5, 4.6 and 4.7 show the nine flow regime maps for the three micromixers at various velocities of cyclooctane and three glycerol/water mixtures. The viscosities of the glycerol/water mixtures are 65 mPa·s, 100 mPa·s and 150 mPa·s. The range of Reynolds numbers for the glycerol/water mixture is 0 to a maximum of 2, and for the cyclooctane phase 0 to a maximum of 135, which is based on the total maximum superficial velocity in the channel. A total of 7 flow patterns, such as Taylor slug flow, Taylor slug with uniform small droplets in the continuous phase, slug flow of a deformed hemispherical cap with overlapping droplets in the continuous phase, inverted slug flow, ring flow, wavy flow, and drop flow are observed. The x-axis and y-axis show the superficial velocities of the glycerol/water mixture and the superficial velocities of the cyclooctane phase in m/s, respectively. Tabel 4.2 provides a reference to the seven observed flow patterns in these micromixers. The next section shows a general description of the flow patterns. A cumbersome elaboration on the details is not preferred, and a more general view on the flow regime maps shows that smaller droplets are generated when the liquids provide higher shear forces (higher pressure or viscosity). Smaller droplets can also be achieved mechanically by the action of the interdigital and especially the split-and-recombine mixer, even at low velocities (5 cm/s). The split-and-recombine mixer is therefore preferred for fast reactions occurring within seconds.

Drop flow, Taylor flow and Taylor flow with small droplets are the predominant flow patterns that are observed in the three mixers at low velocities (typically at total superficial velocities < 0.15 m/s). These flow patterns are of main concern as normally the time needed for a chemical reaction to occur within the microchannel is in the order of several seconds to minutes. Therefore these flow patterns will receive more attention compared to the other flow patterns. Almost all flow patterns are observed in all three mixers, only the superficial velocities at which these flow patterns are occurring is different for each mixer and set of liquids. The only flow pattern which is not observed in all mixers is Taylor flow. In the split-and-recombine mixer only Taylor flow with droplets is observed, as can be expected from the split-and-recombine action of the mixer. The Y-mixer does not show Taylor flow with

Table 4.2: Observed flow patterns and their characteristic features. The channel diameter is 320 μm.

nr	Flow pattern	*Characteristics of the flow pattern*
	Representative picture of the flow pattern	

1   Taylor slug flow

Dispersed droplets larger than the diameter of the channel

2   Taylor slug flow with uniform small droplets

Droplets larger than the diameter of the channel accompanied by droplets smaller than the channel diameter

3   Slug with overlapping droplets

Slug boundaries are broken and slugs are including the continuous phase

4   Inverted slug flow

Large droplets of glycerol/water with small cyclooctane are formed inside larger cyclooctane droplets

5   Ring flow

A glycerol/water flow on the channel wall with a cyclooctane core

6   Wavy flow

The glycerol/water flow on the channel wall travels in waves surrounding the cyclooctane core

7   Drop flow

Drops of cyclooctane with a diameter smaller than the channel diameter

300 μm

small droplets for a viscosity of 65 mPa·s of the glycerol/water mixture. As the viscosity rises, the shear forces rise as well, therefore smaller droplets are more easily formed. The flow regime maps in Figures 4.5, 4.6 and 4.7 show that the flow patterns with smaller droplets are occurring at lower superficial velocities for higher viscosities (e.g. for the Y-mixer from 0.20, 0.15 to 0.14 m/s for 65, 100 to 150 mPa·s, respectively). Taylor slugs of cyclooctane and uniform droplets of cyclooctane in the continuous phase of the glycerol/water mixture are observed for the split-and-recombine, the interdigital, and also at high viscosity in the Y-mixer. Generally for all mixers higher viscosity increases the shear forces, which ultimately results into small droplets and droplets. The glycerol/water phase has a high viscosity, and therefore is more dominated by shear forces, whereas the cyclooctane phase is more dominated by capillary forces. Taylor flow is well known for its well defined flow pattern and surface area and also for the high mass transfer rates achievable by the presence of the film surrounding the Taylor slug and recirculation within the slug (Jovanovic et al., 2010). However, this flow pattern at high viscosity is less useful for mass transfer because recirculation in the droplets and slugs is decreased at Ca numbers higher than 0.5; this is shown to drastically lower the selectivity for the Beckmann rearrangement (Chapter 5.)

The remaining four flow patterns, slug flow with overlapping droplets in the continuous phase, inverted slug flow, ring flow, and wavy flow, all share a high velocity of the (dispersed) cyclooctane phase. In these flow patterns the slug boundaries are broken and the dispersed phase makes an intensive contact with the continuous phase, glycerol/water mixture. As the superficial velocity is high, the residence time in the microchannel is generally too short for reactions to reach full conversion, and therefore these flow patterns are considered less relevant for reaction purposes, and are not extensively considered in this thesis. Of course, one single mixer can be used to feed multiple microchannels to increase the residence time, but this is not covered in this thesis.

4.3.2   The formation of double emulsions or inverted slugs

Although the superficial velocities of glycerol/water and cyclooctane are high (generally between 0.1 - 0.25 m/s) the formation of small droplets inside other droplets, or double emulsions provide very intensive interfacial contact; this is beneficial for

intermixing of the two phases. Droplets of glycerol/water with small cyclooctane droplets are formed inside cyclooctane slugs during inverted slug flow. An inverted slug flow pattern is observed at relatively high flow velocity of the glycerol/water mixture and at high cyclooctane velocity. At high velocity of cyclooctane the inertial forces are high which push the whole mixture of glycerol-water-cyclooctane inside the slug of cyclooctane, whereas at high flow rate of the glycerol/water mixture more droplets are generated due to higher shear forces. These droplets penetrate with high velocity into the boundary of cycloctane. This can be observed in Figures 4.8 a-e, where images are shown at an interval of less than 1 ms to see the details of this inverted slug formation. This double emulsion formation has also been observed by Olbricht and Kung (1992) for various viscosity ratios, where they observe the penetration of a thread of outer phase fluid along the axis of the drop, the outer fluid penetrates the indentation of trailing edge of the drop. This indentation grows and entrains the outer phase liquid inside of the boundaries of slug. These phenomena at higher velocities are beneficial with respect to higher interfacial mass transfer area, however, as mentioned earlier, residence time is low and these flow velocities can only be used to generate emulsions and act as a pre-mixer for multiple microchannels, which however is not investigated in this work.

4.4   Flow regime analysis

4.4.1   Slug velocity for the Taylor flow regime

The flow regimes at relatively low superficial velocities of 0.04 - 0.1 m/s are of interest for the Beckmann rearrangement reaction, as the length of the microreactor does not exceed 1 m and the pressure drop remains within a few bar for complete conversion. Therefore more information is needed on the individual phases and their residence times, as this will determine mass transfer in the microreactor channel. The slug velocity of cyclooctane is in most cases unequal to the superficial velocities of cyclooctane and glycerol/water, $U_{co} = Q_{co}/A$ and $U_{gw} = Q_{gw}/A$, respectively. Here Q_{co} and Q_{gw} are the flow rates of cyclooctane and glycerol/water, respectively, and A is the cross sectional area of the microchannel. The total superficial velocity is defined as $U_{tot} = (Q_{co} + Q_{gw})/A$. However, residence time and liquid hold up are determined by the actual slug velocities. Therefore, slug velocities are measured

(a) Necking of droplet; t=0 ms

(b) Necking of droplet; t= 0.7 ms

(c) Necking of droplet; t= 1.4 ms

(d) Throat development; t=2.1 ms

(e) Detachment of inverted slug; t=2.8 ms

300 μm
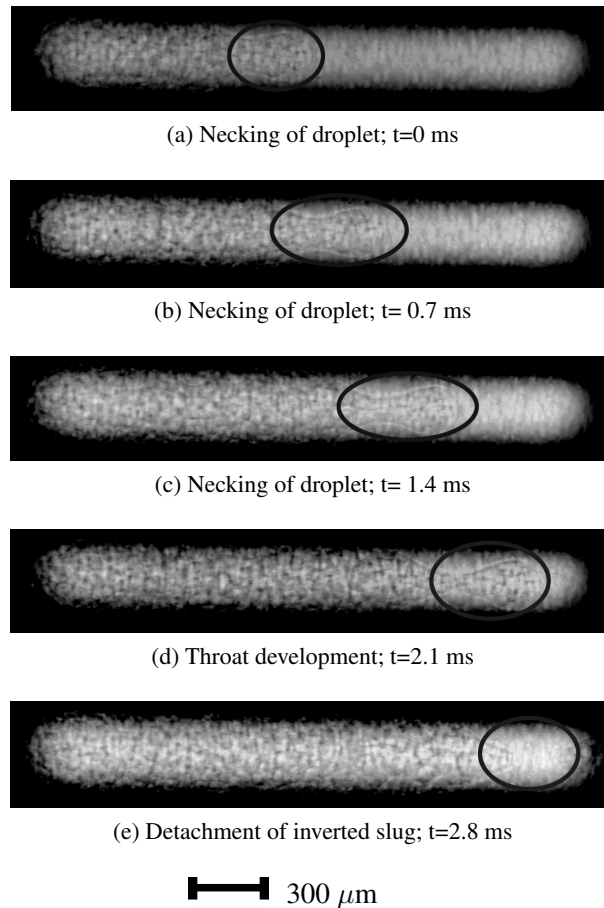
Figure 4.8: Inverted slug flow formation using the split-and-recombine micromixer, with superficial velocities of 0.06 and 0.17 m/s for the glycerol/water mixture (66 mPa·s) and cyclooctane, respectively. The black bar is 300 μm.

by tracking individual slugs of the cyclooctane phase. The flow rate of the glycerol/water mixture is constant (corresponding to a superficial velocity of 0.04 m/s) and the cyclooctane flow rate is varied. Slug velocities are not varying significantly for the same flow rate of cyclooctane for all three mixers. The relation between slug velocity and overall superficial velocity is shown in Figure 4.9. The observed slug velocities are about twice as large as the overall superficial velocities for all three mixers and viscosities mentioned in Table 4.1. For continuity reasons the continuous phase velocity is smaller than the overall superficial velocity, because the continuous phase is in contact with the wall. The Hagen-Poiseuille equation for a circular
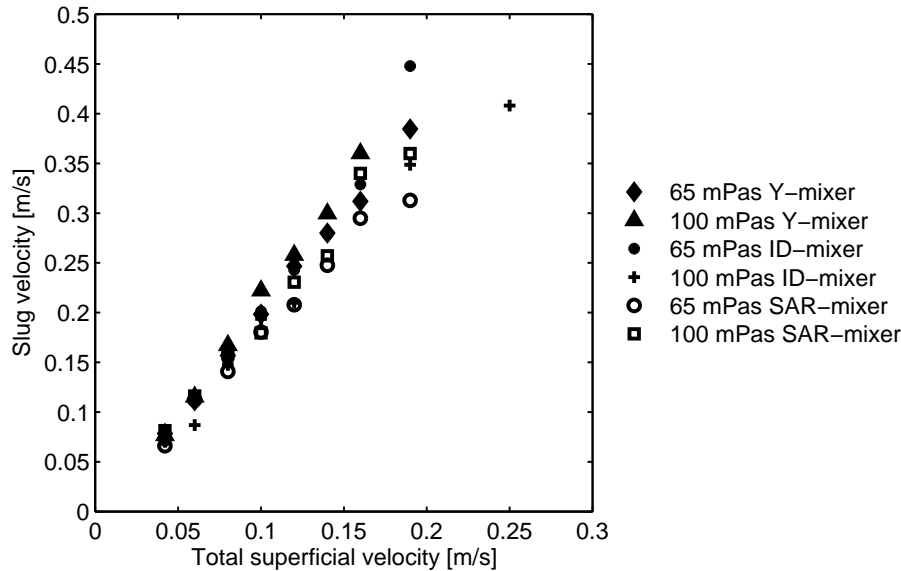
Figure 4.9: Cyclooctane slug velocities are shown as a function of total superficial velocity (U_{tot}) for the Y-mixer, interdigital (ID) mixer, and the split-and-recombine (SAR) mixer for viscosities of 65 and 100 mPa·s.

conduit shows that the maximum velocity is twice the average velocity (Welty et al., 1984), which corresponds to the measured velocities of the slugs. This shows that the cyclooctane slugs are traveling in the inner core of the channel, with distinct residence time, in contrast to the continuous phase glycerol/water, which must have a much broader residence time distribution.

4.4.2   Slug length

Cyclooctane slug length is shown as a function of cyclooctane superficial velocity in Figure 4.10 at a constant superficial velocity of glycerol/water of 0.04 m/s. From the observation it follows that increasing the superficial velocity of cyclooctane increases the slug length to several times the channel diameter. Slugs with a length in the order of 300 μm are observed at a velocity below 0.04 m/s, so $U_{co}/U_{gw} < 1$. Increasing the cyclooctane superficial velocity by a factor three can increase the slug length with a factor 70–180. This shows the importance of the superficial velocity ratio or equivalently the volumetric flow rate ratio, as slug lengths of a factor 180 of
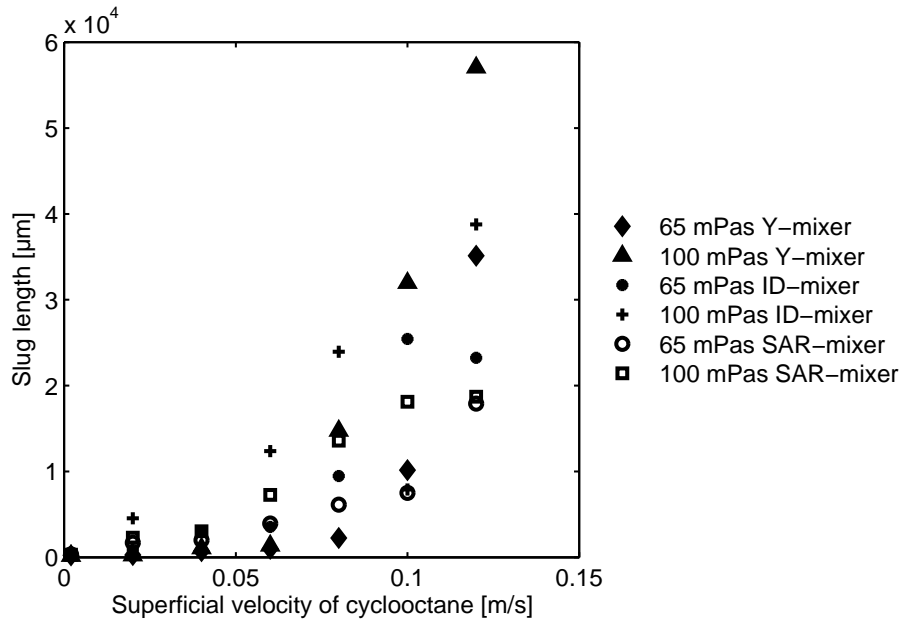
Figure 4.10: Slug lengths (μm) are shown as a function of the superficial velocity of cyclooctane for the Y-mixer, interdigital (ID) mixer, and the split-and-recombine (SAR) mixer for viscosities of 65 and 100 mPa·s. The superficial velocity of glycerol/water was constant at 0.04 m/s.

the channel diameter will decrease two-phase liquid-liquid contact and mass transfer tremendously.

4.4.3   Liquid hold up of Taylor and drop flow

By the liquid hold up and flow rates the average residence times of the two phases in the microchannel can be determined, which is an important design criterion. By definition the liquid hold up ε_a of liquid a is given by:

$$\varepsilon_a = \frac{V_a}{V_a + V_b} \tag{4.1}$$

where V_a and V_b are the volumes occupied by liquids a en b, respectively. This can be rewritten into:

$$\varepsilon_a = \frac{U_a}{u_a} \tag{4.2}$$
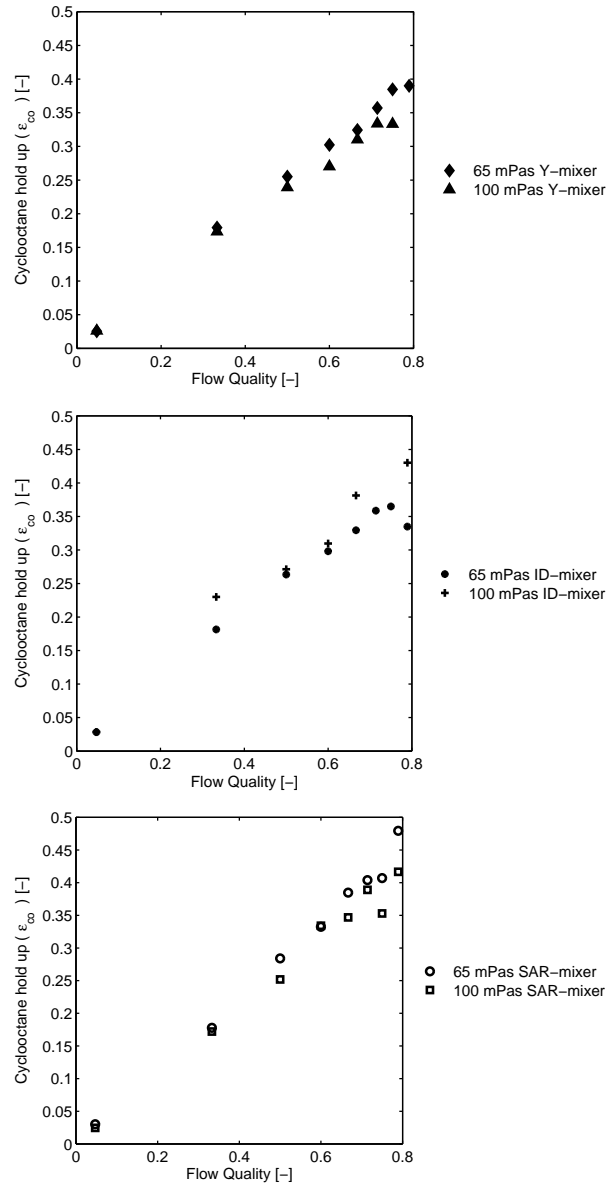
Figure 4.11: Hold ups of the cyclooctane phase (ε_{co}) are shown as a function of the Flow Quality for the Y-mixer, interdigital (ID) mixer, and the split-and-recombine (SAR) mixer for viscosities of 65 and 100 mPa·s. The superficial velocity of glycerol/water was constant at 0.04 m/s. The Flow Quality is defined as $FQ = \frac{U_{co}}{U_{gw}+U_{co}}$.

where U_a is the superficial velocity, which is based on the channel cross-sectional area and u_a is the local velocity of liquid a. This local velocity can be easily determined by video analysis of the droplets, no shape assumptions are required (Warnier et al., 2008). For gas-liquid two-phase flow systems the dependency of the gas hold up on the flow quality, $FQ = \frac{U_g}{U_g + U_l}$, in a unit cell consisting of a gas bubble and a liquid slug is given by Armand and Treschev (Armand and Treschev, 1946):

$$\varepsilon_g = 0.833 \frac{U_g}{U_g + U_l} \qquad (4.3)$$

where U_g and U_l are the gas and liquid superficial velocities, respectively. Warnier et al. (2008) interpreted the constant parameter of 0.833 as the ratio of the bubble cross sectional area over the cross sectional area of the channel. In their work they obtained 0.82 and 0.84 for two different mixers, a cross mixer and a smooth mixer, respectively, for a nitrogen-water system. In liquid-liquid Taylor and drop flow, the hold up (ε) is a function of the flow quality, $FQ = \frac{U_{co}}{U_{gw} + U_{co}}$, as well (where gw and co stand for glycerol/water and cyclooctane, respectively) and can be written by a equation as $\varepsilon_{co} = b * FQ$, here b is a constant like the Armand constant. Figure 4.11 shows hold ups of the cyclooctane phase (ε_{co}) as a function of the flow quality for the Y-mixer, interdigital (ID) mixer, and the split-and-recombine (SAR) mixer for viscosities of 65 and 100 mPa·s and constant superficial velocity of glycerol/water (U_{gw}) of 0.04 m/s. Using the method of least squares for determining the b parameter for the data in Figure 4.11 results in 0.49, 0.45, and 0.58 for the Y-type, the interdigital, and the split-and-recombine mixer, respectively, for a viscosity of 65 mPa·s of the glycerol/water mixture. Similarly, constant values of 0.44, 0.52 and 0.52 are determined for the 100 mPa·s glycerol/water mixture. For a known diameter of the channel, using the model of Warnier et al. (2008), it is possible to calculate the liquid film thickness between the bubble and the channel wall. This calculated thickness is between 40 and 50 μm for a constant glycerol/water velocity of 0.04 m/s. The liquid-liquid interfacial tension is not so large as compared to the work of Warnier et al. (2008), therefore a larger thickness of the film between the bubble and the channel wall is expected. However, by the refraction and deformation of the image by the round channel this liquid film can not be experimentally determined for verification of the model estimate.

The deviation from a straight line model in Figure 4.11 indicates the transition of

Table 4.3: Interfacial areas (m^2/m^3) between the glycerol/water and the cyclooctane phase of the Y-micromixer, Interdigital (ID) micromixer, and the split-and-recombine (SAR) micromixer. The glycerol/water superficial velocity was maintained at 0.04 m/s. The deviation of the method is within 100 m^2/m^3

U_{co}	Viscosity	Y-micromixer	ID mi-cromixer	SAR micromixer
(m/s)	(mPa·s)	(m^2/m^3)	(m^2/m^3)	(m^2/m^3)
0.02	65	6900	7400	16600
0.04	65	7800	9400	20500
0.02	100	6200	6700	12900
0.04	100	5600	6600	14000
Flow regime:		Drop flow	Taylor flow	Taylor flow with small droplets

flow regimes; the transition from Taylor slugs to Taylor slugs with droplets and slugs with overlapping droplets occurs at a flow quality higher than 0.7. The larger deviation of a straight line for the measurements at higher viscosity manifests that more droplets are generated in the continuous phase at a viscosity of 100 mPa·s compared to the 65 mPa·s. Therefore, cyclooctane hold up increases significantly in the continuous phase. However, as far as mixer performance is considered, it is observed from Figure 4.11 that the Y-mixer shows a straight line even at high flow quality values, which confirms that it leads to Taylor slug flow for a larger range of superficial velocities of both cyclooctane and glycerol/water mixture unlike the split-and-recombine and the interdigital mixers. The cyclooctane hold up is higher for the interdigital and the split-and-recombine mixer for flow regimes with small droplets in the continuous phase than the hold-up of the Y-mixer. These mixers effectively increase hold up, which is beneficial for intense phase contact.

4.4.4 Interfacial area between the dispersed and continuous phases

The interfacial area between the dispersed phase and the continuous phase is very important when the dispersed phase is carrying one of the reactants and the continuous phase is carrying the second (or third etc) reactant. Conversion of the main reactant is

only possible by transport through the interface between the two phases. In case of the Beckmann rearrangement only cyclohexanone oxime can be transported though the interface, as fuming sulphuric acid can not dissolve into cyclooctane. Reaction can only take place in the ε-caprolactam/oleum phase, which is mimicked by the glycerol/water phase in this chapter. Generally, the larger the interfacial area between the dispersed and continuous phases the faster the mass transport that can occur. Therefore the mixer must create an interfacial surface area as large as possible. Video imaging data is used to determine the interfacial area between the dispersed and continuous phases for the three mixers. Table 4.3 shows the interfacial area between the glycerol/water phase (U_{gw} of 0.04 m/s) and the cyclooctane phase (U_{co} of 0.02 and 0.04 m/s). These conditions correspond to the Taylor, and the Taylor flow with small droplets regimes. These superficial velocities of the dispersed and continuous phase are also used for the Beckmann rearrangement in Chapter 5 and provide insight into the question why the Y-mixer and interdigital mixer are outperformed by the split-and-recombine mixer. The Taylor flow with droplets flow pattern is observed at a low velocity range in the case of the split-and-recombine mixer, whereas the interdigital and Y-type mixers only are able to generate a small number of small droplets with Taylor flow. The surface area-to-volume ratio of the split-and-recombine mixer is higher by a factor of 2-3 compared to the other mixers even at low velocity and reaches values of 20.000 m^2/m^3, which is considered large.

4.4.5   Interfacial surface area, mass transport and the Beckmann rearrangement

Only a part of the mass transport is determined by the interfacial surface area. Therefore in this section the interfacial areas, which are measured for the glycerol/water mixtures are used to estimate the order of magnitude of the mass transfer, during the Beckmann rearrangement in the micromixers and microchannels used in this work. The conversion measurements of cyclohexanone oxime show the complete conversion to ε-caprolactam in Chapter 5; therefore we know the total mass transfer flux across the interface between the two phases, which together with the interfacial surface area provides an estimation of k. The mass transport across the two phase inter-

phase per reactor volume is determined by:

$$F = k * a * \Delta C \qquad \qquad (\text{mol/m}^3 s) \qquad \qquad (4.4)$$

where k is mass transfer coefficient in m/s, a is the specific surface area in m^2/m^3 between the two phases and ΔC is the concentration difference between the two phases. The mass transfer coefficient k is mainly determined by the effective diffusion coefficient, and therefore also by the viscosity. As ε-caprolactam/oleum solutions have the highest viscosity, the resistance to mass transfer is mainly located in this phase. For an example calculation a 10 wt% solution of cyclohexanone oxime in a ε-caprolactam/oleum mixture of 50 mPa·s shows complete conversion and therefore shows that an estimation of mass transfer coefficient k (during reaction) is in the order of 4×10^{-5} m/s, which is a factor 400 times the case of single diffusion over the channel diameter. This shows the increase in mass transfer which is possible by dispersed liquid-liquid flows.

4.5   Concluding remarks

The work presented in this chapter shows flow regime maps as a function of the velocities of the continuous and dispersed liquid phases. The results show a total of nine flow regime maps with flow patterns as Taylor slug, drop, Taylor slug with droplets, slug with overlapping droplets, ring and inverted slug, wavy and inverted drop and wavy with inverted drops.

- Larger interfacial surface area is created by mechanical means of the mixer design, where the split-and-recombine mixer results in the most intense liquid-liquid contact (20.000 m^2/m^3), larger shear forces (higher velocities and viscosities) increase the interfacial surface area as well.

- Correlations of liquid hold up with flow quality and slug velocity with overall superficial velocity of the liquids are obtained and shows the volume fraction of the continuous and dispersed phase as a function of the overall flow conditions.

- The liquid hold up over flow quality relation shows that the interdigital and split-and-recombine mixer do not have a linear behavior at higher flow qualities, indicating the Taylor flow with droplets regime.

- The slug velocity is found to be twice as large as the overall superficial velocity, therefore the residence time of the dispersed phase is considerably shorter compared to the continuous phase.

- The cyclooctane slug length increases with increasing cyclooctane velocity. The slug length increases extremely if $U_{co}/U_{gw} > 1$; ratios larger than 1 will decrease the interfacial area drastically, which can cause major problems when performing a liquid-liquid reaction in this regime.

- The interfacial area between the glycerol/water mixture and cyclooctane in case of the split-and-recombine mixer is in the order of 20.000 m^2/m^3 and larger by a factor of 2-3 compared to Taylor slug flow in the interdigital and the Y-type micromixers for the same velocity conditions. Taylor slugs with uniform droplets in the continuous phase give a high interfacial area at low velocity (0.08 m/s) in split-and-recombine mixer. This shows that the split-and-recombine mixer gives better mixing efficiency at a low velocity range.

- The split-and-recombine mixer creates more interfacial surface area compared to the Y-type mixer and interdigital mixer at the same velocity range, which explains the higher selectivities that are obtained by this mixer in Chapter 5.

- The mass transfer coefficient in the split-and-recombine mixer during the Beckmann rearrangement is estimated in the order of 4×10^{-5} m/s. For this calculation is assumed that the interfacial surface area is in the order of 20.000 m^2/m^3.

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Selectivity of the Beckmann rearrangement in a Y-mixer, interdigital and split-and-recombine mixer with dispersed liquid-liquid flow

5

Abstract

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 ε-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 to 99+%, 93 to 99+%, and 95 to 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.

5.1   Introduction

5.1.1   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 and was 3.9×10^6 mt/year in 2008 (Editorial (2007, 2009)) and a number of production facilities are expanding their production volume (Alperowicz, 2010). 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 (Dahlhoff et al., 2001). This reaction is catalyzed by Lewis acids and is highly exothermic and extremely fast (Wichterle and Roček (1951a,b); Nguyen et al. (1997)). In industry, fuming sulphuric acid (oleum) is generally used as a catalyst (Fisher and Crescentini, 2000). 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 sulphate. The phases are purified by extraction with benzene and water. This conventional production process has a few drawbacks. Due to the fast kinetics and exothermic behaviour, the production method is limited by the heat produced during reaction. A large recycle loop ($50\times$) in comparison with the cyclohexanone oxime feed is used to limit the temperature rise and to maintain a high selectivity of 99% (Smeets et al., 2004). 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 sulphate.

5.1.2   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 5.1. The mechanism starts with the conversion of the OH group of the oxime into a leaving group. This is typically
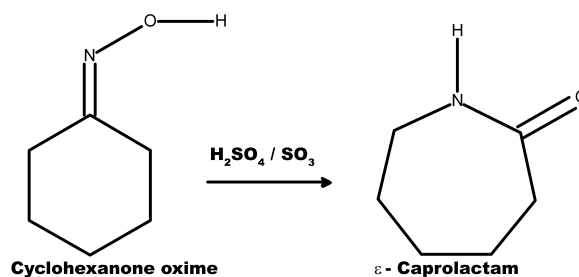
Figure 5.1: The Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam.
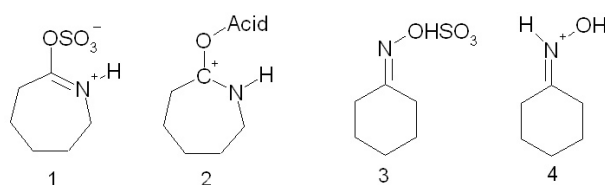
Figure 5.2: Four complexes of cyclohexanone oxime and ε-caprolactam with H_2SO_4 and SO_3 in SO_2 solution(Cavalieri-d'Oro et al., 1992): 1: $CPLSO_3$; 2: $CPLH^+$; 3: $OXSO_3$; and 4: OXH^+. ε-caprolactam is not in the free state but in the form of a complex during reaction. Cyclohexanone oxime can only be in the free state just before mixing and also forms complexes in the reaction.

accomplished by protonation with a strong acid such as sulphuric acid to give an ox-onium 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 sulphuric acid at 60 and 90 °C are described by Ogata et al. (1955). The rate was found to be first order with respect to oxime con-centration. 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 5.2). The formation of cyclohexanone oxime proceeds via a con-certed mechanism by the exerted ring strain. Cavalieri-d'Oro et al. (1992) 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 cy-clohexanone 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 5.2. Wichterle and Roček (1951a,b) 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 pyrosulphuric acid ($H_2S_2O_7$) in the Beckmann rearrangement mechanism in mixtures of ε-caprolactam, sulphuric acid and SO_3.

5.1.3   The Beckmann rearrangement in microreactors

5.1.3.1   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 (Hessel et al., 2004). 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 (1951a,b) are the only authors who published the kinetic rates of the Beckmann rearrangement in fuming sulphuric acid at SO_3 concentrations comparable to 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.

5.1.4   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 to 130 °C (see Chapter 2). The physical properties of these mixtures are mainly determined by the acid over lactam ratio (M-ratio or ($[H_2SO_4]$ + $[SO_3]$)/$[\varepsilon$-caprolactam]). 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 sulphate and HSO_4^- ions. The viscosity

of these mixtures has a large influence on the mixing performance. Bourne (2003) and Ottino (1994) 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 (Anna et al. (2003); Bothe et al. (2006); Garstecki et al. (2006)). For Reynolds numbers below 180 (Hoffmann et al. (2006); Bothe et al. (2006)) a T-mixer gives a single interface between two miscible liquids, however, this generally does not provide a high mass transfer rate as is shown in Chapter 3. 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.

5.1.4.1   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 (Horn et al., 1981) where it is used for heat removal at the boiling point. Cycloalkanes are known for their inertness towards fuming sulphuric acid, as sulphonation 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. (2004) and Taha and Cui (2004). In order to optimize mixing, the liquid slugs must be small but they still have to touch the channel walls in order 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 (Taylor, 1960). These circulations increase mass transfer in the radial direction for low capillary numbers. However, the above 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.

5.1.4.2 Goal

In this chapter selectivities towards 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 above 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. The main question is: what kind of micromixer provides the best performance and at what reactions conditions. Furthermore, will this be adequate for industrial application.

5.2 Experimental

5.2.1 Equipment

5.2.1.1 standard setup
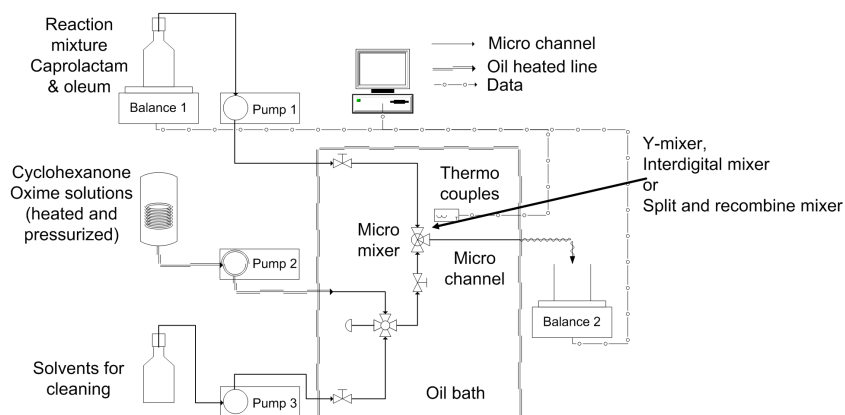
Figure 5.3: Schematic overview of the microreactor setup. The microreactor is a combination of a micromixer and a microchannel. The micromixer in the setup can be interchanged between a Y-mixer, an interdigital mixer, and a split-and-recombine mixer. The 316 stainless steel microchannel has an internal diameter of 250 μm and a length of 50 cm. The cyclohexanone oxime feed line is completely traced to prevent solidification of the oxime.

A schematic of the microreactor setup is shown in Figure 5.3. 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: $([H_2SO_4] + [SO_3])/[\varepsilon$-caprolactam]) is chosen close to unity (approximately 1.3), to reduce the production of ammonium sulphate co-product. Three different micromixers were tested, viz. a Y-mixer, an interdigital mixer, and a split-and-recombine mixer, which are shown in Chapter 4. One of the mixers is connected to a microchannel as described above. 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.

5.2.1.2   Setup for internal recirculation of reaction mixture

A schematic of the microreactor recycle setup is shown in Figure 5.4. The micromixers that are used are two split-and-recombine mixers for the mixing of oleum/ε-caprolactam mixtures with additional oleum and for mixing of oleum/ε-caprolactam mixtures with cyclohexanone oxime in cyclooctane solutions. The microchannel is the same as mentioned in the standard setup. 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 HPLC pump is connected to one of the split-and-recombine micromixers. The outlet of this micromixer is connected to one
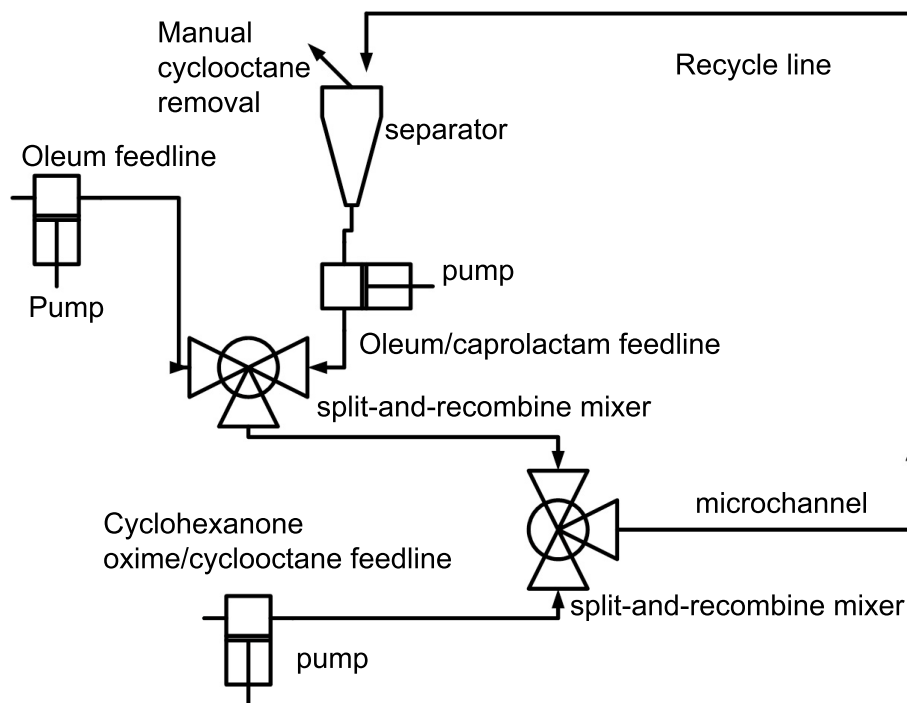
Figure 5.4: Schematic overview of the microreactor setup used for recycle experiments. The microreactor is a combination of a micromixer and a microchannel. Two split-and-recombine micromixers are used for the mixing of oleum/ε-caprolactam mixtures with additional oleum and for mixing of oleum/ε-caprolactam mixtures with cyclohexanone oxime in cyclooctane solutions. The 316 stainless steel microchannel has an internal diameter of 250 μm and a length of 50 cm.

of the feedlines of the split-and-recombine micromixer that is used for the Beckmann rearrangement. The second feedline of this mixer is connected to the cyclohexanone oxime in cyclooctane HPLC pump. The outlet of the reactor microchannel is inserted into a glass separator, where the cyclooctane is manually removed from the top. The separated oleum/ε-caprolactam product is removed at the bottom of the separator and re-injected into the recycle by a Gilson 305 HPLC pump, equipped with high viscosity spring loaded, PTFE sealed, check valves, which completes the recycle. The oleum/ε-caprolactam mixture remains in the recycle and is collected (mainly) in the separator which contains the largest volume within the recycle (1–10 ml). The oleum and cyclohexanone oxime in cyclooctane solution weight loss is recorded by a Sartorius balance. The product sample is collected over time in the separator for at least

5 hour until enough oleum/ε-caprolactam is produced by the reactor. The recycle reactor is started by an initial amount of synthetic oleum/ε-caprolactam mixture of 10 ml (M = 2.3). The reactor is flushed with the cyclooctane phase and the oleum/ε-caprolactam mixture, and fuming sulphuric acid until steady state is reached. In this startup phase the product mixture is disregard, as this is mostly synthetic oleum/ε-caprolactam mixture, needed to initially fill the microchannels. After steady state is reached, the volume of the oleum/ε-caprolactam mixture in the separator is brought back to 1 ml of the scaled volume, at that point the recycle is initiated until enough ε-caprolactam is produced (5 hours). The flow rate of fuming sulphuric acid is 0.028 g/min and the flow rate of the 10 wt% cyclohexanone oxime in cyclooctane solution is 0.14 g/min. The flow rate of the recycled mixture of oleum and ε-caprolactam is 0.2 ml/min. This results in an M-ratio of 2.3.

5.2.2 Measurement procedures

Synthetic reaction mixtures were prepared by carefully admixing of known quantities of known concentrations of oleum, sulphuric 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 dissolve 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 minutes. The sample was collected over a period of 45-60 minutes 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, titra-

tion, and NMR and the cyclooctane samples by GC to determine the total composition.

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

$$S_{proc} = \frac{P_{prod} \cdot F_{cap} - P_{syn} \cdot F_{capsyn}}{F_{oxime}} \tag{5.1}$$

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 %) 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 (Yagoubi et al., 1998). 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%.

5.3   Results

Table 5.1: Conversion of oxime in the Y–mixer and the interdigital mixer. The error in the measurement is $\pm$ 0.3%.

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

5.3.1   Conversion

Table 5.1 shows the conversion of cyclohexanone oxime versus temperature in the reactor setup equipped with the Y-mixer and the interdigital mixer, respectively. The

Table 5.2: Composition of the synthetic ε-caprolactam mixtures with H_2SO_4 and SO_3.

M-ratio	wt% caprolactam	wt% H_2SO_4	wt% SO_3
2.6	31	58	11
2.3	34	55	11
2.0	37	52	11
1.7	41	48	11

initial composition and the flow rate of the synthetic oleum/ε-caprolactam solution are constant at an M-ratio of 2.0 (Table 5.2) 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 the subsequent microchannel is approximately 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 (1951a) 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.

5.3.2   Selectivity

Cyclohexanone oxime concentration.

Figures 5.5 a-c show selectivities towards ε-caprolactam as a function of temperature for different cyclohexanone oxime concentrations. The composition of the oleum/ε-caprolactam solution is kept constant (Table 5.2, 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

Figure 5.5: Figures a-c show 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 - 132 °C. Figures a-c show oxime concentrations of 5, 10, 20, and 30 wt% for an M-ratio of 2.0 measured at a flow rate of 0.2 ml/min of Syn-Cl-A and 0.2 ml/min of cyclohexanone oxime in cyclooctane.

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 to 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 5.5a and 5.5b shows higher selectivities for the interdigital mixer also at high temperatures, compared to the Y-mixer. This can be attributed to the additional surface area for mass transfer, created in the interdigital micromixer by the multi-lamination inlet section (Hessel et al. (2003); Löb et al. (2006)). The selectivities for the 5 wt% solution of cyclohexanone oxime in cycloctane are remarkably lower, even compared to 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.
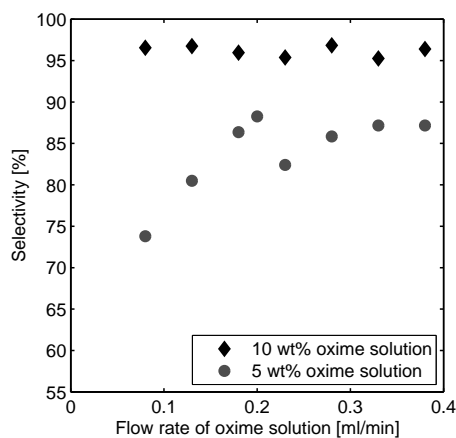
Figure 5.6: Selectivities to ε-caprolactam using the Y-mixer with 5 and 10 wt% solutions of cyclohexanone oxime at a temperature of 111 °C. The flow rate of cyclohexanone oxime in cyclooctane is increased, whereas the flow rate of Syn-CL-A (M-ratio = 2.0) is kept constant at 0.2 ml/min.

Figure 5.6 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 as compared to 10 wt% solutions. This lower selectivity and variation can be attributed to the role of the pyrosulphuric acid ($H_2S_2O_7$) equilibrium in the mixture of oleum and ε-caprolactam, which is discussed in the next section.

Pyrosulphuric acid.

Fuming sulphuric acid or oleum can be represented by $H_2SO_4 \cdot x \cdot SO_3$. If x equals 1, oleum forms pure pyrosulphuric acid with the chemical formula $H_2S_2O_7$:

$$H_2SO_4 + SO_3 \rightleftharpoons H_2S_2O_7 \tag{5.2}$$
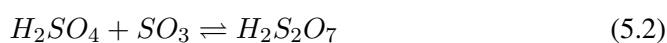
Pure pyrosulphuric acid, which corresponds to oleum with 44.9 wt% free SO_3, crystallizes at ca. 35 °C, the maximum of the freezing-point curve in the oleum range. In addition to oleum, the Beckmann rearrangement mixture contains mainly ε-caprolactam and cyclohexanone oxime, which, however, do not exist in the free state in the reaction system. The most prominent complex that can be found (Cavalieri-d'Oro et al., 1992) is $CPLH^+$, the product of capture of H_2SO_4 by ε-caprolactam, see Figure 5.2. 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 pyrosulphuric acid (equation 5.2), 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 (1951b) determined reaction rate constants in oleum/ε-caprolactam mixtures as a function of SO_3 concentration. As mentioned before, 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 5.5 b and c, Figure 5.8 h, and Figure 5.6) where the selectivities for 5 wt% cyclohexanone oxime solutions are lower than for 10 wt% solutions. As in case of the 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 either higher or lower values. This suggests that the pyrosulphuric acid equilibrium can

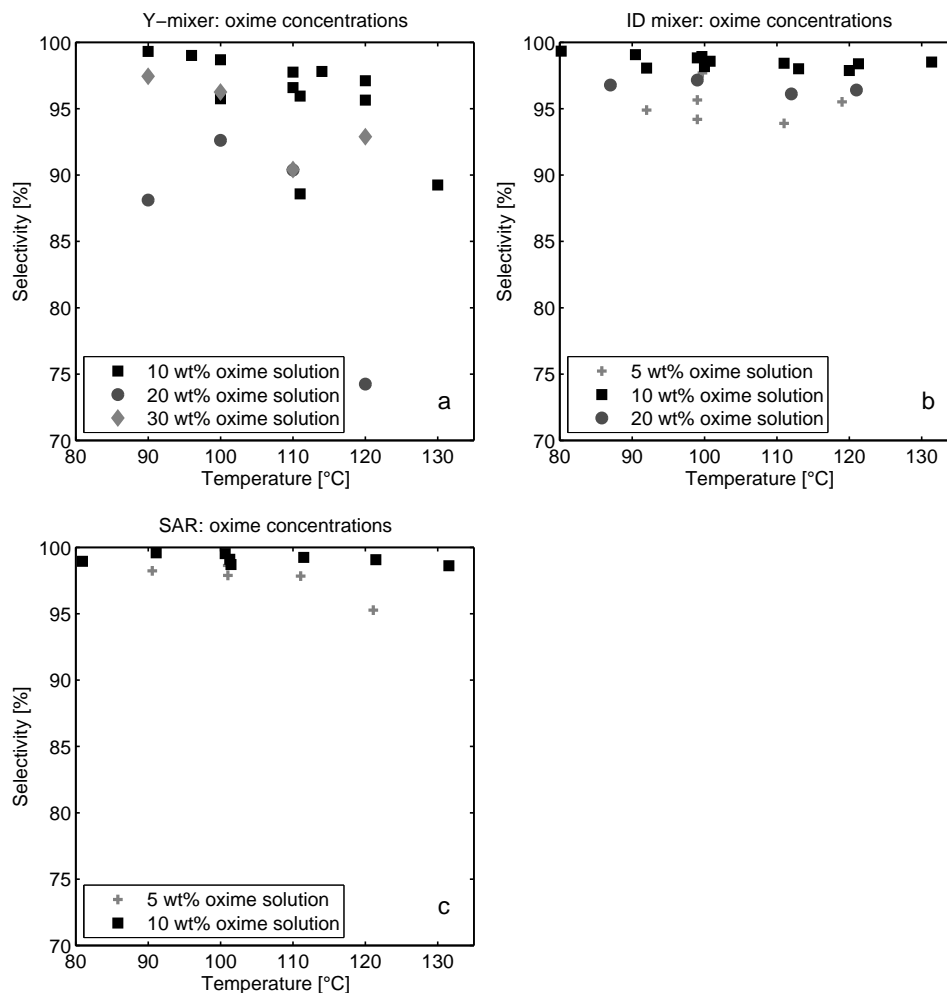also influence the route of reaction, and therefore selectivity.

Figure 5.7: Figures d-f show 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 - 132 °C. Figures d-f show 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.

Composition of the reaction mixture.

Figures 5.7 d, e and 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 5.2).

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 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 towards 99%.

Flow ratio.

Figures 5.8 g, h and 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 before. 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 to that of the 10 wt% solution. This can be attributed to the role of pyrosulphuric acid and the SO_3 to H_2SO_4 ratio, as mentioned before. 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
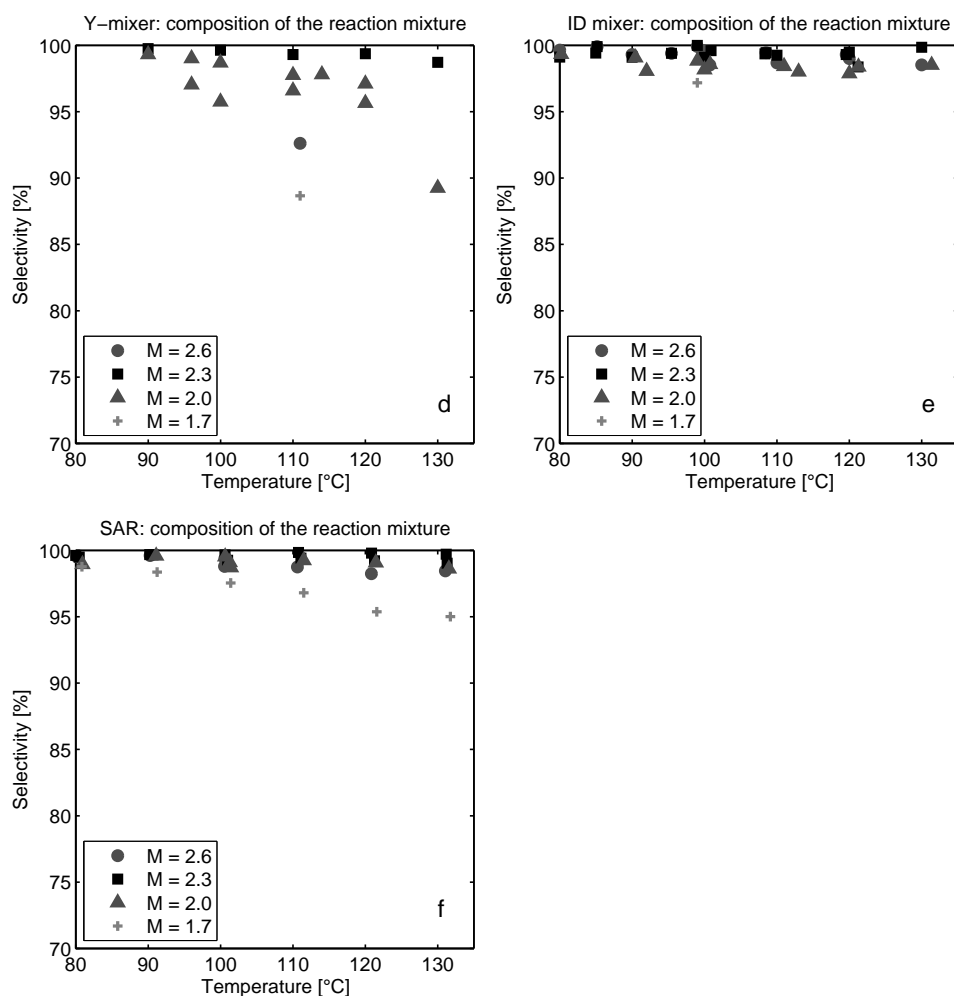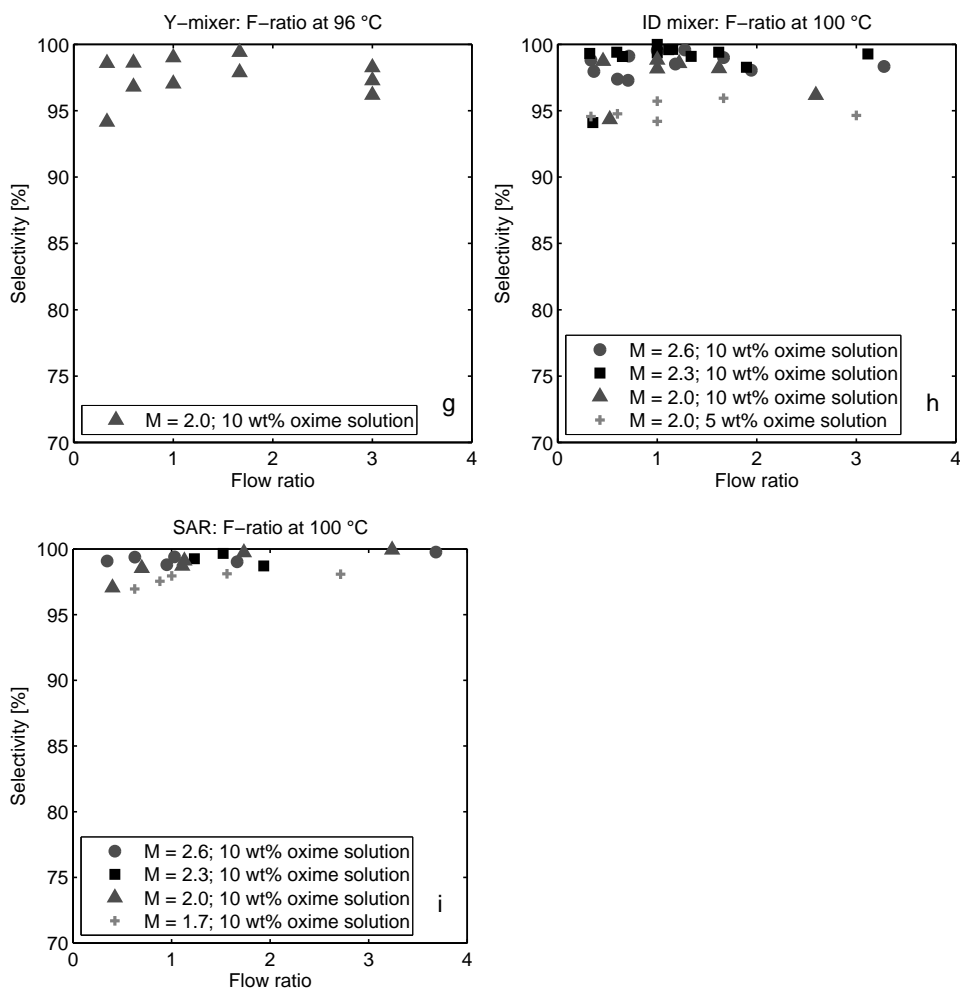
Figure 5.8: Figures g-i show the selectivities to ε-caprolactam measured for the Y-mixer, the interdigital (ID) mixer, and the split-and-recombine (SAR) mixer for a temperature of 100 °C. Figures g-h show selectivities for various flow ratios of Syn-Cl-A over cyclohexanone oxime in cyclooctane. The flow rate ranges from 0.1 to 0.3 ml/min to a total of 0.4 ml/min.

to 1.4 along the reactor by the additionally formed ε-caprolactam. However, in this case all selectivities are below 99%. Smeets et al. (2004) 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, e.g. 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.

5.3.3   Internal recirculation of the ε-caprolactam mixture

Table 5.3: Recycle experiments with oleum/ε-caprolactam mixtures (error 1% in selectivity). CO-ox is the abbreviation of cyclooctane - cyclohexanone oxime solution. The purity is measured by NMR. The M-ratio of the oleum/ε-caprolactam mixture is 2.3 for all recirculation experiments. The reaction temperature is 100 °C. Two control experiments without cyclohexanone oxime are conducted: one with oleum and the second with cyclooctane.

Description	Purity of ε-caprolactam	Recirculation time (min)	flow rate oleum (g/min)	flow rate CO - ox (g/min)	Selectivity
Control experiments:					
Oleum	99.96%	-	0.027	0.0	-
Cyclooctane	98.3%	247	0.0	0.14	-
Recirculation experiments:					
1	98.8%	301	0.028	0.14	99%
2	98.7%	305	0.028	0.14	99%

Recycle experiments are conducted to show that the reactor can perform the Beckmann rearrangement with constant recycling of the oleum/ε-caprolactam mixture, feeding of pure fuming sulphuric acid, addition of the cyclohexanone oxime in cyclooctane solution, and continuous separation of the cyclooctane - oleum/ε-caprolactam emulsion, which is a demonstration of the reliability of operation of the microreactor with hazardous chemicals. The reactor performed well during four recycle experiments at 100 °C, of which the results of two are shown in Table 5.3. The control experiment where pure fuming sulphuric acid is added to a synthetic oleum/ε-caprolactam mixture (99.95%) shows that the purity of this mixture is not reduced by oleum (99.96%). The control recycle experiment with large amounts of pure cyclooctane (without cyclohexanone oxime) shows that the purity of the

oleum/ε-caprolactam mixture is reduced by a pure cyclooctane solution (with no cyclohexanone oxime). This is possible by small amounts of impurities present in the cyclooctane solution and/or by reaction of the cyclooctane itself, which can not be resolved by the used NMR method. This introduces an uncertainty of 0.6% in the measured selectivity by the cyclooctane solution. The experiments show that the selectivity (99%) measured for an M-ratio of 2.3 is comparable to former results at this M-ratio.

5.3.4   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 as compared to the industrial approach. This implies that the industrial recycle ratio thus can be decreased from 50 to 7 by means of micro technology. 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 approximately 0.5, the critical limit above which no internal circulation occurs in the liquid 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 number of microchannels needed for production. Apparently, the micromixers used in this study are reaching their operation 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 during experiments under too extreme conditions. Therefore other methods are needed to control the Beckmann rearrangement

in microreactor systems, which is shown in the next chapter.

The continuous production of ε-caprolactam is possible in a recycle reactor, which is a demonstration of the reliability of the microreactor with hazardous chemicals. The same selectivity is found within experimental error to former experiments at the same conditions. The recycle experiments show that the cyclooctane introduces part of the purity reduction of the oleum/ε-caprolactam, however, this remains within the statistical error of the method and has no effect on the results.

5.4   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 to 2.0) for which the selectivity is above 99%, compared to 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 towards ε-caprolactam at selectivities of 99%. As the Ca number is approximately 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.

The continuous production of ε-caprolactam is possible in a recycle reactor, which is a demonstration of the reliability of the microreactor with hazardous chemicals. The same selectivity is found within experimental error to former experiments at the same conditions.

Pyrosulphuric 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 to 5%, if compared to experiments with a double amount of cyclohexanone oxime. The pyrosulphuric 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.

The best performing micromixer is certainly the split-and-recombine micromixer, for all conditions under investigation, which answers one of the research questions. However, the selectivity is not high enough for industrial application. Therefore, other methods for operation of an industrial microreactor needs to be considered, which is shown in the next chapter by the description of a cascade microreactor, which is able to reach high selectivity for low M-ratios as well.

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Selectivity of the Beckmann rearrangement in the split-and-recombine mixer with mixing at low temperature followed by rapid heating for high selectivity

6

Abstract

The selectivity of the Beckmann rearrangement of cyclohexanone oxime, dissolved in cyclooctane, into ε-caprolactam is determined for conditions with a high concentration of ε-caprolactam, meaning that the M-ratio $(([H_2SO_4] + [SO_3])/[\varepsilon\text{-caprolactam}])$ is as low as 1.7 to 1.4. The microreactor consists of one low temperature mixing zone followed by a high temperature reaction zone. The mixing is conducted at 65 °C in a split-and-recombine micromixer followed immediately by a second zone at high temperature (100 - 127 °C) for complete conversion of cyclohexanone oxime. Selectivities of 99% are found for these conditions, almost independent on the temperature of the high temperature zone. The selectivity of the Beckmann rearrangement for the same mixer, reactants, and flow velocities at a single temperature for mixing and reaction at 130 °C was found to be 95%, as discussed in Chapter 5. This means that by decreasing the mixing temperature, and therefore suppressing the reaction during mixing, the selectivity is increased by 4% at industrial relevant oleum and ε-caprolactam concentrations.

6.1   Introduction

One of the greatest benefits of microreactors is the excellent heat transfer by the small distance between the reactants and the (cooled or heated) reactor wall. However, the mass transfer is generally more challenging as the Lewis number ($Le = \alpha/D$, where α is the thermal diffusivity and D is the mass diffusivity) is high for liquids. The bulk of chemical processes requires premixing of all reactants for process initiation and intensive mixing for high conversion and selectivity (Hessel et al., 2005). As is shown in Chapter 3 and Chapter 5, the selectivity of the Beckmann rearrangement is very much dependent on the mixing conditions of the reactants. The selectivity of a chemical reaction is of course dependent on the reaction rate to the desired product and the reaction rate to by-products; these reaction rates are on their own dependent on their *local* concentrations. So far this is only textbook chemistry, which is elaborately described by Bourne (2003), Balgyga and Bourne (1990), Ottino (1994) and Angst et al. (1982) who state that the highest selectivity is reached for well mixed reactants. In a large number of reactors the mixing and the reaction are conducted at the same temperature, as this is generally the most straightforward scenario. However, this approach is not suited for the Beckmann rearrangement as cyclohexanone oxime is liquid above 90 °C; at this temperature the reaction rate with fuming sulphuric acid is very high (Wichterle and Roček (1951); Nguyen et al. (1997)). Mixing is generally slower at low Reynolds numbers (below 10) that are attained in microreactors, even if the reactants are diluted with cyclooctane as described in Chapter 5. In this chapter a method of separating reaction and mixing by two different temperature zones is experimentally verified to determine if selectivity of the Beckmann rearrangement can be high at high temperatures and low Reynolds numbers as well. Effectively lower temperature decreases the second Damköhler number, which is defined in reacting systems that include also interphase mass transport as the ratio of the chemical reaction rate to the mass transfer rate or $\mathrm{Da}_{II} = \frac{kC_0^{n-1}}{k_g a}$, where k_g is the global mass transport coefficient and a is the specific surface area. The second zone increases the reaction rate, however, as the reactants are premixed at low temperature the rate towards the by-products, as for example octahydrophenazine (Jodra et al., 1981), which is formed at high cyclohexanone oxime concentrations, is decreased. This approach is beneficial as part of the heat released by the reaction is released at a higher temperature, which makes it easier to re-use the energy in other processes. Generally,

an ε-caprolactam production facility produces around 200.000 tonnes/year, which corresponds to a constant release in energy of 6 MW during production. By using cyclooctane as a dilutant, the mixing can be done at low temperature (20 - 70 °C), where the reaction rate is much smaller. By applying one of the greatest benefits of microreactors, the excellent heat transfer, the well mixed reaction mixture can be rapidly heated up to temperatures where the reaction rate is high (between 90 - 130 °C for the Beckmann rearrangement). Mixing is already completed at low temperature, therefore at high temperature the reaction rate towards the main product is the highest, or in other words, the selectivity will have the highest thermodynamically possible value of $S_{max} = r_{main}/(\sum r_i)$, where r_{main} is the reaction rate towards the desired product ε-caprolactam and $\sum r_i$ is the sum of all the possible reactions with the main reactant cyclohexanone oxime. Therefore this will yield into a high selectivity, and within limits independent of temperature of the second temperature zone. In this chapter is experimentally verified if this applies to the Beckmann rearrangement at industrially relevant high concentrations of ε-caprolactam in oleum (M-ratio of 1.4 or lower).

6.2   Experimental

A schematic of the microreactor setup is shown in Figure 6.1. The experimental setup is used for mixing the reactants in temperature zone 1 and subsequently increase the temperature of the mixture in zone 2. A split-and-recombine mixer (SAR) is used as the low temperature (pre-)reaction mixer. The design of the stainless steel split-and-recombine mixer is shown in Chapter 4. An overview of the experiments is provided in Table 6.1. The microreactor is considered as the combination of a micromixer and a 316 stainless steel microchannel with an internal diameter of 250 μm and a length of 1 meter; 50 cm of the microchannel is submersed in the first low temperature zone, this capillary is attached to an additional capillary of 50 cm in zone 2 (high temperature zone). The external diameter of the microchannel is 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
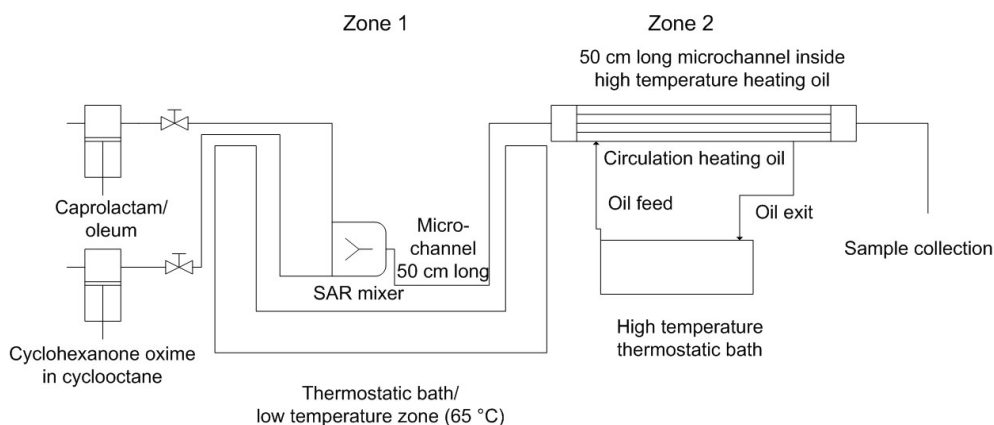
Figure 6.1: Schematic overview of the experimental setup. HPLC pumps deliver the ε-caprolactam/oleum solution and the cyclohexanone oxime cyclooctane solution to the split-and-recombine micromixer. The micromixer is attached to a steel 1/16 inch capillary with an internal diameter of 250 μm, which is submersed in the first low temperature zone, the extention of this capillary is attached to an additional capillary, which is placed inside a tube with circulating high temperature fluid.

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 split-and-recombine mixer, valves, and preheater channels are immersed into a 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 directly connected microchannel in zone 2 was inserted into a large tube (diameter 1.5 cm, length 40 cm) with circulating thermostatic oil from a Lauda ecoline thermostat. The temperature in zone 2 was recorded by an additional thermocouple in the recirculation thermostatic oil.

6.2.1   Measurement procedures

Synthetic reaction mixtures were prepared by carefully admixing of known quantities of known concentrations of oleum, sulphuric acid, and ε-caprolactam. The resulting synthetic mixtures were measured by HPLC, titration, and NMR for verification of the chosen composition. Cyclohexanone oxime/cyclooctane solutions were prepared

Table 6.1: Experimental conditions and the initial M-ratio $(([H_2SO_4] + [SO_3])/[\varepsilon\text{-caprolactam}])$, temperatures of the high temperature zone and cyclohexanone oxime concentration used for these experiments with the split-and-recombine mixer.

M-ratio	Temperature (°C)	Cyclohexanone oxime concentration (wt%)
1.7	100	9
1.7	110	9
1.7	120	9
1.7	127	9

according to the desired mass fractions and heated if necessary to completely dissolve all cyclohexanone oxime. 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 split-and-recombine mixer and subsequent microchannel and contacted with the cyclohexanone oxime/cyclooctane solution. The reactor and feed channels were flushed for at least 30 minutes. The sample was collected over a period of 45-60 minutes and the weight gain of the product sample as well as the weight loss of the one of the reactants, the synthetic oleum/ε-caprolactam mixture, were recorded, the difference accounts for the amount of the second reactant, viz. the 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 was calculated by the same method as was used in Chapter 5. By this method the selectivity (measured in %) is determined within a measurement error of 1%.

6.3 Results and Discussion
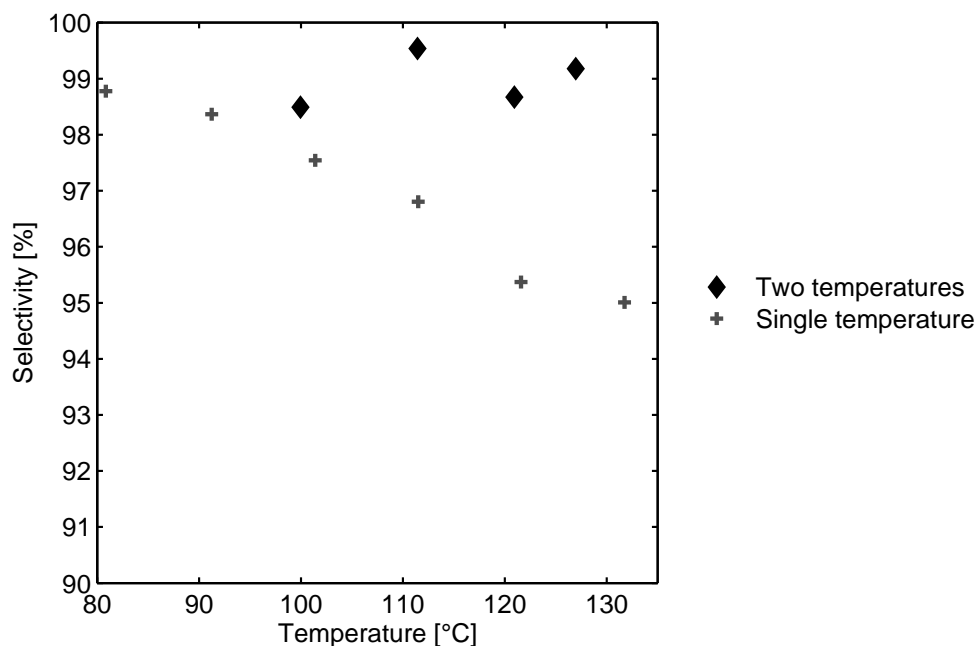
Figure 6.2: The selectivities to ε-caprolactam measured for the split-and-recombine (SAR) mixer for temperatures from 80 - 132 °C. The M-ratio between 1.7 - 1.4 is corresponding to a viscosity between 50 and 150 mPa·s (Chapter 2). The data of the split-and-recombine mixer with an M-ratio of 1.7 was also shown in Chapter 5 and is included here for comparison with the experiments with two temperature zones. The temperature of the low temperature mixing zone was 65 °C. The selectivity (measured in %) is determined within a measurement error of 1%.

Figure 6.2 shows the results of the selectivities measured in the split-and-recombine micromixer with the mixing zone at 65 °C and subsequently the microchannel in zone 2 at the indicated temperatures in the figure; this is of course not the actual temperature of the reaction mixture, as this will be higher by the reaction heat of cyclohexanone oxime conversion (see Figure 3.7). The initial composition and the flow rate of the synthetic oleum/ε-caprolactam solution are constant at an M-ratio of 1.7 and a flow rate of 0.2 ml/min. The flow rate of the 9 wt% solution of cyclohexanone oxime in cyclooctane is 0.2 ml/min. The residence time of the reactants in the mixer and the subsequent microchannel is approximately 10 seconds. For comparison
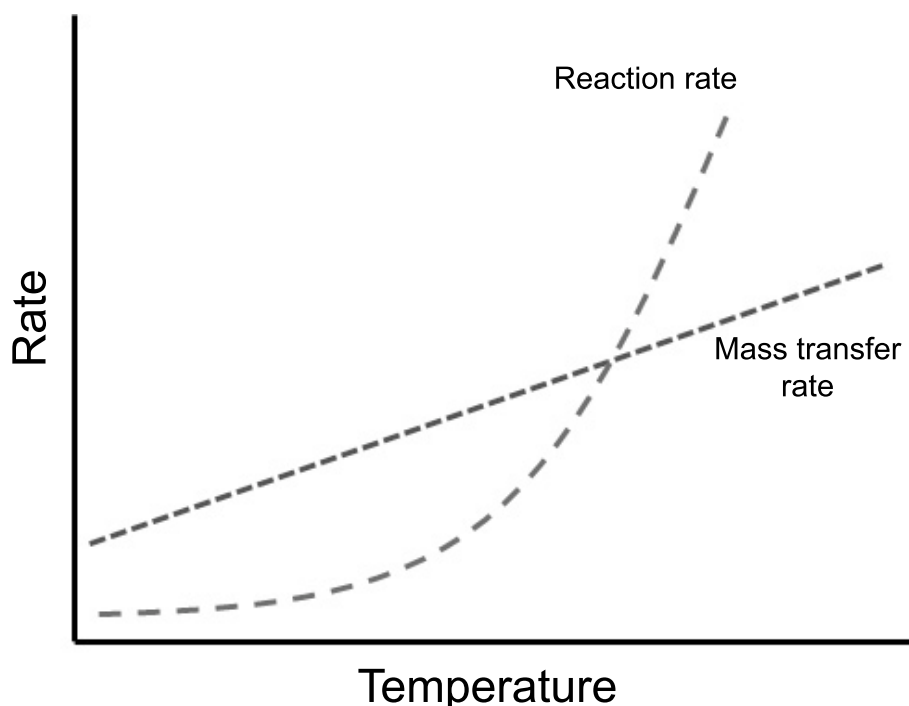
Figure 6.3: Schematic representation of the increase in mass transport and of the increase reaction rate as a function of temperature.

the selectivities of the Beckmann rearrangement shown in Chapter 5 for mixing and reaction at the same temperature are shown in Figure 6.2 as well. The Beckmann reaction conducted at two temperature zones all show selectivities around 99%, whereas the corresponding selectivities measured in a single temperature zone show selectivities as low as 95%. The initial M-ratio $(([H_2SO_4] + [SO_3])/[\varepsilon\text{-caprolactam}])$ for these experiments is 1.7, which after introduction of cyclohexanone oxime decreases to 1.4, which is comparable to industrial values. The selectivity results in Chapter 5 show the decrease in selectivity for all the three used mixers at these conditions. This was attributed to the decrease of internal circulations inside the slugs as the capillary number is approximately 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. High selectivities are reached for low M-ratios as well by separating the mixing zone from

the reaction zone. This is of course the first requirement for upscaling of the Beck-
mann reaction by microtechnology. Figure 6.3 shows a schematic representation of
the rate of reaction and the rate of mass transfer. At a certain temperature the reaction
rate will increase exponentially to a rate which is higher than the mass transfer rate,
of course this temperature will differ for other reactions and other process conditions.
However, the concept will be the same and a temperature can be found for which
the reaction rate is slower than the mass transfer rate, this can be chosen as the tem-
perature of the mixing zone. Subsequently the second temperature should increase
the reaction rate to ensure complete conversion at the exit of the microchannel. In
this way one can think of a situation for the Beckmann rearrangement where mixing
is conducted at even lower temperature, e.g. 20 °C, which was not possible in the
current setup, by the high pressures (higher than 600 bar) which were needed in the
small channels of the split-and-recombine mixer. For example a conventional static
mixer can be used, which can feed a number of high temperature microchannels for
rapid heat up to the reaction temperature, and prevention of exothermic increase of
the reaction mixture temperature by the heat of reaction, which can be tremendous if
the reaction heat is not removed (Hlidkova-Kadlecova et al., 1986). At high temper-
ature the conversion of the cyclohexanone oxime is completed with high selectivity
as the mixing is already completed at low temperature. By these measurements is
shown that the same high selectivities can be reached by microreactor technology for
comparable low M-ratios as in industry, this is the most important prerequisite for
industrial application of microreactor technology for the Beckmann rearrangement
of cyclohexanone oxime. However, addition equipment for mixing of cyclohexanone
oxime with cyclooctane, separation of cyclooctane from the reaction mixture, and
of course the microchannel heat exchanger is needed for application. Part of the in-
vestment can be regained by the better heat management possible by a microchannel
reactor. This makes the selection for a microchannel reactor an economical choice,
which requires further investigations.

6.4   Concluding remarks

In this chapter a method is tested were the mixing is completed at a lower temperature
of 65 °C and the rapid heating in a microchannel to 100 - 127 °C is used to completely
convert cyclohexanone oxime into ε-caprolactam at high selectivity at high tempera-

tures for the Beckmann rearrangement. Selectivities around 99% were measured for these samples. This is a very large increase in selectivity for this low value of the M-ratio ($([H_2SO_4] + [SO_3])/[\varepsilon$-caprolactam]) of 1.7 - 1.4. Selectivity should be optimized for conditions with an M-ratio as low as possible as less ammoniumsulphate co-product is formed in this way. As the conversion of cyclohexanone oxime can take place at higher temperatures more of the reaction heat could be reused in other processes, making the Beckmann rearrangement to ε-caprolactam more energy efficient. However, a careful analysis of the process economics is therefore needed.

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Flow distribution in a circular symmetrical 10 channel microreactor

7

Abstract

In the scale up of chemical micro process technology it is important to guarantee reproducible reaction conditions in a large number of parallel microchannels. One of the characteristic problems in microreactors is to distribute the incoming fluid equally over the microchannels. A fluid maldistribution would induce unequal residence times in different channels, with undesirable consequences for the product distribution of a chemical reaction being conducted inside the reactor. In this chapter the flow distribution in a circular symmetrical 10 channel microreactor is tested. This microreactor is designed for its capability of upscaling; circular symmetrical microchannels around a larger cooling tube is a concept where crossover and leakage is less likely as there is no need for bonding of microstructured stacks of plates, as is needed for non circular symmetrical concepts. Moreover, the tubes needed for cooling can have larger diameters e.g. centimeter range, which makes the requirements for the purity of the cooling liquid less stringent. However, plate like stacked microchannels certainly have shown excellent performance in upscaling microtechnology, therefore a circular symmetrical design should not be seen as a substitution, but rather as an addition to scale up of micro technology. An equal flow distribution over the microchannels is a first requirement for well-defined and reproducible reaction conditions, and is therefore investigated with the most straightforward flow distributor: a "large" liquid chamber (0.5 ml) in front of all microchannels. The flow distribution is tested with a series of liquids varying in viscosity and flow rate. Fur-

thermore, the behavior of liquid mixing of liquids with varying viscosities is investigated. Glycerol/water mixtures with viscosities above 50 mPa·s provide a regular flow distribution, with standard deviation of 3% over the 10 channels of the microreactor. Water, with a lower viscosity, provides a decreased flow distribution with a standard deviation of 5%, which can be understood by the lower pressure drop over the microchannels, when this is compared to the pressure with liquids of a higher viscosity. Simultaneous operation of two liquids with different viscosities significantly reduces the quality of the flow distribution. This is due to the viscosity changes and the pressure fluctuations caused by these changes. Therefore multiple steady states for the liquid distribution over the microchannels are possible, which leads to a maldistribution over the channels. Although this makes the 10 channel microreactor less adequate for mixing of the reactants, as is concluded in Chapter 3 as well, the distributor of the 10 channel microreactor is very well capable of distributing premixed viscous liquids. This coincides with the conclusion of Chapter 6 where a low temperature premixer is suggested as a method to gain high selectivity for the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam.

7.1   Flow distribution

In chemical micro process technology it is important to guarantee well-defined and reproducible reaction conditions in microchannels, and a high throughput should be achieved for scale up (Tonkovich et al., 2005). For this purpose, the process fluids are guided through a large number of parallel microchannels, where heat exchange and/or chemical reactions occur. One of the characteristic problems in microreactors is to distribute the incoming fluid equally over the microchannels. A fluid maldistribution would induce unequal residence times in different channels, with undesirable consequences for the product distribution of a chemical reaction being conducted inside the reactor. When a process with various competing side reactions and by-products is considered, the contact time of the process fluid in the reaction region should be as well defined as possible in order to maximize the selectivity of the process (Hessel et al., 2004). Various concepts for the equal flow distribution of fluids over a multitude of microchannels have been developed (Rebrov et al., 2010). One concept relies on guiding the incoming fluid through a flow splitter with subsequent bifurcations (Chen and Chen (2002); Wada et al. (2006); Luo et al. (2008)). Bejan and

Errera (1997) found that such a fractal tree-like network structure (observed widely in natural structures such as cracks in a dry ground, arteries or veins and lungs) gave flow uniformity, at least in the absence of channel dimensional variations, and as long as the length of the straight channel after each channel bend is sufficient for a symmetrical velocity profile to develop. The most widely used design for equal flow distribution is based on a comparatively wide inlet region leading into a multitude of narrow microchannels. The principle of this design lies in the pressure barrier of the microchannels. The narrower the microchannels are, the higher the pressure drop will be in the channels themselves as compared with the pressure drop in the flow distribution chamber, and the more uniform the flow distribution will be. Optimizing the geometry of the flow distribution and collecting chamber ensures equal pressure drop over the microchannels. Delsman (2005) modelled the flow distribution over a set of microchannels for five different geometries of the flow distribution and collecting chambers. He obtained the best results for a case with inlets and outlets in-line with the channels and asymmetrical flow distribution and collecting chambers.

Although a large number of distributors exists to provide a regular flow distribution, in most cases the most straightforward one will be the most economical, and only when the necessity exists a more elaborate flow distributor will be installed. Therefore the most straightforward flow distributor, a larger liquid chamber before the microchannels, is tested for applicability for scale up of the Beckmann rearrangement of cyclohexanone oxime towards ε-caprolactam. The liquid flow rates and/or velocities are estimated by a number of approximations: as a first approximation the reaction rate and mass transfer are possible in the order of seconds (which is shown elaborately in Chapter 3). Furthermore, most microchannels are in the order of 50 - 500 μm. As an approximation the pressure drop over the microchannel is limited to ca. 10 bar (the same as the industrial design described by Smeets et al. (2004)). These approximations lead to an inlet velocity of the reaction mixture of around 0.1 - 0.2 m/s. Considering a production rate of 200.000 tonnes/annum for an ε-caprolactam production facility this leads to ca. 7–16 million microchannels with a radial dimension of 200 μm. This seems a rather large number, however a volume of $1 \times 1 \times 0.5$ m^3 can contain ca. 3 million microchannels, which puts the volume of an industrial microreactor in perspective. The flow rates that are needed in the microchannels used in this chapter are therefore in the order of 1 ml/min. The microreactor tested in this chapter is designed for its capability of upscaling; circular symmetrical mi-

crochannels around a larger cooling tube is a concept where crossover and leakage are less likely as there is no need for bonding of microstructured stacks of plates, as is needed for non circular symmetrical concepts. Moreover, the tube needed for cooling can have a larger diameter e.g. centimeter range, which makes the requirements for the purity of the cooling liquid less stringent. An equal flow distribution over the microchannels is a first requirement for a regular operation, and is therefore investigated with the most straightforward flow distributor: a large liquid chamber before all microchannels. The flow distribution is tested with a series of liquids varying in viscosity and flow rate. Furthermore, the behavior of liquid mixing of liquids with varying viscosities is investigated in this straightforward flow distributor. Glycerol/water mixtures and water are used as testing liquids, because of the comparable viscosities with oleum/ε-caprolactam mixtures and cyclohexanone oxime. The mass and heat transfer in a rectangular microchannel is addressed in Chapter 3, where is shown that the microchannel is capable to perform almost isothermally. However, the mass transfer with a single side inlet is not sufficient with high viscous liquids. Therefore only the flow distribution is tested for this 10 channel microreactor.

7.2   A circular 10 channel reactor

In this chapter a circular multichannel microreactor is investigated, which is schematically shown in Figure 7.1. The left picture shows the microchannels descending in a helical form around an inner cooling cavity, which is shown in the right cross section. Into this cavity a dipped steel pipe can be inserted to provide the cooling liquid. The main advantage of the circular design is the symmetrical arrangement of the microchannels, by this arrangement the reactor provides identical conditions for all channels. Furthermore, only the channels containing reactants are on microscale, whereas the cooling tube can remain relatively large; this decreases the demands on the purity of the cooling liquid. By the circular arrangement leakage of reactant liquids towards the cooling liquid is completely prevented. No welded metal-metal connections are used for separation between the cooling liquid and reactant liquids. More details are shown in the experimental section.
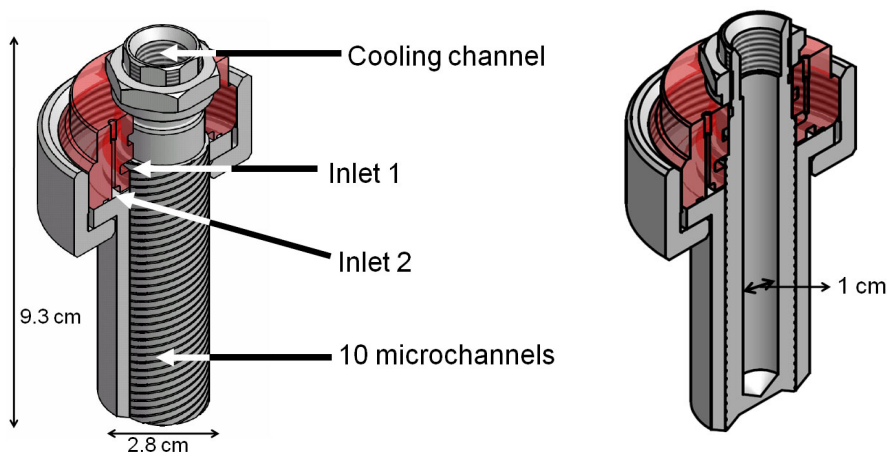
Figure 7.1: Schematic representation of the 10 channel microreactor. The left picture shows the helical descending microchannels and the connections to the inlets. The right schematic cross section shows the inner cooling channel as well, which is symmetrically surrounded by the helical microchannels ($200 \times 400 \ \mu$m). The cooling channel is fed by a smaller dipped steel pipe (not shown here) into the cooling cavity.

7.3 Experimental

7.3.1 Equipment and procedures

In this section the experimental set-up and the experimental procedures for the investigation of the flow distribution in the multi-channel microreactor are provided. The total experimental set-up consists of the feed section, the 10 channel microreactor, the fluid collection and the analysis section. An overview of the different parts of the set-up is provided in the following sections.

7.3.1.1 Feed section

The feed section consists of three different parts: a container for liquid 1 with viscosities in the range of 1-300 mPa·s, a container for liquid 2 with a viscosity of 1 mPa·s and two HPLC pumps. A glycerol/water mixture is used to match the high viscosities of the reaction mixture (50-300 mPa·s). Water (1 mPa·s) is used as the low viscosity liquid, as this is in the same order of magnitude as cyclohexanone oxime (4–8 mPa·s, Chapter 2). Viscosities in the range of 50 to 300 mPa·s are obtained by
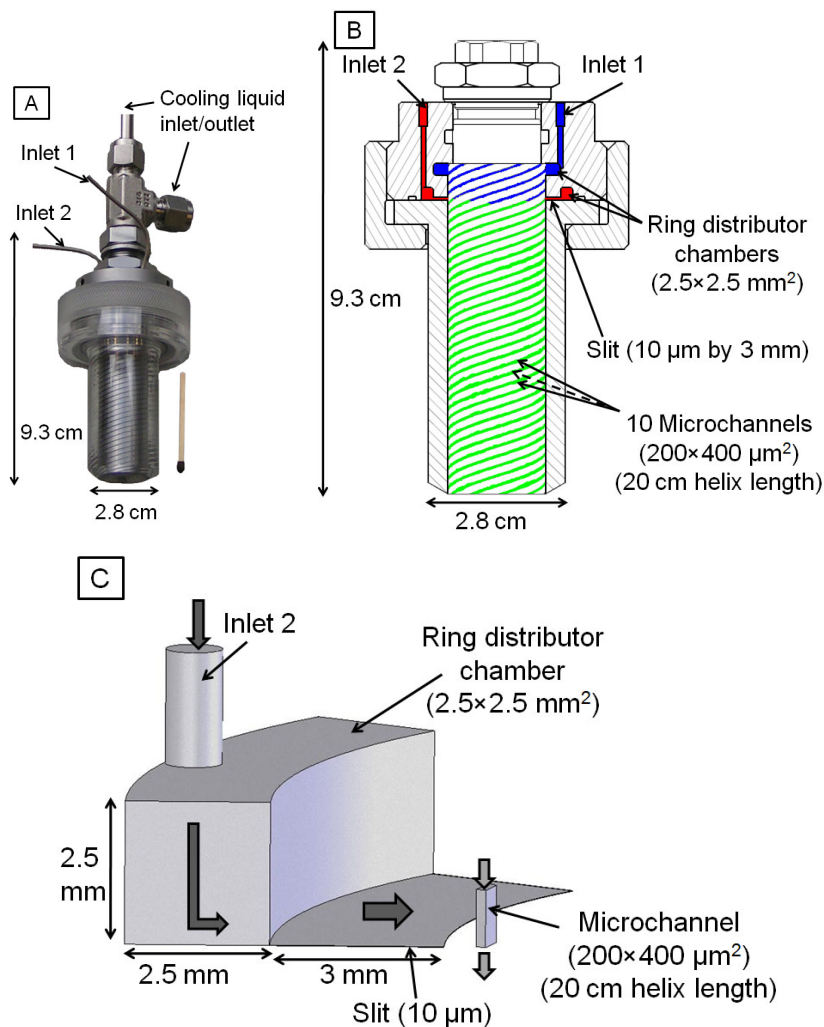
Figure 7.2: The picture A shows the microreactor with 10 microchannels, with an attached cooling pipe. The schematic representation B shows the liquid flows in color, inlet 1 in blue, inlet 2 in red, and mixed liquids in green. The inlets of the microreactor are connected to two ring shaped chambers. The ring shape of inlet 1 is directly connected to the helical microchannel, whereas the second inlet ring shape is connected to the microchannels by a small 10 μm slit. Schematic C shows the details of inlet 2 with the attached slit (heigth 10 μm length 3 mm) and microchannel (200×400 μm^2). The direction of the liquid flow is indicated by grey arrows.

mixing glycerol with water according to Lide (1999). The viscosities of glycerol and water are 1500 mPa·s and 1 mPa·s, respectively. Two different pumps are used for the 10 channel microreactor. A Pharmacia LKB-2150 HPLC pump is used for low viscous liquids. The flow rates for this pump are in the range of 0.01-5 ml/min and the pressure-range is 0-600 bar. A Gilson 305 HPLC pump is used for both high and low viscosity liquids. Flow rates for this pump are in the range of 0.125-25 ml/min and the pressure range is 0-300 bar. At the inlet of the pumps, 10 μm filters are installed. Stainless steel tubing (outer diameter 1/16 inch, inner diameter 0.5 mm) for the Gilson 305 HPLC pump and PEEK (polyetheretherketone) tubing (outer diameter 1/16 inch, inner diameter 0.03 inch) for the Pharmacia LKB-2150 HPLC pump and Valco connectors are used for high pressure outlet connections to the stainless steel tubing (outer diameter 1/16 inch, inner diameter 0.5 mm) of the inlets of the microreactor.

7.3.1.2   The 10 channel microreactor

All flow distribution experiments are performed in the 10 channel microreactor (Figure 7.2). The reactor consists of a stainless steel AISI 304L core and an outside made of Perspex®. The reactor has two inlets: inlet 1 for highly viscous liquids and inlet 2 for low viscous liquids. Both inlets are connected to a ring chamber distributor (2.5×2.5 mm²) around the periphery of the microreactor, which is connected to the ten microchannels. The inlet 2 is connected to the microchannels by a 10 μm slit (Figure 7.2 C) with a length of 3 mm around the periphery of the microreactor, which provides a small side inlet into the main channel. The purpose of this slit is to give better flow distribution of the liquid with a low viscosity and match the linear flow velocities of the volumetric flow ratio of 1:10 used for the experiments. The microchannels, rectangular (200 by 400 μm), have a helical form and a length of 20 cm. The helix has a diameter and a pitch of 2 cm. A cooling channel is situated on the inside of the microreactor (internal diameter 10 mm). The viscous liquids are distributed over the channels by inlet 1, while the low viscous liquids are distributed by inlet 2 into the 10 μm slit.

7.3.1.3   Fluid collecting section

The outlets of the microreactor channels are connected to ten rubber tubes (inner
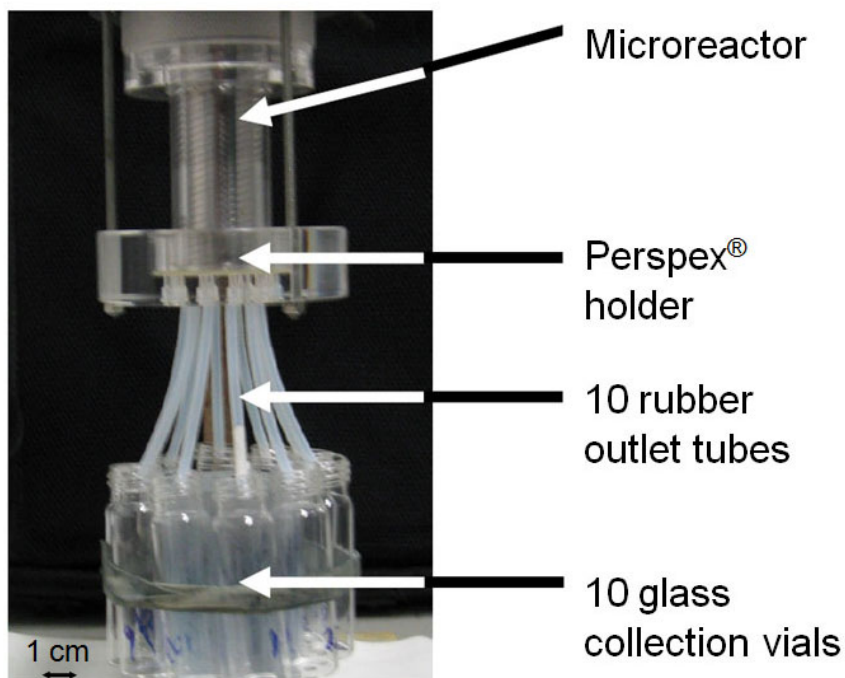
Figure 7.3: 10 channel microreactor with the attached tubes to separately collect the liquids from each individual channel.

diameter 1.6 mm), which lead the outflow into ten glass vials (Figure 7.3), which allow the outflow of each microchannel to be collected separately. The ten glass vials with the collected outflow of each channel were tested gravimetrically. Next to the gravimetrical method the outlet liquids were titrated to show intermixing of the liquid flows. At a constant flow ratio of 10:1 (highly viscous liquid : low viscous liquid) a solution of nitric acid (3.0 M) was used for inlet 2. A solution of sodium hydroxide (0.04 M) was used as titrant to determine the amount of nitric acid per channel. Phenolphthalein was used as pH indicator and a SCHOTT Instruments GmbH TITRONIC® universal titrator was used for the titration.

7.3.2   Experimental procedures

At the start of each experiment, the 10 channel microreactor is rinsed with water until the complete reactor is filled with fluid. First the flow distributions for both inlets are

tested separately with water by keeping one inlet flow at zero and varying the other inlet flow. The flow rates for inlet 1 are varied between 0.5 and 10 ml/min, while the flow rates for inlet 2 are varied between 0.1 and 2.0 ml/min. The flow distribution is also tested for inlet 1 with glycerol/water mixtures. The flow rate is varied between 0.5 and 10 ml/min and the viscosity between 50 and 300 mPa·s, in accordance with the desired flow rates defined in the introduction. In these tests, the flow rate of inlet 2 is kept at zero for all experiments. Finally the flow distribution is investigated for both inlets simultaneously at a constant flow ratio of 10:1 (highly viscous liquid : low viscous liquid) using glycerol/water mixtures for the highly viscous liquid and a nitric acid solution (3.0 M) as low viscous liquid. The start-up procedure for the experiments consists of a first rinse of the reactor with water through both inlets, then stop the pump for inlet 2 and use the glycerol/water mixture for inlet 1 at the desired flow rate. When steady flow is reached, the nitric acid solution is pumped through inlet 2 at the desired flow rate to obtain a flow ratio of 10:1 at steady state. Next the ten glass collecting tubes are placed under the reactor in order to collect the outflow of each channel. The flow rate of the glycerol/water is varied between 1 and 10 ml/min and the flow rate of the nitric acid solution between 0.1 and 1 ml/min, while keeping the flow ratio at 10:1. The viscosity of the glycerol/water mixture is kept constant at about 50 mPa·s.

7.4   Data analysis

7.4.1   Flow distribution

As a measure for the quality of the flow distribution, i.e. the evenness of the flow distribution, the relative standard deviation is used, which is defined as:

$$\sigma_r = \frac{1}{\bar{F}} \sqrt{\frac{\sum (F_i - \bar{F})^2}{n-1}} \tag{7.1}$$

with $\bar{F}$ the mean flow rate per channel, F_i the flow rate per channel, and n the number of channels. An increase in the relative standard deviation is equivalent to a less even flow distribution over the channels.

7.5   Results and Discussion

7.5.1   Flow distribution of the main inlet (inlet 1)
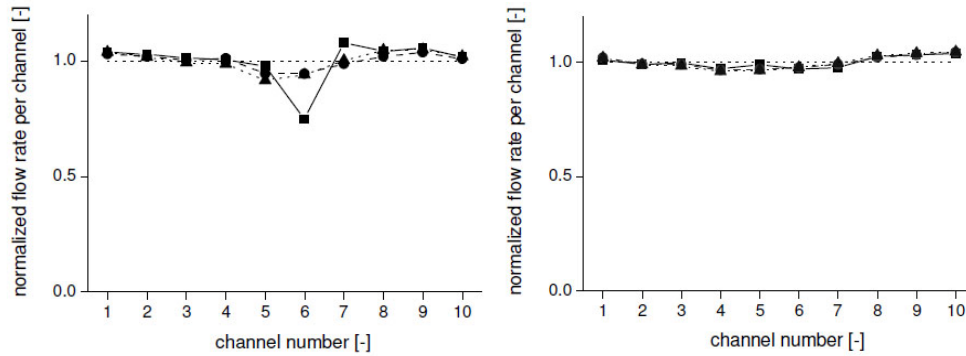
Figure 7.4: Flow distribution over the channels for inlet 1 for water (left) and glycerol/water mixtures (right). The normalized flow rate per channel is given for different inlet flow rates for water or glycerol/water mixtures (50–300 mPa·s): 1 ml/min (■), 5 ml/min (●), 10 ml/min (▲). The viscosity is varied between 50 and 300 mPa·s, however, almost no differences between these viscosities is measured. Channel number 1 is closest to inlet 1 and counted clockwise till number 10 (which is followed by number 1).
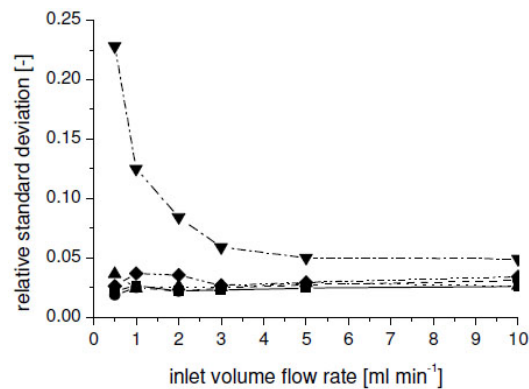
Figure 7.5: Relative standard deviation as a measure for the flow distribution as a function of the flow distributor inlet volumetric flow. Experimental results for inlet 1 for water and glycerol/water mixtures of different viscosities: 1mPa·s (▼), 50 mPa·s (■), 100 mPa·s (●), 200 mPa·s (▲), 300 mPa·s (♦).

The flow distribution in the 10 channel circular symmetric reactor is tested with various flow rates and liquids with various viscosities. The reactor has two inlets, which are not the same. Inlet 1 is the inlet for the main stream, inlet 2 is used as a side feed with a smaller dimension for smaller inlet flow rates. This is typical for the Beckmann rearrangement, where the main stream is an ε-caprolactam/oleum mixture and the side feed is used for molten cyclohexanone oxime. The total flow rate for the Beckmann rearrangement in this reactor should be in the order of 2 ml/min by the main inlet (inlet 1) of the channels and 0.2 ml/min by the side inlet slit (inlet 2) to provide a reasonable production rate of ε-caprolactam in these channels, which is mentioned in section 7.1. The two inlets are first tested separately. A typical flow distribution plot for inlet 1 tested with water (left) and glycerol/water (right) mixtures is shown in Figure 7.4. Here the normalized flow rates of the ten microchannels are plotted. These plots show that, especially for low flow rates of water the channels closer to the inlet of the flow distributor have higher flow rates, whereas the channels at a greater distance have lower flow rates. However, the effect of the viscosity of the glycerol/water mixtures (right figure) is evident. For an inlet volume flow between 0.5 and 10 ml/min no significant deviations from uniform flow distribution can be observed. The standard deviation of the flow rates for inlet 1 of the microreactor with water and glycerol/water mixtures is plotted in Figure 7.5. For viscosities of the glycerol/water mixture between 50 and 300 mPa·s, and flow rates in the range of 0.5–10 ml/min, the relative standard deviation remains below 5%. Furthermore, no significant difference is observed for different viscosities between 50 mPa·s and 300 mPa·s. However, glycerol/water mixtures with viscosities above 50 mPa·s show a better distribution than water of 1 mPa·s. This difference is caused by the difference in pressure drop. A higher pressure drop results in a better flow distribution. The maximum flow distribution uniformity for viscosities between 50 and 300 mPa·s has a relative standard deviation of about 3%. The relative standard deviation is taken as a measure for the quality of the flow distribution. For higher flow rates the relative standard deviation is lower, so a better flow distribution is obtained. Two different regions can be distinguished, depending on the inlet flow rate. For low inlet flow rates the relative standard deviation decreases with higher inlet flow rates. At a transitional flow rate of about 3 ml/min, the flow distribution is independent of the inlet volume flow rate. The pressure drop is known to have a large influence on the flow distribution (Hessel et al., 2004), explaining the fact that higher flow rates, and thus higher

pressure drop, results in a better flow distribution. The fact that the flow distribution remains constant at a value of about 5% for higher velocities is partly caused by the inaccuracy of the manufacturing process (ca. 2 %). The design of the flow distributor is not optimal, since distribution is not equal for liquids with a low viscosity, however, for highly viscous liquids as the Beckmann reaction mixture the distributor works well at the flow rate around 1 ml/min per microchannel.

7.5.2   Flow distribution for the small side inlet (inlet 2)
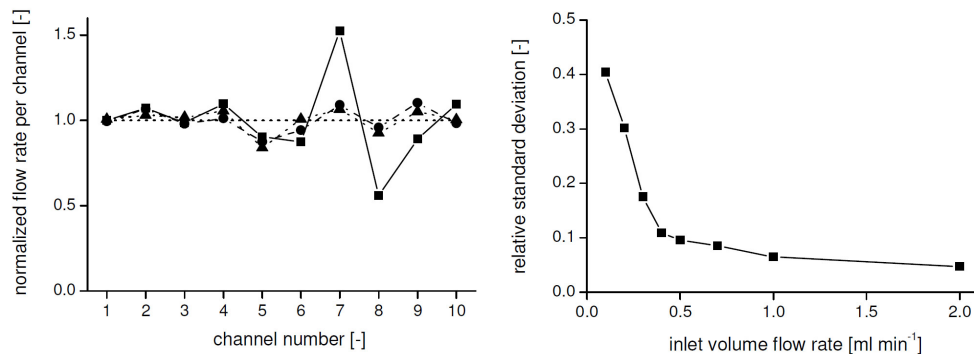
Figure 7.6: Flow distribution over the channels for inlet 2 for water (left). The normalized flow rate per channel is given for different inlet flow rates of water: 0.2 ml/min (■), 0.5 ml/min (●), 1 ml/min (▲). The right figure shows the standard deviation of inlet 2. Channel number 1 is closest to inlet 1 and counted clockwise till number 10 (which is followed by number 1).

A typical flow distribution plot for water for inlet 2 can be seen in Figure 7.6 (left). The normalized flow rate per channel against the channel number is plotted. The inlet to the flow distributor is closest to channel number 3. For an inlet volume flow of 0.2 ml/min the flow maldistribution is very high as can be seen by the fact that channel 7 has about 1.5 times and channel 8 about 0.5 times the flow rate it would have in case of an optimal flow distribution. In Figure 7.6 (right) the relative standard deviation, as a measure for the quality of the flow distribution, is plotted for different inlet flow rates. For higher flow rates the relative standard deviation is lower, so a better flow distribution is obtained. Again two different regions can be distinguished, depending on the inlet flow rate. The relative standard deviation decreases with higher inlet flow rates. The flow rate does not have much influence on

the flow distribution for flow rates higher than 0.5 ml/min. The best flow distribution uniformity has a relative standard deviation of about 5%. The transitional flow rate for this inlet is significantly lower than for inlet 1, because of the 10 μm slit in this distributor. This slit causes a higher pressure drop for lower flow rates and therefore a better flow distribution is obtained. However, at the aimed flow rate of 0.2 ml/min the standard deviation remains rather high.

7.5.3 Simultaneous operation of the inlet sections
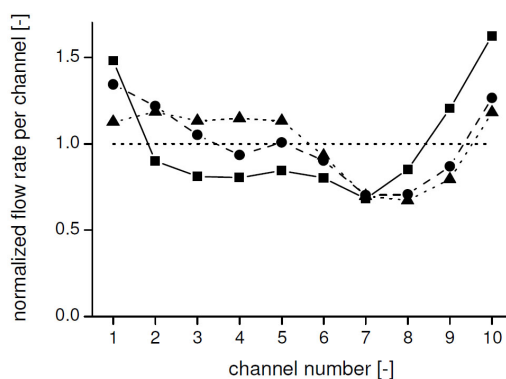
Figure 7.7: Flow distribution over the channels of the glycerol/water mixture fed by inlet 1, with flow ratio of 10 : 1 (inlet 1 : inlet 2). The normalized flow rate per channel is given for different inlet flow rates of the glycerol/water mixture: 1 ml/min (■), 5 ml/min (●), 10 ml/min (▲). Channel number 1 is closest to inlet 1 and counted clockwise till number 10 (which is followed by number 1).

Simultaneous operation of both inlets influences the viscosity of the mixture and has a large influence on the flow distribution over the microchannels. In these experiments only a glycerol/water mixture of 50 mPa·s is used for inlet 1, since glycerol/water mixtures of higher viscosities lead to comparable flow distributions. A nitric acid solution (3.0 M) was used for the side slit inlet (inlet 2). By titration with a sodium hydroxide solution the flow distribution for each inlet could be determined separately. The flow ratio between the two inlets is in all cases 10 : 1 (inlet 1 : inlet 2). The start-up procedure for the experiments is an important factor influencing the flow distribution, when both inlets are tested simultaneously. It is important to first establish a high pressure drop over the channels, before the low viscous liquid is fed into the microreactor. A typical flow distribution plot for inlet 1 is shown in Figure
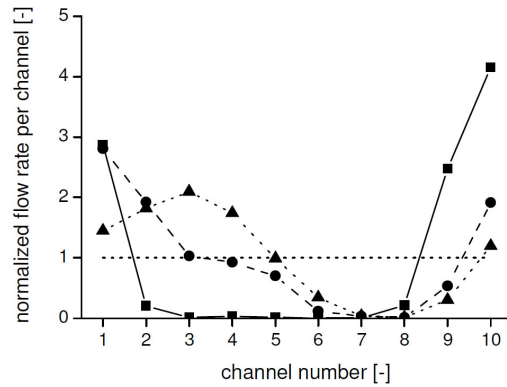
Figure 7.8: Flow distribution over the channels for the nitric acid solution fed by inlet 2, with flow ratio of 10 : 1 (inlet 1 : inlet 2). The normalized flow rate per channel is given for different inlet flow rates of the nitric acid solution: 0.1 ml/min (■), 0.5 ml/min (●), 1 ml/min (▲).
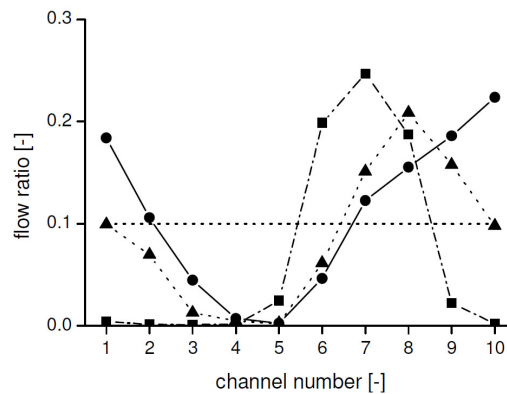
Figure 7.9: Flow ratio per channel of the nitric acid solution to the glycerol/water mixture (50 mPa·s), for an inlet flow ratio of 10 : 1. Results are shown for three different inlet flow rates for inlet 1: 1 ml/min (■), 5 ml/min (●), 10 ml/min (▲).

7.7, while Figure 7.8 shows a typical plot for inlet 2. Large deviations from uniform flow distribution are observed, especially for the nitric acid solution of inlet 2. There are a number of channels for which almost no nitric acid was detected. This can again be explained by pressure drop: there are multiple stable possibilities with the same pressure drop over the channels. A sudden local pressure drop loss in some channels is created by an uneven distribution of low viscous liquid over the channels, at the moment the low viscous liquid is fed into the channels. In order to compensate for this sudden local pressure drop loss, more low viscous liquid will flow through these channels, causing the pressure drop to decrease more. Therefore, a higher volumetric flow rate in these channels is observed to compensate for the differences in pressure drop between the microchannels. That is also why similar trends are observed for both inlets. For higher inlet flow rates the flow distribution is improving slightly, probably due to the fact that the flow distribution for inlet 2 is better in this case. The sudden local pressure drop loss will be better distributed over the channels, causing both flows to be better distributed over the channels. Figure 7.9 shows the flow ratio in the ten individual channels, which should be 0.1 ($\frac{\text{nitric acid solution}}{\text{glycerol/water solution}}$) shown by the dashed line. This flow maldistribution will lead to unequal residence times and deviating flow ratios per channel. In some channels the flow ratio is very close to zero, whereas in other channels the flow ratio is much higher than the inlet flow ratio of 10 : 1 (highly viscous liquid : low viscous liquid). However, for the glycerol/water mixture, the viscosity will decrease with increasing flow ratio, whereas for the liquids used for the Beckmann rearrangement to ε-caprolactam the viscosity will increase with increasing flow ratio, as more cyclohexanone oxime is converted to ε-caprolactam. This will *increase* the viscosity (Chapter 2) instead of decreasing the viscosity as with glycerol/water mixtures that are mixed with water as shown here. This increase in viscosity will probably cause the flow distribution for the Beckmann rearrangement to be slightly better than for the glycerol/water experiments, since higher viscosities will give better flow distribution. Still for the Beckmann rearrangement the flow ratio distribution of the cyclohexanone oxime (4–6 mPa·s) to the reaction mixture (50–300 mPa·s) would resemble the one for the glycerol/water experiments. This flow ratio distribution together with unequal residence times would lead to a lower overall conversion, because in some channels the reaction will not be completed within the length of the microchannels. Since some channels will contain more cyclohexanone oxime, more reaction heat will be produced, causing the

temperature to rise significantly in these channels, leading to a reduced selectivity of cyclohexanone oxime towards ε-caprolactam. If the reaction would not be completed at the end of the channel, the reaction will continue after leaving the channels, without cooling, leading to higher temperatures and again a reduced selectivity. Therefore, the current 10 channel microreactor is not tested with the Beckmann rearrangement of cyclohexanone oxime. Furthermore, the results in Chapter 3 show that the reaction can not be completed within the channel with only a single side inlet. However, the results in Chapter 6 show that premixing the Beckmann rearrangement liquids at low temperature lead to the highest selectivity at low M-ratio. This would eliminate the need of mixing in the microchannels, and the flow distributor investigated in this chapter would be sufficient, as this distributor is well capable of distributing a single high viscous liquid with an acceptable flow distribution with a standard deviation of 3%.

7.6   Concluding remarks

When the inlets were tested separately and at higher flow rates, close to uniform flow distribution over the 10 channels in the microreactor was observed for the experiments with water and the viscous liquid (glycerol/water). At lower flow rates the relative standard deviation, as a measure for the quality of the flow distribution, is dependent on the flow rate. At flow rates above 3 ml/min, the relative standard deviation is constant. The maximum obtained flow distribution uniformity for inlet 1 with water had a relative standard deviation of 5%. For the experiments with highly viscous liquids for inlet 1, better flow distribution was observed for all flow rates in the range of 0.5-10 ml/min, and no transitional flow rate was observed. The maximum flow distribution uniformity had a relative standard deviation of 3%. Better flow distribution was observed for the highly viscous liquids in comparison with the low viscous liquid, because of a higher pressure drop over the channels. For inlet 2, which was only tested with water, the transitional flow rate was observed at 0.5 ml/min, and the maximum obtainable flow distribution uniformity was found to have a relative standard deviation of 5%. The lower transitional flow rate for inlet 2, compared to inlet 1, is caused by the higher pressure drop for this distributor, due to the 10 μm slit in this distributor.

When both inlets were tested simultaneously, inlet 1 with a highly viscous liquid and

inlet 2 with a low viscous liquid, the flow distribution was very poor for both inlets. The explanation for this effect lies in the fact that there are multiple stable possibilities with the same pressure drop over the channels. A sudden local pressure drop loss in some channels was created by an uneven distribution of low viscous liquid over the channels, at the moment the low viscous liquid was fed into the channels. In order to compensate for this sudden local pressure drop loss, a higher volumetric flow rate will occur in this channel to compensate for the differences in pressure drop between the microchannels. With higher flow rates the flow distribution slightly improves, because of better flow distribution for both inlets individually. Because of deviating residence times and flow ratios over the channels, this flow maldistribution will lead to a lower selectivity and overall conversion for the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. Therefore, the current design of the flow distributor is not used for the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam, moreover, the results in Chapter 3 already showed that complete conversion by a single small side inlet is not possible within the microchannel.

However, the work done in Chapter 6 by using two temperatures, one for a mixing zone and one for a reaction zone, could be very beneficial for flow distribution. In this way the liquids are premixed in one premixer where the liquids have a low residence time. These liquids are subsequently distributed over multiple microchannels for a rapid temperature increase. The flow distribution is more straightforward as viscosity of the reaction mixture does not change anymore by the introduction of a second reactant. This would make the use of a straightforward pre chamber distributor, as tested in this chapter, possible, which would certainly simplify the scale up by microreactor technology.

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Conclusions and outlook
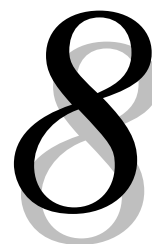
8.1 Conclusions

The research presented in this thesis focusses on the demonstration and feasibility of a microreactor system for one of the main bulk chemical processes in industry, viz. the Beckmann rearrangement of cyclohexanone oxime towards ε-caprolactam. The relevant material properties of the liquids used in this thesis are provided. The microreactor performance, during direct injection of molten cyclohexanone oxime into a mixture of ε-caprolactam and oleum, is discussed. The characteristics of liquid-liquid dispersed flows created by the micromixers in this work are visualized by high speed imaging. The selectivity of the Beckmann rearangement is demonstrated in a number of micromixers for the liquid-liquid dispersed flows. A selectivity enhancement for ε-caprolactam/oleum mixture with a low M-ratio $(([H_2SO_4]+[SO_3])/[\varepsilon\text{-caprolactam}])$ is found for a microreactor system with a low temperature zone for mixing followed by a high temperature zone for complete conversion of cyclohexanone oxime. The flow distribution is studied for a ten channel circular symmetrical microreactor.

The relevant material properties of the liquids used in this thesis are shown. Densities of the measured ε-caprolactam/oleum mixtures vary between 1.54 and 1.38 g/cm^3 and decrease linearly with temperature with an thermal expansion coefficient of around 5×10^{-4} K^{-1}. The density also has a linear relationship with composition. The viscosity of the ε-caprolactam/oleum mixture shows a decrease with temperature and it has a high dependence on the ε-caprolactam/oleum mixture's M-ratio. Lower M-ratio lead to higher viscosities. The solubility of cyclohexanone oxime in cyclooctane is high enough for application as an inert solvent in the Beckmann rearrange-

ment. The surface tension of ε-caprolactam/oleum mixtures decreases with temperature and is the highest for low M-ratios. The surface tensions of cyclooctane with cyclohexanone oxime solutions are much lower compared to the ε-caprolactam/oleum mixtures, however, they decrease with temperature as well. The surface tension of the model liquid glycerol/water has the same magnitude as ε-caprolactam/oleum mixtures at temperatures at which the Beckmann rearrangement is normally conducted (90–120 °C).

Modeling work shows that a side inlet micromixer in the microreactor is not sufficient for mixing a small molten cyclohexanone oxime flow into an ε-caprolactam/oleum mixture. The mass transfer in a single microchannel is mainly taking place by diffusion and convection can be neglected. For a side inlet micromixer the microchannel should be 5.4 m long in order for the reaction to be completed within the length of the channel for an inlet velocity of 0.1 m/s. Rapid viscosity increases are caused by the transfer of cyclohexanone oxime into the ε-caprolactam/oleum mixture, which can lead to different reaction pathways. A diffusion path of the cyclohexanone oxime stream between 2 and 5 μm was shown to be sufficient for mixing of the liquids in the microchannel. For this diffusion path the reaction is completed within the length of the microchannel (50 cm) for an inlet velocity of 0.1 m/s and would still have a residence time in the range of seconds, therefore a split-and-recombine micromixer is an excellent candidate for the direct reaction of cyclohexanone oxime and an ε-caprolactam/oleum mixture. The reaction of molten cyclohexanone oxime in a split-and-recombine mixer is possible at relatively high M-ratio with high selectivity. However, already at M-ratios of 2.0 the split-and-recombine mixer is repeatedly blocked by viscous by-products of the Beckmann rearrangement. Therefore, other possibilities for intensifying the mixing are needed. This makes the use of an inert solvent for cyclohexanone oxime necessary to reach higher selectivity and prevent blockage of the split-and-recombine micromixer.

The liquid-liquid flow behavior of an ε-caprolactam/oleum mixture with a cyclohexanone oxime in cyclooctane solution is modeled by the liquid-liquid flow of glycerol/water with cyclooctane. These model liquids have comparable liquid properties as the liquids used for the Beckmann rearrangement. This makes study of the liquid-liquid flow behavior possible at room temperature by a high speed camera equipped microscope. Flow regime maps as a function of the velocities of the continuous and dispersed liquid phases show various patterns as Taylor slug, drop, Taylor slug with

droplets, slug with overlapping droplets, ring and inverted slug, wavy and inverted drop and wavy with inverted drops. Larger interfacial surface area is created by mechanical means of the mixer design, where the split-and-recombine mixer results in the most intense liquid-liquid contact (20.000 m^2/m^3), larger shear forces (higher velocities and viscosities) increase the interfacial surface area as well. Correlations of liquid hold up with flow quality and slug velocity with overall superficial velocity of the liquids are obtained and shows the volume fraction of the continuous and dispersed phase as a function of the overall flow conditions. The slug velocity is found to be twice as large as the overall superficial velocity, therefore the residence time of the dispersed phase is considerably shorter compared to the continuous phase. The cyclooctane slug length increases with increasing cyclooctane velocity. The slug length increases extremely if $U_{co}/U_{gw} > 1$; ratios larger than 1 will decrease the interfacial area drastically, which can cause major problems when performing a liquid-liquid reaction in this regime. The interfacial area between the glycerol/water mixture and cyclooctane in case of the split-and-recombine mixer is in the order of 20.000 m^2/m^3 and larger by a factor of 2-3 compared to Taylor slug flow in the interdigital and the Y-type micromixers for the same velocity conditions. Taylor slugs with uniform droplets in the continuous phase give a high interfacial area at low velocity (0.08 m/s) in split-and-recombine mixer. This shows that the split-and-recombine mixer gives better mixing efficiency at a low velocity range.

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.

<u>Y–mixer.</u> 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.

<u>Interdigital mixer.</u> 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%.

<u>Split-and-recombine mixer.</u> The application of the split-and-recombine mixer

provides a broader range of conditions (M-ratio of 2.6 to 2.0) for which the selectivity is above 99%, compared to 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 towards ε-caprolactam at selectivities of 99%. As the Ca number is approximately 0.5 for this higher ε-caprolactam concentration, the lower selectivities are attributed to a decrease in recirculation in the liquid packages of the dispersed flow, and therefore less mass transfer, in the liquid slugs.

The continuous production of ε-caprolactam is possible in a recycle reactor, which is a demonstration of the reliability of the microreactor with hazardous chemicals. The same selectivity is found within experimental error to former experiments at the same conditions.

Pyrosulphuric acid. Experiments where the composition of the reaction mixture, a mixture of mostly $CPLH^+$, SO$_3$ and H$_2$SO$_4$, has a molar ratio of unity for SO$_3$ and H$_2$SO$_4$, show remarkably lower selectivities. Y-mixer, interdigital mixer, and split-and-recombine mixer lead to selectivities decreased by 2 to 5%, if compared to experiments with a double amount of cyclohexanone oxime. The pyrosulphuric acid equilibrium is suggested to influence selectivity because less SO$_3$ or H$_2$SO$_4$ is available as catalyst and/or dehydration agent if the molar ratio is unity.

A selectivity enhancement for an ε-caprolactam/oleum mixture with a low M-ratio (the $([H_2SO_4] + [SO_3])/[\varepsilon$-caprolactam] is between 1.4–1.7) is found for a microreactor system with a low temperature zone for mixing followed by a high temperature zone for complete conversion of cyclohexanone oxime. A lower temperature of 65 °C is used for mixing, whereas rapid heating in a microchannel to 100 - 127 °C is used to completely convert cyclohexanone oxime into ε-caprolactam at high selectivity at high temperatures for the Beckmann rearrangement. Selectivities around 99% were measured for these samples. This is a very large increase in selectivity for this low value of the M-ratio (1.7 - 1.4). Selectivity should be optimized for conditions with an M-ratio as low as possible as less ammoniumsulphate co-product is formed in this way. As the conversion of cyclohexanone oxime can take place at higher temperatures more of the reaction heat could be reused in other processes,

making the Beckmann rearrangement to ε-caprolactam more energy efficient. However, a careful analysis of the process economics is therefore needed.

The flow distribution of the circular symmetrical ten channels microreactor is acceptable for high viscosity liquids with a considerable pressure drop over the microchannels. The flow distribution shows a maldistribution when operated with mixing liquids of dissimilar viscosity. The change in the viscosity causes pressure fluctuations, which results in an uneven flow distribution over the channels. However, the work done in Chapter 6 by using two temperatures, one for a mixing zone and one for a reaction zone, could be very beneficial for flow distribution. In this way the liquids are premixed in one premixer where the liquids have a low residence time. These liquids are subsequently distributed over multiple microchannels for a rapid temperature increase. The flow distribution is more straightforward as viscosity of the reaction mixture does not change anymore by the introduction of a second reactant. This would make the use of a straightforward pre chamber distributor possible, which would certainly simplify the scale up by microreactor technology.

8.2 Outlook

Microreactor systems have the potential of being used for their excellent heat transfer for industrial applications. However, the mass transfer in microchannels remains a challenging issue as mixing is only possible by diffusion on the micro scale. In this study it is shown that mixing is one of the key parameters of the Beckmann rearrangement. However, making the dimensions of the mixers even smaller than used in this study makes the application of microreactors unlikely as physical blockage of the microchannels and micromixers can not be prevented practically. Therefore, other possibilities need to be considered. Mixing of viscous liquids is very well possible with more macroscale static mixers, where the linear velocities can be kept very high to maintain a very small residence time. However, this is only possible when the reaction can be prevented from occurring inside of the mixer, as this would lead to run-away reactions of the Beckmann rearrangement. This can be done by introducing the liquids at a low temperature, as was a done in Chapter 6 with a micromixer. The use of a macro static mixer at low temperature has more potential as the pressure drop is far less compared to micromixers. The outlet of the static mixer can feed a considerable amount of microchannels, which make a rapid increase in temperature possible

and at the same time prevent run-away reaction by a too rapid increase of temperature. This approach shows potential for the application in industry as the application of macro static mixers is already proven technology in that area. The application of multiple microchannels with a fractal structure or bifurcation of the channels will provide an acceptable flow distribution, which can be used for rapid heat exchange. This is a smaller hurdle to take as compared to combined mixing and heat exchange in a microreactor.

List of symbols

Roman Symbols

a	Layer thickness of cyclohexanone oxime	m
a	Specific surface area	m^2/m^3
A	Cross sectional area of the microchannel	m^2
A_{ch}	Cross sectional area reaction channel	m^2
A_m	Cross sectional area metal	m^2
b	Layer thickness of oleum/ε-caprolactam	m
b	Constant for liquid hold up of cyclooctane	-
Ca	Capillary number; $Ca = \mu_d u_d / \sigma$	-
c_a	Concentration of cyclohexanone oxime	mol/m^3
c_i	Concentration component i	mol/m^3
$C_{p,R}$	Heat capacity reaction mixture	J/kg·K
ΔC	Concentration difference between two phases	mol/m^3
d	Layer thickness of cyclohexanone oxime	m
d	Diameter	m
D	Diffusion coefficient	m^2/s
Da_{II}	The second Damköhler number; $\mathrm{Da}_{II} = \frac{kC_0^{n-1}}{k_g a}$	-
d_c	Characteristic length	m
D_{eff}	Effective diffusion coefficient	m^2/s
D_0	Diffusion coefficient at the inlet temperature	m^2/s
E_{act}	Activation energy	kJ/mol
f	Liquid-liquid interface location	m
F	Mass transport across the two phase interphase per reactor volume	$mol/m^3 s$

$\bar{F}$	Mean flow rate per channel	ml/min
F_{cap}	Total amount of ε-caprolactam and converted oxime in the product reaction mixture	g
F_{capsyn}	Amount of ε-caprolactam in the synthetic mixture	g
F_i	Flow rate per channel	ml/min
F_{oxime}	Amount of converted cyclohexanone oxime in the product mixture	g
FQ	Flow quality	-
g	Width of reaction mixture	m
ΔH_R	Reaction enthalpy	J/mol
k	Mass transfer coefficient	m/s
k_g	The global mass transport coefficient	m/s
k_0	Pre-exponential factor	s^{-1}
Le	Lewis number; $Le = \alpha/D$	-
M-ratio	$([H_2SO_4] + [SO_3])/[\varepsilon\text{-caprolactam}]$	-
n	Number of channels	-
R	Gas constant	kJ/mol·K
r_a	Reaction rate of cyclohexanone oxime	mol/m^{3}s
Re	Reynolds number; $Re = \frac{\rho d v}{\mu}$	
r_i	Reaction rate of component i	mol/m^{3}s
r_{main}	Reaction rate of main component	mol/m^{3}s
S	Scaling factor	m
S_{max}	Maximum selectivity	%
S_{proc}	Selectivity process	%
t	Time	s
T_c	Temperature of the cooling liquid	K
T_m	Temperature of the metal	K
T_R	Temperature of the reaction mixture	K
$T_{R,in}$	Inlet temperature of the reaction mixture	K
O_{ch}	Perimeter reaction channel	m
O_{cool}	Perimeter cooling channel	m
p	Pressure	Pa

Pe	Peclet number; $Pe = d_c \cdot v / D$	-
P_{prod}	Purity of ε-caprolactam in the product mixture	%
P_{syn}	Purity of ε-caprolactam of the synthetic mixture	%
u	Velocity vector	m/s
U_a	Superficial velocity of liquid a	m/s
u_a	Local velocity of liquid a	m/s
U_C	Overall heat transfer coefficient cooling liquid	W/m^{2}K
U_{co}	Superficial velocity cyclooctane	m/s
u_d	Velocity dispersed phase	m/s
u_{dl}	Dimensionless velocity	-
U_g	Gas superficial velocity	m/s
U_{gw}	Superficial velocity glycerol/water	m/s
U_l	Liquid superficial velocity	m/s
U_R	Overall heat transfer coefficient reaction mixture	W/m^{2}K
U_{tot}	Total superficial velocity	m/s
v	Mean velocity liquid	m/s
V_a	Volume occupied by liquid a	m^3
v_{avg}	Average velocity liquid	m/s
V_b	Volume occupied by liquid b	m^3
w	Total width of channel	m
w_{oleum}	Weight fraction of oleum	-
x	x-coordinate	m
z	z-coordinate	m
$\hat{z}$	Scaled z-coordinate	-

Greek Symbols

α	Thermal diffusivity	m^2/s
ε_a	Liquid hold up of liquid a	-
ε_{co}	Liquid hold up of cyclooctane	-
ε_g	Gas hold up	-
η	Viscosity	Pa $\cdot$ s
λ_m	Heat conductivity of the metal	W/m·K
λ_R	Heat conductivity of the reaction mixture	W/m·K
μ	Viscosity	mPa·s
μ_d	Viscosity dispersed phase	mPa·s
μ_0	Inlet viscosity	mPa·s
ρ	Density	kg/m^3
ρ_R	Density of the reaction mixture	kg/m^3
σ	Surface tension	N/m
σ_r	Relative standard deviation of flow distribution	-

List of publications

Journal Publications

- Zuidhof, K.T., Croon, M.H.J.M. de, Schouten, J.C. (2010). Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam in microreactors. AIChE Journal, 56(5), 1297-1304.

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- Zuidhof, K.T., Croon, M.H.J.M. de, Schouten, J.C. (2008). Micro reactor application for the Beckmann rearrangement to ε-caprolactam. Proceedings of the 10th International Conference on Microreaction Technology (IMRET-10), April, 06-10 2008, New Orleans, La. (pp. 83f). New York, NY: AIChE.

- Zuidhof, K.T., Croon, M.H.J.M. de, Schouten, J.C. (2008). Determination of the selectivity of the Beckmann rearrangement to caprolactam in a micro reactor. In H. Komiyama (Ed.), Green Chemical Reaction Engineering for a Sustainable Future. Proceedings of the 20st Int. Symp. on Chemical Reaction Engineering (ISCRE-20), 7-10 September 2008, Kyoto, Japan. (pp. 320-321). Society of Chemical Engineers, Japan.

- Zuidhof, K.T., Croon, M.H.J.M. de, Schouten, J.C. (2008). Influence of micro mixers on the selectivity of the Beckmann rearrangement to caprolactam. Proceedings of the IXth Netherlands Catalysis and Chemistry Conference (NCCC IX), 03-05 March 2009, Noordwijkerhout. (pp. 127-127).

- Zuidhof, K.T., Croon, M.H.J.M. de, Schouten, J.C. (2008). Influence of reactant mixing on selectivity towards ε-caprolactam in the Beckmann rearrange-

ment of cyclohexanone oxime in a micro reactor. 1st Smart Synthesis and Technologies for Organic Processes Conference (SYNTOP). Germany, Potsdam.

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- Zuidhof, K.T., Croon, M.H.J.M. de, Schouten, J.C. (2007). Micro reactor application for the Beckmann rearrangement to ε-caprolactam. Netherlands Process Technology Symposium 2007 (NPS 7), 28-30 October 2007, Veldhoven, The Netherlands. (pp. p.-54). Netherlands, Veldhoven.

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About the author

Niek Zuidhof was born in Geldrop on May 24th, 1980. He finished general secondary education (VWO) at the Strabrecht college in Geldrop in 1998. After this he continued his education at the Eindhoven University of Technology. In 2004 he obtained his M.Sc. in Chemical Engineering on the topic of "The oxidation of ethane on CuO in a microreactor" in the group of prof.dr.ir. J.C. Schouten. In 2004 he started his Ph.D. research at the Laboratory of Chemical Reactor Engineering under the supervision of dr. M.H.J.M. de Croon, and prof.dr.ir. J.C. Schouten. His work focused on the development, testing, and modelling of the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam in microreactors. Currently, he is working as a process engineer on the development of thin film solar cells in the Research and Development group of Scheuten Solar and TNO Research in Venlo and Eindhoven.