Continuous metal scavenging with a flow liquid-liquid extraction unit

Continues liquid-liquid extraction using coiled flow inverter

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Abstract

Development of microscale equipment is mainly focused on reaction, mixing and heat transfer, however for implementation in the process industry also separation is required. In particular, equipment is missing that suits (i) the integration in a full-flow chain (ii) and production capacities of kilo- and pilot-labs in industry, which amounts to product- and solvent flows of 1-10 kg/day and 10-100 l/day. A new device called coiled flow inverter enhances mixing by inverting the flow due to 90° bends can be utilized for extraction purposes.

The goal of this project was to investigate immiscible liquid-liquid extraction with a coiled flow inverter operated in segmented flow mode combined with online phase separation – to characterize performance and to exploit range of capacity increase as compared to smaller single straight tube of same flow pattern. To do so the flow pattern within the CFI is studied, extraction performances are measured and compared with a straight tube and a membrane and slit separator are used for phase separation. To do these tests two model systems with different interfacial tension were used as advised by the European Federation of Chemical engineering (EFCE), water-acetone(10wt%)-toluene (17.8 mN/m) and water-acetone(10wt%)-butyl acetate (9.2 mN/m).

First the partition coefficient was measured using the shake flask method and compared to literature. The partition coefficients found are 0.86 wt/wt and 0.98 wt/wt for the toluene and butyl acetate system respectively, this corresponds with values found in literature (EFCE). Based on these values the equilibrium concentration and extraction efficiency are calculated.

Flow pattern maps for both model systems were made and it was found that the slug length does not increase with increasing flow rate as long as the aqueous volume fraction remains constant. When changing the aqueous volume fraction it was found that for the toluene system slugs lengths varied from three times tube length to one tube length. For the butyl acetate the slugs varied from 5 times the tube length for high aqueous volume fractions to drop flow for low aqueous volume fraction.

Concerning the extraction efficiency the toluene and butyl acetate system show similar behavior and comparable performance within the CFI. The difference in interfacial tension does not have a significant effect in the extraction efficiency, both systems reach efficiencies above 90%. Comparing both model systems with a straight tube show that the CFI shows better performance at higher flow rates most likely due to flow inversions and Dean vortices. For systems with lower interfacial tension the advantage of the CFI can already be seen at flow rates of 10 ml/min where for high interfacial tension systems the advantage starts at 30 ml/min. One of the remarkable differences between the CFI and the straight tube is the development of a parallel flow within the straight tube at high flow rates while the CFI maintains operating in the slug flow regime. Parallel flow can be seen at 50 ml/min and 40 ml/min for the toluene and butyl acetate system respectively.

The effect of the aqueous volume fraction on the extraction performance was studied. The difference in interfacial tension causes the slightly lower performance (~10%) at low aqueous fraction for the butyl acetate test system when using the CFI. When increasing the aqueous volume fraction, and thus the aqueous slug length, it was found that the straight tube shows a lower extraction efficiency. This can be caused by the larger stagnant zone within the aqueous slugs. The CFI performed better at these parameters because of its flow inversions which mixes the stagnant zone, and causing an increase in the surface-to-volume ratio.

Online phase separation was tested using a slit separator for a slit height of 0.4 and 0.8 mm, and by using a 0.5 μm Zefluor PTFE membrane in an IMM microreactor. Entrainment of the organic phase was observed using the membrane hence 20% of the retentate was organic phase for flow rates of up to 20 ml/min. Higher flow rates were not tested due to the large pressure drop over the membrane. Although it was expected for the slit height of 0.8 mm to perform better compared to 0.4 mm (based on theoretical calculation) the contrary was observed. Using a slit height of 0.4 mm a maximum of 20% breakthrough was observed for flow rates up to 120 ml/min and 32 ml/min for the toluene and butyl acetate test system respectively.
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1. Introduction

Over the past few years new devices were developed to reduce residence time, show better mixing performance, improve heat transport and have improve safety. These points are referred to by Hessel et al. [1] as transport intensification. Modern devices as spinning-disk, membrane reactors, micro- and millireactors are notable examples to exploit the transport intensification principles. Among these, microreactor technology is considered to be most potential in process intensification [1]. Microprocess technology is defined as miniaturized reaction systems with characteristic dimensions of internal structures ranging from sub-micrometer to sub-millimeter regime [2]. One of the advantages of microprocessing are the short diffusion paths for heat and mass transfer due the extremely large surface-to-volume ratios. The decrease in linear length scales will reduce volume, heat loss etc. Aside from that, the miniaturized unit operations require less space, energy and materials.

Using these short scales has opened a new field of opportunities the so called Novel Process Windows (NPW)[1]. NPW constitute a chemical intensification field with so far hardly or non explored process windows (e.g. for temperature, pressure, concentration, or solvent choice), major part of flow chemistry uses that idea. NPW also offer new horizons in process design with regard to integration and simplification. At the edge of chemical and process-design intensification are new chemical transformations which need input from both NPW sides. Especially those flow reactions need a proper online flow integration and demand for proper flow separations, this is this study is focused on.

![Figure 1.1: A schematic view of the Novel Process Windows [1].](image)

The majority of the research in the microprocess field has been focused on reaction, mixing and heat-transfer. Some research has also been done on micro distillation, adsorption/desorption and liquid-liquid extraction for purification [2, 3]. Liquid-liquid extraction has generated most interest to be used in microscale processing [4]. In microdevices surface tension forces dominate over gravitational, viscous and shear forces this causes liquid-liquid flow to have predefined flow patterns. Extraction requires good mixing and enhanced mass transfer a coiled flow inverter (CFI) has the potential to be a very good device for microextraction.

Domination of the surface tension force makes conventional phase separation methods based on gravity and density differences not applicable. Separation of flows consisting of immiscible liquids can be based on capillary forces in the channels of the microdevice, coated channel walls, membranes and preferential wettability. Performing reaction, extraction and phase separation online the system will fit in the NPW of process simplification & integration.
1.1. Problem statement

Previous work has shown that homogeneous metal catalysts extraction can successfully be combined with reaction in microscale flow equipment. However the industry demands larger throughputs and thus scale up of the equipment.

1.2. Objectives

The objective of the study is to investigate immiscible liquid-liquid extraction with a coiled flow inverter (CFI) combined with online phase separation.

- Determine which flow patterns are within the coiled flow inverter, i.e. if segmented flow can be maintained at high flow rates and how its flow pattern map looks like.
- Characterize the performance of the coiled flow inverter in single stage liquid-liquid extraction, and explore possible capacity limits of operation.
- Design a setup for continuous liquid-liquid extraction at high flow rates with online phase separation.
- Achieve phase separation with a minimal amount of breakthrough.
- Compare extraction performance of the CFI with the extraction performances of a straight tube.
- Demonstrate scale up by operation at a solvent capacity potentially close to pilot-scale (10-100 l/day).

1.3. Scope of study

The study will mainly focus on extending previous work [5] to higher flow rates and research in this process windows above mentioned performance criteria. The range of flow rates to be tested is chosen to be 2-120 ml/min. Two phase separation devices were tested which separate on the principle of preferential wettability, namely a membrane separator and a slit separator. A comparison was made between the CFI and a straight tube.
2. Theory
2.1. Microfluidics

Flow chemistry in microscale equipment is defined by the characteristic dimensions of the internal structure. Fluid channels in this scale typically range from sub-micrometer to the sub-millimeter scale. Some advantages of this technique are as follows [1]:

- Unique flow: laminar flow for single flows or defined multiphase flows.
- Short diffusion paths for heat and mass transfer.
- High surface-to-volume ratios for phase contact areas.
- High share of solid wall material, leading to a short path to the catalyst.

These advantages make microscale systems suitable for liquid-liquid extraction. Short diffusion paths and high surface-to-volume ratios mean fast mass transfer and thus short residence times. The defined multiphase flow patterns make two phase flow very controllable for e.g. separation. Several studies have been performed on the control and changing of the flow pattern [6, 7]. Figure 2.1 shows six different flow patterns as defined by Kashid et al. [8]. These different flow patterns can be induced by changing the two-phase velocity, flow rate ratio or the use of internally structured microchannels.

![Figure 2.1: Examples of possible flow regimes in a microchannel. [8]](image)

The differences and advantages of microscale operation compared to macro scale operation can be explained by the difference in dominant forces. Important forces that play a role in fluid dynamics are: gravitational, surface tension, viscous and inertia forces. Microscale operations are characterized by the dominance of surface tension forces over the other forces, which is in contrary with macroscale operations. The extent to which forces dominate over others can be expressed in dimensionless numbers, table 2.1 gives an overview of some relevant dimensionless numbers, what ratio they represent and typical micro values.

### TABLE 2.1: IMPORTANT DIMENSIONLESS NUMBERS FOR MICROSCALE OPERATION [9].

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Physical interpretation</th>
<th>Typical micro value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond number</td>
<td>( \frac{\rho L^2 g}{\mu} )</td>
<td>gravitational force over surface-tension force</td>
<td>( 1 \cdot 10^{-3} )</td>
</tr>
<tr>
<td>Capillary number</td>
<td>( \frac{\mu u}{\sigma} )</td>
<td>viscous force over surface-tension force</td>
<td>( 1 \cdot 10^{-4} )</td>
</tr>
<tr>
<td>Weber number</td>
<td>( \frac{\rho L^4 u^2 g}{\mu} )</td>
<td>inertial force over surface-tension force</td>
<td>( 1 \cdot 10^{-7} )</td>
</tr>
</tbody>
</table>
Slug flow (A in figure 2.1) is defined as a type of two phase flow pattern that consists of elongated slugs with equivalent diameter usually many times that of the channel diameter, separated by slugs of a different phase [10]. Which phase forms the slugs (round edged) and which phase forms the continuous phase is influenced by the channel wall and the affinity of the phases with the channel wall. One of the great advantages in slug flow is that of a finite number of 90 degree bends at equal intervals along the length of each circulation which permits precise tuning of the flow rate down to 1 mL/h. Slug flow with the impinging stream contactor (Fig. 2.2) to a symmetric 120° Y-piece mixing element made of acrylonitrile butadiene styrene (ABS) with one inlet and two outlets to separate the two immiscible liquid phases (aqueous and organic), as illustrated in Figure 3. The splitter was comprised of Teflon with a steel internal diameter, being fitted into one of the outlets. The splitter element with one inlet and two outlets to separate the two liquid phases. The operat-

2.2. Micromixing

Mixing in macroscopic systems is mainly carried it in the turbulent regime. Microscopic systems which are governed by laminar flows usually relies on diffusive or convective mixing. In order to perform mixing in microscopic systems active or passive mixers are applied. Figure 2.3 shows some examples of passive and active mixers. The main difference between those categories is the external energy input needed for mixing. Active mixers require an external force for mixing, e.g. a pressure disturbance. Passive mixers however mix without external forces, but use flow forces induced by pumps and micro structures to mix the liquid. Passive mixers are easier to fabricate and provide adequate flow rates as needed in chemical process industry [3, 12].

![Micromixer classifications](image)

Figure 2.3: Micromixer classifications [3].

Multilamination and split-and-recombine mixers are common ways to perform diffusive and convective mixing respectively. For convection, the concept of chaotic advection is also a major sub principle. Chaotic advection can be achieved with alternating helical flows, curved microchannels like bent, spiral or helical coils which are easy to fabricate have shown to offer effective mixing due to the chaotic advection [3].

Static mixers with internal structures have limitations for very viscous fluids since it can cause severe pressure drop which can result in high pumping costs. A coiled flow inverter (CFI) was developed by Nigam to overcome this limitation [13, 14]. The configuration of a CFI consists of a finite number of 90 degree bends at equal intervals along the length of
the tube. A schematic view of a coiled flow inverter is shown in figure 2.4 below, the figure also shows an images of the flow inversion induced by the bends. The CFI has also been realized as 2-D planar version in chip format as helical micromixer with similar benefits reported.

![Figure 2.4: Schematic view of a coiled flow inverter with three bends and velocity profile within the tube][15]

A way to describe the amount of Dean vortices is the dimensionless Dean number (see equation 1). Dean vortices are induced by turns within a channel, thus repeating these turns will allow the Dean effect to intensify a helical coiled tube uses this principle. Within the CFI these vortexes will be inverted creating even more chaotic advection and thus reducing the axial dispersion. Figure 2.5 show the velocity vectors in a CFD simulation of a CFI at different Dean numbers to show the development of Dean vortices, it can be seen that at Dean = 70 the Dean vortices are fully developed. The large amount of axial mixing in the CFI reduces the amount of back-mixing and makes the CFI tends towards ideal plug flow [9, 15, 16].

\[
De = Re \sqrt{\left(\frac{D}{R}\right)}
\]  

Figure 2.5: CFD simulation velocity vectors in a CFI (d_t =0.5mm) at different Dean numbers [17].
2.3. Microextraction and phase separation

To perform microextraction good dispersion, contacting and constant phase separation of two immiscible phases is needed. Macroscale extraction is usually performed in large columns using dispersions. Enhanced mixing can be achieved using microscope equipment due to the higher surface-to-volume ratio and shorter diffusion paths [1]. Some of the above mentioned micromixers and also the CFI can be used both for single- and two-phase mixing (as needed for extraction). In some cases specialized two-phase micro-flow contractors exist, which are here however not considered because their scale-up is deemed more difficult as for the fist mentioned equipment.

In microscale equipment multiphase flows have defined patterns, hence there are multiple ways to contact the organic and the aqueous phase. Using guided structures or surface-treated channel walls one can achieve phase separation all along the channel path, while still allowing a contact interface [18]. Membrane contactors for extraction and separation have been developed, but have a relative small contact area. Micromixers which create fine dispersions of droplets which are typical below 50 μm, (e.g. interdigital mixers) make use of an even shorter diffusion path and large interfacial areas [19-22].

However there remains an issue to separate the phases, a solution is extraction performed in slug flow. In parallel flow the mass transfer is diffusion driven whereas in slug flow rapid extraction can be achieved due to internal circulations [2]. Utilizing a chaotic advection mixer like a CFI can enhance the convective mass transport. Being able to separate the two phases easily when using slug flow is a major advantage. Several researches have been done on the concept of slug flow microextraction see Table 2.2 [11, 21, 23, 24].

**TABLE 2.2: STUDIES CONCERNING EXTRACTION IN SLUG FLOW REGIME [11, 21, 23, 24].**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Operational conditions</th>
<th>System</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kralj et al. (2007)[21]</td>
<td>0.3 x 0.4 x 0.15 (W x L x D mm)</td>
<td>DCM/DMF/Water</td>
<td>Thermodynamic equilibrium is achieved with slug flow regime</td>
</tr>
<tr>
<td>Kashid et al. (2007)[11]</td>
<td>ID: 0.5 – 1 mm L: 100 – 300 mm 5 – 60 mL/h</td>
<td>Kerosene/acetic acid/water Water/iodine/kerosene Water/succinic acid/butanol</td>
<td>90% efficiency, increase in flow rate extraction performance drops due to mass-transfer limitations Thermodynamic equilibrium achieved with slug flow regime</td>
</tr>
<tr>
<td>Jovanovic et al. (2012)[24]</td>
<td>ID: 0.25 mm L: 400 mm 6 – 36 ml/h</td>
<td>Toluene/2-butanol/water</td>
<td></td>
</tr>
<tr>
<td>Okubo et al. (2008)[23]</td>
<td>ID: 0.5 – 1 mm Up to 300 ml/h</td>
<td>Dodecane/phenol/water</td>
<td>90 % extraction in 100 s, increase performance with increased flow.</td>
</tr>
</tbody>
</table>

After extraction, in macro scale often separation methods like settling or distillation are used [25]. In microscale the use of a separator which uses the principle of preferential wettability of a liquid on a solid material is more common [2] e.g. coated channel walls, membranes (fig 2.6) or slit separators (fig 2.7). In these separators the aqueous phase has strong affinity with steel [11] or glass [26], whereas the organic phase shows strong affinity with e.g. teflon or hydrophobic membranes [22]. This technique is very well suitable for use in microscale since surface tension forces dominate rather than gravitational forces.
There is however a constraint with these separation techniques; the pressure difference between the hydraulic pressure and the capillary pressure. If the hydraulic pressure (which is induced by the pumps) of one phase exceeds the capillary pressure of the membrane, or the slit for which it does not have preferential wettability, breakthrough will occur and the phases are not fully separated [21, 22, 26, 27]. Membranes are held by micro devices (as shown schematically in figure 2.6) the design of the micro device is very important. If e.g. the channels are too deep, the phase that is supposed to flow through the membrane will not have proper contact with the membrane and will be entrained by the retentate.

![Figure 2.6: Schematic view of a membrane [21].](image)

A slit separator was developed by Gaakeer et al. [26] that uses glass and teflon bars with stainless steel spacers, these bars and spacers make it possible to vary the height of the slit from 0.1 to 2.0 mm this makes it suitable for a wide range of systems and flow rates. Figure 2.7 shows a schematic view of the slit separator, the flow divider at the top of the devices flattens the velocity profile for better separation.

![Figure 2.7: Schematic view of slit separator device [26].](image)
3. Experimental

To measure the extraction performance of the system two test systems as recommended by the European Federation of Chemical Engineering (EFCE) [28] were used and are stated in table 3.1. The two selected systems are used with a concentration of 10 wt% acetone based on previous studies [5, 19].

**TABLE 3.1: MODEL SYSTEMS TO EVALUATE THE EXTRACTION PERFORMANCES OF THE CFI.**

<table>
<thead>
<tr>
<th>Model systems</th>
<th>Raffinate phase</th>
<th>Component</th>
<th>Extract phase</th>
<th>Δσ* [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water</td>
<td>Acetone</td>
<td>Toluene</td>
<td>17.8</td>
</tr>
<tr>
<td>2</td>
<td>Water</td>
<td>Acetone</td>
<td>n-Butyl-acetate</td>
<td>9.2</td>
</tr>
</tbody>
</table>

*Interfacial tension [29]*

3.1. Used equipment

The setup used in the experiments is shown in figure 3.1. Two syringe pumps of type Chemyx Fusion 200 syringe infusion pumps. Three syringes are connected to a 1/8” outer diameter (OD) PFA tube with 1.55 mm inner diameter (ID). The tubes are connected to a union cross (1) (1/8”) where the aqueous phase enters from the side (and the organic phase enters in the centre (blue and clear liquid in fig 3.1 respectively). After the union cross the tube will extent to a PFA tube with 1/4” OD and 1/8” ID which was used in the coiled flow inverter (2). The PFA tube is coiled around a steel cylinder of 1” OD (resulting in a curvature ratio of 10) and has three 90° bends resulting in a total length of 2130 mm. Leaving the CFI the tube narrows to 1/16” OD and 400 μm ID which leads to the separation device (3), fig 2.7 shows a schematic view of the slit separator. To drain the slit separator two 1/16” OD and 400 μm ID PFA tubes are connected to the bottom of the device and lead to the waste collector, during running experiments no flow was observed in these tubes. The slit separator was compared to a membrane separator where a 44 mm x 14 mm 0.5 μm Zefluor membrane, cut from a round 47 mm disk, was placed in a MMS-V3-sus micro reactor made by IMM (10 channels of LxWxD = 38 mm x 500 μm x 280 μm).

![Figure 3.1: Experimental setup used for flow map, performance characterization and separator performance.](image-url)
For the comparison of the performance of the CFI with the straight tube the setup shown in figure 3.2 was used. The straight tube was put in one big coil since the size of 2130 mm made the setup too large to fit in the fume hood. It is assumed the coil is large enough to neglect the formation of Dean vortices and assume it can be.

![Figure 3.2 Experimental setup for comparison CFI with straight tube.](image)

3.2. Flow map

The flow map was constructed using a (blue) colored aqueous phase and a clear organic phase to be able to distinguish the two phases. The aqueous phase was colored by dissolving 5 g/L stock solution methylene blue, made from solid methylene blue from Sigma Aldrich, into demineralized water until a light blue color was seen. The pictures at high flow rates (> 10 ml/min) were taken with a MotionPro X3 high speed camera with a Canon lens mounted. Acetone was left out of both systems, which influences the interfacial tension, how acetone influences the interfacial tension can be found in appendix II.

For the toluene test system (table 3.1) the pictures at low velocity are also taken with the high speed camera at the exit of the CFI. For test system two (table 3.1) the pictures at low flow rates are taken with a Canon EOS 400D SLR camera. These pictures are taken at the inlet of the CFI due to extraction of methylene blue by the butyl acetate which made it difficult do distinguish the organic and the aqueous phase. Setup as shown in figure 3.1 was used for these experiments where the slit separator has a slit height of 0.4 mm.

3.3. Extraction performances

The extraction performances in terms of the extraction efficiency (calculated via 2) is studied as a function of the total flow rate and aqueous volume fraction at a fixed flow rate. The aqueous volume fraction is defined as the aqueous flow rate divided by the total flow rate. First the partition coefficient had to be determined as a function of the aqueous volume fraction, the method provided by the OECD guidelines for testing [29] was used.

\[
E = \frac{C_{2,\text{out}} - C_{2,\text{in}}}{C_{2,\text{sat}} - C_{2,\text{in}}}
\]

(2)

The concentration at the inlet is equal to 0 since no acetone is added to the organic phase in the beginning, the outlet concentration is measured using a GC-FID. Calibration curves of both test systems can be found in appendix I.
24.32 gram acetone (≥99.5% pure ACS reagent, Sigma Aldrich) was dissolved in demineralized water in a 250 ml volumetric flask, yielding a 10 wt% acetone solution. Two Terumo 20 ml syringes are filled with the solution and connected to the setup. One 50 ml HSW syringe is filled with clean organic phase (≥99.5% pure ACS reagent, Sigma Aldrich). The CFI is filled with the mixture at the experimental flow rate without the separator until the CFI is filled with slugs of equal length, i.e. a steady state is reached. As soon as the steady state is reached the slit separator is added with a slit height of 0.4 mm. The setup is allowed to reach a new steady state before an experiment can be started, this will generally up to two residence times. A sample can be taken as soon as the steady state is reached, two more samples are taken with one residence time in between samples. Samples are taken by holding a GC autosampler vial directly under the organic outlet. When breakthrough of the aqueous phase occurs it has to be made sure that there is no water in the sample vial. This can be done by emptying the organic outlet tube, now it will first fill with organic phase and takes some time before the aqueous phase comes out again.

3.4. Separator performances

To gain insight in the performance of the different separators a system of only demineralized water and toluene or butyl acetate was used. Important for the slit separator is to make sure it is level in all directions before starting an experiment, a digital spirit level was used to make sure the device was level. At low flow rates the setup was given the time to reach a steady state. Next the waste collection tubes were removed and at both outlets a measuring cylinder of 10 ml was put at the outlet to collect the samples. It was made sure that the switch took place when a slug of the opposite phase was exiting the separator so no chemicals were spilled.

At high flow rates this procedure was not possible due to the adhesive forces of the liquid, it was not possible to take samples without stopping the flow to change the tubes and thus disturb the steady state. A larger amount is collected and start-up effects cannot be neglected, this caused some extra breakthrough. These results are a little bit less reliable but give a very good indication of the performance of the slit separator.

The slit separator was tested for a slit height of 0.4 mm and 0.8 mm. For the comparison with membrane separation a PTFE Zefluor membrane was used with average pore size of 0.5 μm [21].
4. Results and Discussion

4.1. Partition coefficient

The partition coefficient at equilibrium was determined as a function of the aqueous volume fraction for both test systems in batch using the shake flask method (OECD [29]). Table 4.1 shows the comparison of the experimentally determined values with the literature values, as can be seen the experimental values agree with the values found in literature [28]. Results of the partition coefficient as function of the aqueous volume fraction can be found in figure 4.1.

<table>
<thead>
<tr>
<th>Model systems</th>
<th>Partition coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Water-Acetone (10wt%)-Toluene</td>
<td>0.86</td>
</tr>
<tr>
<td>2) Water-Acetone (10wt%)-Butyl acetate</td>
<td>0.98</td>
</tr>
</tbody>
</table>

As can be seen the experimentally determined partition coefficient of the toluene-acetone-water system has a slight experimental error, hence the wavy pattern. The trend however can clearly be seen, at low aqueous volume fractions the partition coefficient increases with increasing aqueous fractions. When the thermodynamic maximum is reached at an aqueous volume fraction of 0.5 the value remains constant at 0.86 ± 0.04 for the toluene system and 0.96 ± 0.02 was reached at an aq. volume fraction of 0.4 for the butyl acetate system. The increase in partition coefficient at low aqueous volume fractions can be explained by the large volume of the organic phase. The partition coefficient is calculated by dividing the weight fraction of acetone in the organic phase by the weight fraction of acetone in the aqueous phase. Due to the large volume of the organic phase the concentration acetone in the organic phase is lower, hence the lower partition coefficient.

The partition coefficient measured using the shake flask method is considered to be the thermodynamic equilibrium partition coefficient. Since these values are in line with literature sources the concentration measured in the organic phase is considered to be the equilibrium concentration. This value (as function of the aqueous volume fraction) can be found in figure 4.2 and is used in equation 2 to calculate the extraction efficiency.
Figure 4.2: Equilibrium concentration as function of the aqueous volume fraction.

Figure 4.2 also show the trend lines used to calculate the equilibrium concentration for every aqueous volume fraction. Table 4.2 shows their equations and accuracy. The concentrations were measured using GC-FID, the calibration curve can be found in appendix I.

**TABLE 4.2: TREND LINE EQUATIONS FOR CALCULATION OF EQUILIBRIUM CONCENTRATION.**

<table>
<thead>
<tr>
<th>Toluene system</th>
<th>Butyl acetate system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear model</td>
<td>Linear model</td>
</tr>
<tr>
<td></td>
<td>( f(x) = p_1 x + p_2 )</td>
</tr>
<tr>
<td>Coefficients:</td>
<td>Coefficients:</td>
</tr>
<tr>
<td>( p_1 = 1.724 )</td>
<td>( p_1 = 1.4733 )</td>
</tr>
<tr>
<td>( p_2 = 0.0108 )</td>
<td>( p_2 = 0.0171 )</td>
</tr>
<tr>
<td>Goodness of fit:</td>
<td>Goodness of fit:</td>
</tr>
<tr>
<td>R-square: 0.9978</td>
<td>R-square: 0.9978</td>
</tr>
</tbody>
</table>
4.2. Flow map

Flow maps were constructed for both test systems (table 3.1) to study the effect of the flow rate and flow rate ratio to the flow regime. Flow maps are only constructed for a maximum of 10 ml/min for each phase for the comparison with literature [8, 30]. In figures 4.3 and 4.5 the blue round slugs are the aqueous phase and the clear continues phase is the organic phase. The organic phase has preferential wettability on the PFA tube this ensures the organic phase to be the continuous phase [6].

4.2.1. Water-Acetone-Toluene

As can be seen in figure 4.3 the flow regime does not change with change in flow rate or change in aqueous fraction. The slug length however does change with change in volumetric flow rate. As expected the phase with the largest volume fraction (highest flow rate) has the largest slugs. Gravitational forces have got little to no influence to the formation of the flow profile, the Bond number is 0.66 which indicates surface tension forces dominate over gravitational forces.

![Flow map of water-toluene system](image)

Previous researchers [30] $(d_h = 0.5 \text{ mm})$ have found a decrease in slug length with aqueous fraction of 0.5 and an increasing total flow rate. The slug length in this research remains more constant this is most likely due to the much larger tube diameter of 3.2 mm. There was no difference in flow patterns observed between the inlet and the outlet of the CFI, there was no coalescence or breakage of the slugs.
At even higher flow rates no other flows than slug flow were seen, however at a certain point the slugs are not uniform and flow in an irregular pattern (right in fig 4.4). A deformed interface (approximately 1 cm in tube, left in fig 4.4) in the beginning of the CFI is causing this irregular flow profile. The flow rate is so high the viscous forces are having influence on the formation of the flow patterns instead of the surface tension forces solely (Capillary number reaches $1 \cdot 10^{-2}$). Deformed interface was never observed further down the CFI.

Figure 4.4: Flow profile at 90 ml/min total flow rate. Left: Directly after CFI inlet, Right: At CFI outlet tube.

Exploiting slug flow in flow rates which bridges lab to pilot scale, one ‘microfluidic’ flow pattern stays the same as a whole and if a proper setting is used even in its details makes it essentially almost an ideal situation.

4.2.2. Water-Acetone-Butyl acetate

The results of the butyl acetate system are similar to those of the toluene system although the interfacial tension is much lower (see table 3.1). The difference occurs when the organic fraction is 0.6-0.83. At these fractions the flow changes from slug flow to slug-drop flow or drop flow. The slug-drop flow in this case means that for several seconds there is slug flow which changes to drop flow, and after a few seconds back again to slug flow. It is not clear why these particular combinations of flow rates show unstable flow patterns. It looks like the liquid from the two sides gets ripped off before both sides have reached the centre of the tube, hence the irregularity in position with respect to the centre of the tube.

Figure 4.5: Flow map of n-butyl acetate-water system.
When drop flow was observed it was seen that the aqueous drops accelerated under the influence of gravity. This can be explained using the Bond number, the extent to which the surface tension forces dominate the gravitational forces. Bo is 1.06 for the butyl acetate test system so the gravitational forces do have influence on the system. The capillary number exceeds that of the toluene system, viscous forces will have more effect and dominate at lower flow rates for the butyl acetate system. However the flow rate at which this phenomenon will occur was not reached.

4.3. Extraction performance as function of the total flow rate

The influence of the extraction efficiency was studied as a function of the total flow rate where the aqueous volume fraction was kept constant at 0.5. A comparison was made between the CFI and a straight tube of equal length and diameter. For determination of the concentration in the organic phase a GC-FID calibration curve was made and can be found in appendix I.

4.3.1. Toluene system

Figure 4.6 shows the extraction efficiency of the toluene test system as a function of the total flow rate in comparison with the straight tube. A maximum of 120 ml/min was taken due to pump limitations.

It can be seen that at flow rates below 10 ml/min (De = 25) the extraction efficiency increases from 80% to ~90% for both the CFI and the straight tube. This leads to the conclusion that the sole residence time (508 s for 2 ml/min, 8 s for 120 ml/min) has much less influence than the internal circulations and mixing within and between slugs. At flow rates above 30 ml/min (De = 77) the CFI shows an almost constant extraction efficiency of 92% ± 4 percentage point (pp) even at flow rates up to 120 ml/min (7.2 l/h, 52 m³/a). The efficiency of the straight tube starts to decrease at flow rates above 30 ml/min and falls back to 75% ± 5 pp. The better performance of the CFI results from the Dean vortices and flow inversion which enhances the mixing and hence the mass transfer contact area and a more uniform concentration profile.

Figure 4.6: Extraction efficiency as a function of the total flow rate of the toluene test system as a function of the total flow rate with schematic view of flow pattern development in straight tube.

Whereas the CFI operates in the slug flow regime for all flow rates it was observed that for the straight tube also deformed interface at 30 ml/min and unstable parallel flow at 50 ml/min (fig 4.7) were observed. The change in flow pattern occurs with increasing flow rate.
which indicates that other forces start dominating over the surface tension forces [31]. The change in flow pattern causes a reduction of about 1.5 times the mass transfer area.

Figure 4.7: Unstable parallel flow in straight tube, blue colored liquid is the aqueous phase.

4.3.2. n-Butyl-acetate system

Similar experiments were carried out for test system 2 using butyl acetate, due to limitations of the separator these experiments were carried out with a maximum of 45 ml/min (see section 4.5).

It can be seen in figure 4.8 that the as well the CFI as the straight tube show the same trend as the toluene test system. The CFI performs better than the straight tube which was also expected (CFI 94% ± 2 pp, straight tube 74% ± 8 pp). Different from the toluene system is the flow rate at which the performance of the straight tube starts deviating from the CFI, at 10 ml/min (De = 24) the CFI shows a better performance of 15%.

In figure 4.8 a schematic view is given of the flow pattern development within the straight tube. It clearly shows that the lower extraction efficiency is not solely caused by the difference in flow pattern. At low Dean numbers where the Dean vortices are not fully developed (fig. 2.5) the CFI performs better than the straight tube, resulting in the fact that the flow inversion must be causing the better performance.

Figure 4.8: Extraction efficiency as a function of the total flow rate of the butyl acetate test system as a function of the total flow rate with schematic view of flow pattern development in straight tube.
4.4. Extraction performances as function of the aqueous volume fraction.

The extend to which the aqueous volume fraction effects the extraction efficiency and the acetone yield was studied for both test systems. The total flow rate was kept constant at 20 ml/min for the toluene test system and, due to breakthrough of the aqueous phase in the slit separator (see section 4.5), at 10 ml/min for the butyl acetate system. The aqueous volume fraction was varied from 0.1 to 0.9, the results are shown below. It has to be noted that at these flow rates the difference between the CFI and the straight tube is rather small, at higher flow rates the effect of the aqueous volume fraction can be present.

4.4.1. Toluene system

Figure 4.9 shows the extraction efficiency as a function of the aqueous volume fraction at 20 ml/min (De = 51). The data in fig. 4.9 at a volume fraction of 0.5 correspond with the 20 ml/min point in fig. 4.6 in section 4.3.

The extraction efficiency decreases ~10 pp for the CFI with an increase in aqueous volume fraction. It can be concluded that the system has difficulties reaching the thermodynamic equilibrium when more aqueous phase is present. This can be explained by the length of the slugs (see flow map in fig. 4.1), a larger aqueous slug results in a low surface-to-volume ratio and a larger stagnant zone within the slug. The slow process of diffusion limits the system from reaching to equilibrium fast. The performance of the straight tube are similar to the performance of the CFI, it can be seen that at high aqueous fractions the CFI shows 10 pp better performance compared to the straight tube. Due to the lack of flow inversion and Dean vortices in the straight tube the stagnant zone within the large aqueous slugs will be larger compared to those within the CFI.

![Figure 4.9: Extraction efficiency as a function of the aqueous volume fraction, total flow rate: 20 ml/min.](image)

Figure 4.10 shows the acetone yield which is defined as the moles acetone in the organic phase at the outlet divided by the moles that entered the setup in the aqueous phase. The yellow line shows the thermodynamic equilibrium measured using the shake flask method provided by [28], the dashed part of the yellow line is extrapolated and not verified with experiments. The extraction efficiency shows the difference between the yellow line and the measured points.
As can be seen the aqueous volume fraction has a severe influence on the acetone yield. The amount of organic phase present to extract the acetone also decreases, at a certain point the toluene is saturated but due to the large excess of aqueous phase there is still a lot of acetone left to be extracted. Depending on the desired product the right aqueous volume fraction can be chosen and up to 80% of the original solute can be extracted.

The points at an aqueous fraction of 0.1 appear to be above the thermodynamic equilibrium line, which is in reality impossible. The difference can arise from some experimental error in sampling the CFI and straight tube, second the concentrations measured are based on a fitted calibration curve with a small error. The ratio between the two points is correct (see also fig 4.9 above) the absolute value should be at/below the yellow line.

Figure 4.10: Acetone yield as a function of the aqueous volume fraction, total flow rate: 20 ml/min.
4.4.2. n-Butyl-acetate system

The same experiments were carried out for the butyl acetate test system, however at a lower flow rate of 10 ml/min (De = 24) due to limitations of the slit separator. For the butyl acetate test system shows lower performance for low aqueous volume fractions. The extraction efficiency shows a maximum around an aq. vol. frac. of 0.5. The performance at high aq. vol. frac. remain above 90%. The straight tube shows a 10 pp less performance at aqueous fractions of 0.5 and up, the larger stagnant zone within the large aqueous slugs reduces the extraction performance.

Figure 4.11: Extraction efficiency as a function of the aqueous volume fraction, total flow rate: 10 ml/min.

Figure 4.12 shows the acetone yield and the deviation from the thermodynamic equilibrium. The dashed parts of the yellow line are extrapolated and not experimentally verified. The thermodynamic yield for this system is at low aqueous fractions slightly higher (~10%) compared to the toluene test system. However due to the lower interfacial tension and thus the lower efficiency the yield achievable is comparable to the previous system.

Figure 4.12: Acetone yield as a function of the aqueous volume fraction, total flow rate: 10 ml/min.
4.5. Separator performance

Two possible separators were tested: a slit separator which operates on basis of preferential wettability and a membrane. For the slit separator two configurations were used, a slit height of 0.4 mm and 0.8 mm the width and depth of the slit were kept constant. A breakthrough limit of 20% was set as the limit of operation, If the breakthrough was equal or below 20% it was possible to perform extraction performance experiments.

4.5.1. Toluene system

Gaakeer et al. posted in his research [26] a rule of thumb for breakthrough in the slit separator, the capillary pressure should at least be twice as high as the hydraulic pressure in the opposite slit. Figure 4.13 shows this limit in a graphical representation. The orange line is the threshold given by Gaakeer et al., according to the figure breakthrough of the organic phase through the glass slit will occur at a slit flow rate of 30 ml/min (total flow rate 60 ml/min). Increasing the slit height to 0.8 mm should overcome this problem, however it should be taken into account that the absolute capillary pressure is much lower at this slit height.

Figure 4.13: Hydraulic and capillary pressures of slit separator with slit height 0.4 mm and 0.8 mm respectively according to [26].

4.5.1.1. Variation of total flow rate

Figure 4.14 shows the aqueous and organic fraction at the glass and teflon outlet respectively of the slit separator with a slit height of 0.4 mm. It was expected from figure 4.13 that the organic phase would breakthrough the glass slit first, however the opposite was observed. Breakthrough of water through the teflon slit occurred at a total flow rate of 24 ml/min and raises to almost 20% for flow rates above 80 ml/min. Toluene starts breaking through at 28 ml/min and also raises to 20% of the glass outlet.
Below in figure 4.15 a slit height of 0.8 mm was used and although it was expected that less breakthrough would have been observed (based on fig. 4.13), however at lower flow rates than the 0.4 mm slit toluene and water start to breakthrough the glass and teflon slit respectively. The difference observed between the 0.4 and 0.8 mm slit can be explained by the absolute capillary pressure, at a slit height of 0.8 mm it is approximately half the value it is with a slit height of 0.4. This pressure is not high enough to block the liquid from flowing through the slit.

The membrane shows good performances at the permeate side, no water flows through the membrane, however at the retentate side 20% of the flow is organic phase at a flow rate of 6 ml/min. This probably due to the microchannels in the microreactor which are too deep and hence entrainment of the organic phase by the aqueous phase occurs. Another drawback of the membrane is the pressure drop over the membrane and the microchannel device, this resulted in pump failure at flow rates above 20 ml/min. There was no back pressure regulator installed nor was there a variation in pressure drop over the two outlets. Methods with different pressure drops at the outlets were tried to create better separation, however due to the pressure differences in combination with the slug flow pattern the flow within the CFI became discontinues.
For the selection of the most ideal separator for this setup the main focus was on the organic side at a wide range of flow rates. Therefore the slit separator with slit height 0.4 mm was chosen to work best for this test system.

**Varying water volume fraction**

The slit separator was not tested before by Gaakeer et al. [26] on the influence of the aqueous volume fraction, i.e. with organic and aqueous slugs which are not of the same size. Therefore the separators were tested with the same settings as mentioned in section 4.4.

Figure 4.17 shows the fraction aqueous and organic phase coming out of the glass and teflon outlet respectively. It can be seen that at low aq. volume fractions a very small amount of toluene breaks through the glass slit. At larger aq. volume fractions however the aqueous phase breaks through the teflon slit and pollutes the organic phase, where 10-20% of the outlet consist of aqueous phase. At an aqueous volume fraction of 0.1 the aqueous slugs are ~6 times larger than the organic slugs. In combination with the lower flow rate of the organic phase this results in less hydraulic pressure in the teflon slit and hence easier breakthrough of the aqueous phase through the teflon slit. The organic phase breaks through the glass slit at the same aq. volume fractions because it is dragged along with the aqueous phase. This phenomenon could be caused by the aqueous phase which remains in the teflon slit increasing the pressure which makes it more difficult for the organic phase to flow through the teflon slit.
After the results from section 4.5.1.1 it is expected that increasing the slit height to 0.8 mm will cause more liquid to breakthrough. Figure 4.18 shows the results and at high aq. volume fractions more aqueous phase breaks through the teflon slit compared to the 0.4 mm. At an aq. volume fraction of 0.1 the same hydraulic pressure problem occurs as with the 0.4 mm slit at the glass slit, and hence 30% of the glass outlet consists of organic phase. At high aq. fractions the organic phase passes only through the teflon slit and is no longer dragged along through the glass slit.

Figure 4.18: Glass and teflon outlet respectively for a slit height of 0.8 mm total flow rate 20 ml/min.

For the membrane a lower total flow rate (10 ml/min) was used during these experiments due to pump limitations. It can be seen in figure 4.19 that there is no breakthrough of the aqueous phase through the membrane at any aq. volume fraction, however at low aq. volume fractions a large amount of organic material is lost at the retentate side. Even when 90% of the system consists of aqueous phase 10% of the retentate outlet is still organic phase not passing the membrane and very hard to analyze.

Figure 4.19: Retentate and permeate outlet respectively for 0.5 μm Zefluor membrane total flow rate 10 ml/min.
4.5.2. *n*-Butyl-acetate system

The interfacial tension has a major role in the use of the slit separator, it is one of the parameters which dictate the capillary pressure. Using the butyl acetate test system which has a much lower interfacial tension compared to the toluene test system will cause the operating threshold in figure 4.20 to lower down. Hence the expected maximum flow rate for good separation is set to ~15 ml/min (30 ml/min total) for a slit height of 0.4 mm. Theoretically increasing the slit height to 0.8 mm will create stable separation at higher flow rates. However in the previous section it was found that the absolute capillary and hydraulic pressure need to be sufficiently high to assure good separation. Where the capillary pressure for this test system in the 0.4 mm slit is 47.8 Pa the threshold for the toluene system was 46.0 Pa at the same slit height, it is expected that the slit separator shows bad separation for this test system.

![Figure 4.20: Theoretical performance of slit separator with slit height 0.4 mm and 0.8 mm respectively according to [26].](image)

4.5.2.1. Variation of total flow rate

The experiments in the section above were repeated for the butyl acetate test system. The lower interfacial tension was expected to cause more difficulties in using the slit separator, as can be seen in figure 4.21 this hypothesis was confirmed. Breakthrough of up to 40% on both sides occurred at flow rates above 32 ml/min which made it hard to do extraction performance tests with the setup. The large breakthrough can be accounted to the crossing of the threshold capillary pressure. The breakthrough at lower flow rates indicate that the principle of separation on basis of preferential wettability is difficult for systems with low interfacial tension, most likely because the capillary pressure is too low.
Based on the results seen with the toluene system it was expected that increasing the slit height to 0.8 mm would cause both phases to breakthrough more easily. Figure 4.22 shows the results of these experiments and it can be seen that 40% breakthrough at both sides is occurring at flow rates of 10 ml/min. However at higher flow rates (25-30 ml/min) the 0.8 mm slit seems to perform better at the teflon side and a decrease in breakthrough was also observed at the glass outlet. However due to the large amount of breakthrough at low flow rates the slit height of 0.8 mm was not used during other experiments.

The influence of the lower interfacial tension does not provide much benefits nor disadvantages when using the membrane as separator. Comparing fig 4.19 and fig 4.23 it can be seen that both figures show similar behavior. There is 10% more breakthrough at the retentate side using the butyl acetate system. When adding back pressure regulators to improve separation the same discontinuous flow was observed as before.

Figure 4.21: Glass and teflon outlet respectively for slit separator with slit height 0.4 mm.

Figure 4.22: Glass and teflon outlet respectively for slit separator with slit height 0.8 mm.

Figure 4.23: Retentate and permeate outlet respectively for 0.5 μm Zefluor membrane
Varying water volume fraction

The variation in slug length with unequal organic and aqueous slugs has a larger influence on the system with lower interfacial tension. It can be seen in figure 4.24 that 20% breakthrough of the aqueous phase already occurs through the teflon slit at an aq. volume fraction of 0.5. Increasing the aq. volume fraction does not have an significant influence tot the breakthrough. At the glass slit breakthrough occurs for very large organic fractions and with increasing aq. volume fraction the butyl acetate is pushed through the glass slit by the hydraulic pressure caused by the aqueous phase in the teflon slit.

Figure 4.24: Glass and teflon outlet respectively for a slit height of 0.4 mm total flow rate 10 ml/min.

Increasing the slit height to 0.8 mm decreases the performance of the separator as a function of the aq. volume fraction severely. Breakthrough of up to 80% occurs at almost all aq. volume fractions remarkable is the good separation at an aq. volume fraction of 0.9. Following the trend at the teflon outlet, and looking to the results of the toluene system it was expected that an aq. volume fraction of 0.9 would have given the largest breakthrough of up to 50% for the teflon slit. Since this is not the case it is expected there was an error made during the experiments, it could be that the separator was not fully level when the experiment was conducted this has influence on the performance.

Figure 4.25: Glass and teflon outlet respectively for a slit height of 0.8 mm total flow rate 10 ml/min.
Figure 4.26 shows the effect of the aqueous volume fraction in separation performance of the membrane separator. It can be seen that entrainment of the organic phase is more at low aq. vol. fractions. Compared to the toluene test system the amount of organic entrainment is similar.

![Graph showing effect of aqueous volume fraction on separation performance](image1)

![Graph showing comparison of organic and aqueous phases](image2)

Figure 4.26: Retentate and permeate respectively for the membrane separator total flow rate 10 ml/min.

It can be concluded from the above results that the slit separator with a slit height of 0.4 mm shows the best performance. Flow rates of up to 32 ml/min can be achieved with acceptable separation. The design of the membrane separator can be adjusted in further research to improve the performance. If a very pure organic phase is needed the membrane separator is a good alternative and can be of good use at high aqueous volume fraction.
5. Summary, Conclusion and Further studies

5.1. Conclusions

Summary and conclusions from this study are:

- A setup was designed to use a coiled flow inverter with online phase separation.
- The CFI used in this study only operates in the slug flow regime, where the slug lengths remains constant for aqueous volume fractions of 0.5.
- Slug length is mainly influenced by the variation in volume fraction of the two phases, not the total flow rate.
- The straight tube operates in the slug flow regime for lower flow rates, but in the parallel flow regime for higher flow rates.
- Systems with high interfacial tension can successfully separated with a maximum breakthrough of 20% up to flow rates of 120 ml/min using a slit separator with a slit height of 0.4mm. However the separator is limited in using systems with low interfacial tension.
- At lab scale production volumes the membrane works with a clean permeate phase, improper separator design causes some organic phase to be entrained to the retentate.
- The CFI shows extraction performance close (95%) to the thermodynamic equilibrium.
- Successful scale up of the coiled flow inverter was achieved up to flow rates of 120 ml/min (7.2 l/h, 52 m³/a). With an aqueous volume ratio of 0.5 and 10wt% acetone load the production capacity is over 1 t/a acetone yield.
- For systems with high interfacial tension the CFI shows up to ~23% better extraction performances compared to a straight tube, However only for flow rates above 30 ml/min. For systems with low interfacial tension the advantages of the CFI can be exploited at flow rates starting at 10 ml/min and show up to ~26% better performance.
- At high aqueous volume fractions the CFI shows better extraction performances of ~10%.

5.2. Further studies

Due to time limitations there are some experiments left to be done to complete the picture.

- Further experiments using a helical coil, operated in straight manner with no flow inversions, to compare with the results of the CFI.
- Study a better engineered membrane separator e.g. hollow fiber membranes for good comparison with the slit separator and extend the possibilities of the setup, e.g. systems with low interfacial tension.
- Determine where the difference in flow pattern between CFI and straight tube originates from.
- Explore the upper flow rate threshold for which gravity dominates and no slug flow is stable anymore, i.e. further scale up to pilot plant scales (10-100 l/h) using e.g. larger inner diameter.
- Test the setup for an industrial application and test its workability in the process industry.
6. Acknowledgements

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7. Bibliography


Appendix

Appendix I: Calibration curves

To determine the calibration curve for the two systems, known amounts of acetone were dissolved in the desired organic phase and put into the GC. The area of the acetone peak was then divided by the area of the organic phase peak, this is plotted on the x-axis in figure I.1. Next the calibration curves were fitted using excel. The accuracy of both curves shown with $R^2$ is close to one, the points that are not exactly on the line are distributed above and below. These two parameters show that the calibration curve is accurate and no standard error is made, therefore these two curves are used.

![Figure I.1: Left calibration curve toluene system, right calibration curve butyl acetate system.](image-url)
Appendix II: Interfacial tension

Figure II.1: Interfacial tension curves as function of acetone mass fraction. Blue: Butyl acetate system, Green: Toluene system. [28]