Experimental and numerical investigation of micromixing devices for application in liquid-liquid extraction

Tobias Haderer, Axel Wojik, Rolf Marr
Department of Chemical Engineering and Environmental Technology
University of Technology Graz
Inffeldgasse 25, A-8010 Graz, Austria

Stefan Martens
Fluent Deutschland GmbH
Birkenweg 14a, D-64295 Darmstadt, Germany

Matthäus Siebenhofer
VTU-Engineering GmbH
Parkring 18, A-8074 Grambach/Graz, Austria

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Abstract

Micromixers recently have attracted attention for various applications in chemical engineering [**1**] but the use of micromixing devices in liquid-liquid extraction has been reported rarely [**2**]. Therefore design and extraction efficiency of laminar flow micromixing reactors was investigated. Investigation was carried out by performing mass transfer experiments in a concurrently operated T-micromixer with rectangular cross section of the mixing channel (width of 700 and height of 200 microns) and by simulating the hydraulics. The reason for limited extraction efficiency was deduced from results of interface simulation. Then improvement of the mixing capability of the micromixer for constant flux but extended channel height was investigated.

1. Introduction

Industrial scale liquid-liquid extraction is carried out in mixer-settler units or extraction columns. As a result of large size of industrial extractors, mixing performance is not very effective and as a consequence extraction efficiency decreases. From miniaturization of the mixing space towards channels in the range of some microns a significant improvement in overall extraction efficiency is expected. Mass transfer inside microchannels is limited in most cases to diffusion because of the laminar flow pattern. Diffusion distance in the range of some microns can be realized enabling excellent mass transfer. Investigation focused on the comparison of extraction efficiency for several operation conditions and simulation of the corresponding hydraulics of mixing.

2. Experimental Methods and Analyses

Mass transfer experiments were based on extraction of acetone from organic feed (n-hexane) with the solvent water. Extraction efficiency was determined for different operating conditions by varying the process parameters flow rate and phase ratio at constant temperature The mixing step was performed with a *mgt Design T-Mixer* microreactor (mikroglas chemtech GmbH) with rectangular cross section of the mixing channel (width of 700 and height of 200 microns). The whole reactor, made of FOTURAN$^{®}$-glass, consists of 20 mixing channels arranged in parallel. *Figure 1* shows the construction principle of the mixer.

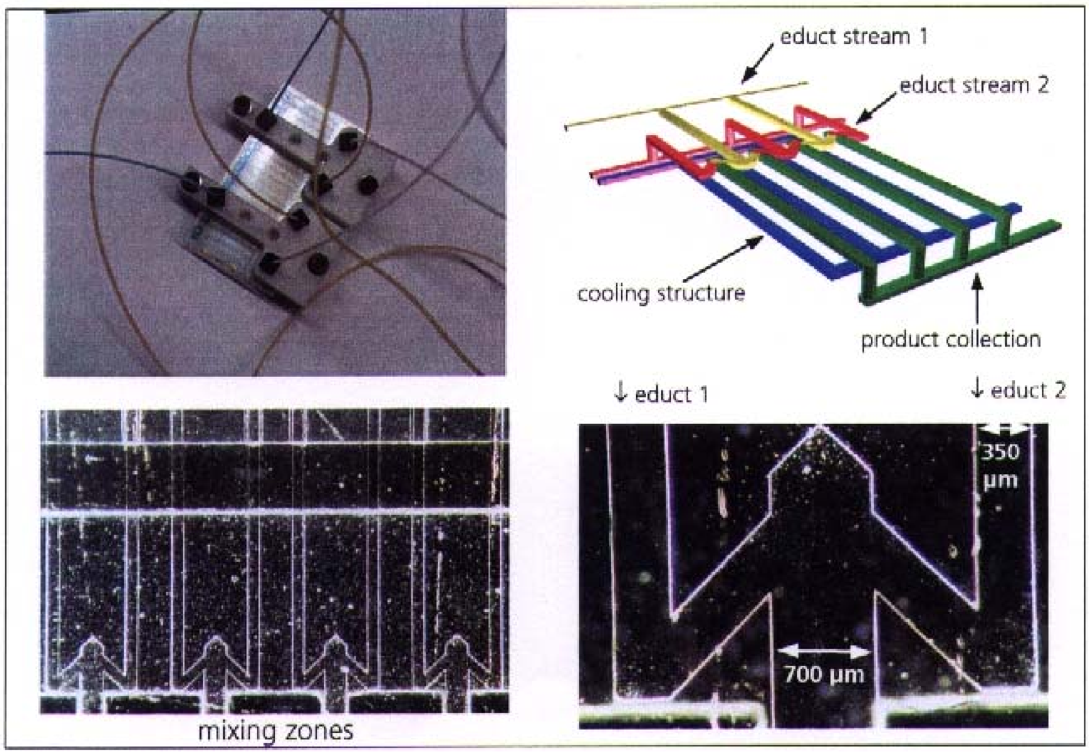

Figure 1: Construction principle of the investigated micromixer with schematic flow and microscopic image of the inlet microchannels

The investigated mixer was originally designed for heat exchange tasks wherefore the channel height was set to 200 µm to improve heat transfer in z-direction. A cooling circuit arranged below the mixing channels guarantees constant operating temperatures. In standard application the microreactor is used for homogeneous liquid phase reactions with focus on constant reaction temperatures so far. To compensate poor heat conductivity of the glass material the ratio of height to width of 200 µm : 700 µm was designed as small as possible.

The rectangular channel design may not be an advantage implicitly for the purpose of performing liquid-liquid extraction processes because of unfavorable flow pattern. Therefore Computational Fluid Dynamics calculations were executed to investigate hydrodynamics of the channel geometry. The results were compared with data from mass transfer experiments. In a next step simulation of hydrodynamics for channel dimension of 700 µm * 700 µm cross-sectional area was performed.

The mixing principle of the reactor is based on non-dispersive contact of both liquids in a T-type mixing channel by forming two accumulated films inside the microchannel. Laminar flow of the liquid layers is a boundary for non-dispersive mixing. At maximum total flow rate of 20 ml/min the Reynolds-number Re according to *equation 1* of less than 2.38 was calculated.

$$\mathrm{Re} = \frac{w \cdot l}{\nu} = 2.38 \tag{1}$$

Re [-]	*Reynolds-number*
w [m/s]	*velocity*
l [m]	*characteristic length*
v $[m^2/s]$	*kinematic viscosity*

Accordingly mass transfer in microchannels is limited to diffusion. Following the general definition of mass transfer in *equation 2*, the flux increases with increasing mass transfer coefficient which is calculated from the diffusion coefficient D and the boundary layer thickness *δ,* according to *equation 3*.

$$\dot{N} = k \cdot A \cdot \Delta c \tag{2}$$

N [mol/s]	*flux*
k [m/s]	*mass transfer coefficient*
A $[m^2]$	*Interfacial area*
Δc $[mol/m^3]$	*concentration difference*

$$k = \frac{D}{\delta} \tag{3}$$

D $[m^2/s]$	*Diffusion coefficient*
δ [m]	*boundary layer thickness*

In microchannels the boundary layer thickness and therefore the diffusion distance is very small. Due to diffusion distances in microchannels in the range of approximately 0.5 and several hundred microns mass transfer can be kept at optimum conditions [**3**]. These considerations are valid for micromixers, where the mixing principle is based on alternating multilamination of fluid layers.

Phase separation was carried out in a gravity mini settler. Extraction efficiency of the microreactor was determined by recording both, overall mass transfer as well as mass transfer in the settler.

In addition the flow pattern was computed with Computational Fluid Dynamics (Fluent 6.1) to determine the available mass transfer area. The interface was computed with a multiphase CFD approach (Volume of Fluid (VOF)) for two microchannels with different channel dimensions (rectangular cross section: width of 700, height of 200 microns and width of 700, height of 700 microns respectively). From the comparison of both simulation routines with the results from mass transfer experiments the effect of the design of the mixing facility on extraction efficiency was explained.

The extraction experiments were carried out in an apparatus arrangement according to *Figure 2*. Piston pumps were used for providing total flow rate of the liquids of 4 to 24 g/min. Between pump (P1) and microreactor the feed stream was directed over a sensor-block (Bürkert), which was needed for temperature and pressure registration with an accuracy of ±0.1 K and ±0.01 MPa. A pressure control valve was integrated in the sensor block. A second line of the same setup was installed to feed the solvent (distilled water) into the microreactor.

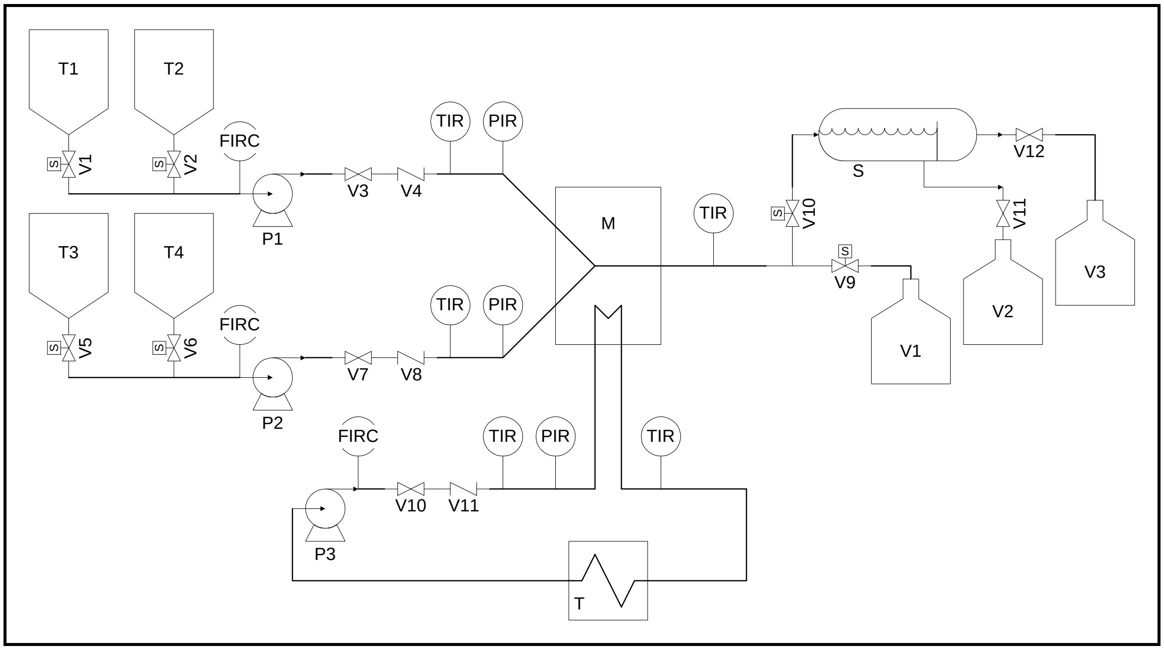

Figure 2: Experimental setup of the microplant: (T1) Feed storage tank, (T3) Solvent storage tank, (T3, T4) Purge tanks, (P1) Feed pump, (P2) Solvent pump, (P3) Pump for heat transfer medium, (T) Cryostat, (M) Microreactor, (S) Settler, (V1) Waste vessel, (V2) Raffinate vessel, (V3) Extract vessel, (V1, V2, V5, V6, V9, V10) Solenoid valves, (V3, V7, V10) Pressure control valves, (V4, V8, V11) Check valves, (V11, V12) Valves

Inside the microreactor the immiscible liquids were mixed. After passing a temperature sensor and a control valve the mixed phase was discharged into a gravity settler. The whole microreactor was equipped with a temperature control loop. Constant temperature of several feed liquids in the storage tanks and the gravity settler was provided by separate temperature control loops. The mass flow rate of the hexane feed and the aqueous solvent were recorded continuously. For this purpose each storage tank was placed on a balance with integrated RS-232c interface. The recorded mass data were processed in the control software LabView7, National Instruments.

2.1. Analysis

The acetone concentration of the feed, the extract phase and the raffinate phase was determined with density probe (Anton Paar, type DMA45) under temperature control of the sample. The temperature of the samples was kept constant at 293.15 K. Different portions of acetone were dissolved in n-hexane and water respectively to provide mixtures for calibration of the density probe in a concentration range of 0 to 5 Vol-%.

3. Results and Discussion

Extraction of acetone from n-hexane into the solvent water in the *mgt Design T-Mixer* microreactor was investigated in two series of experiments. In the first series the total flow rate was varied and in a second series the phase ratio of feed and solvent was varied.

From experimental results the mass balance was calculated. The composition of the extract phase and the raffinate phase was then compared with the operation diagram based on McCabe Thiele projection. Finally the extraction efficiency was calculated from the ratio of the experimentally obtained process data and the theoretical equilibrium composition data according to *equation 4*.

$$Eff = \frac{c_E}{c_{E,equ}} \cdot 100 \qquad (4)$$

Eff [%]	*Extraction efficiency*
c_E *[-]*	*Concentration of acetone in the extract phase*
$c_{E,equ}$ *[-]*	*Concentration of acetone in the extract phase at equilibrium*

To determine the contribution of the settler to the overall extraction efficiency the experiments were repeated in the same experimental setup except the microreactor which was substituted with a T-type mixer.

3.1. Extraction at a constant phase ratio and increasing total flow rate

In the first series of experiments, the influence of the total flow rate on extraction efficiency was investigated. All experiments were carried out at constant temperature of 293 K.

In this series of experiments the total flow rate was increased from 4 to 24 g/min, while the phase ratio of hexane feed and aqueous solvent was held constant at 1. *Table 1* shows the flow conditions of the experiments.

Feed [g/min]	Solvent [g/min]	Total flow rate [g/min]
2	2	4
4	4	8
6	6	12
8	8	16
10	10	20
12	12	24

Table 1: Flow conditions of the experiments for total flow rate of 4 to 24 g/min

The results of the overall extraction efficiency at low total flow rate are shown in *Figure 3*. The results obtained in experiments with the *mgt Design T-Mixer* indicate a slight decrease in efficiency from 70 to 55% with increasing total flow rate.

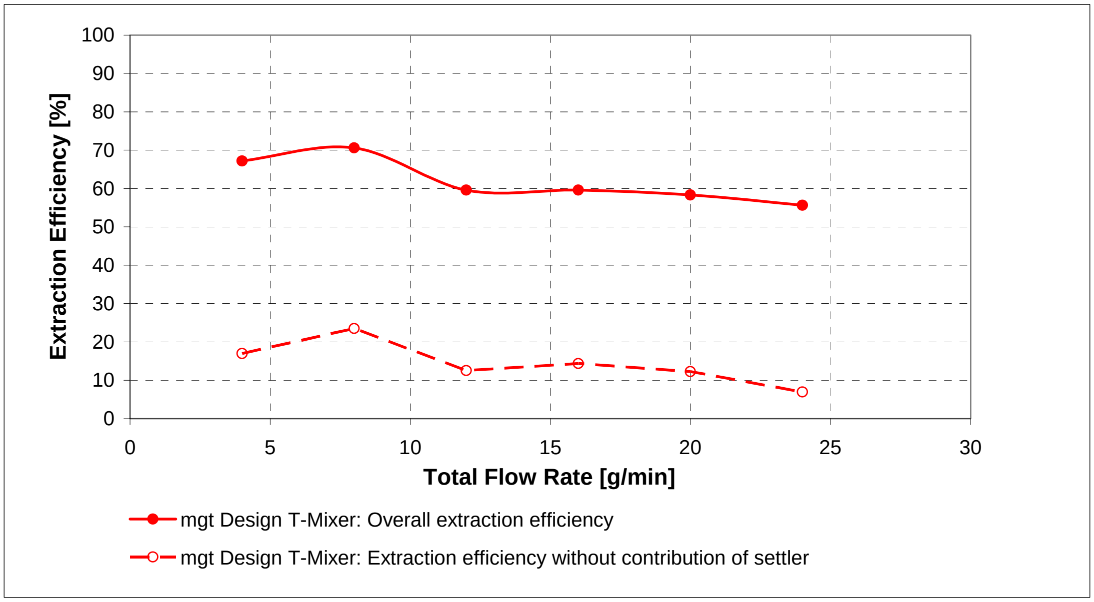

Figure 3: Total flow rate dependence of the overall extraction efficiency and the extraction efficiency without contribution of the settler (broken lines) respectively at constant phase ratio of feed and solvent of 1 for the *mgt Design T-Mixer* microreactor; T=293 K

3.1.1. Contribution of the settler

For consideration of the contribution of the settler all experiments were repeated in the same experimental setup except the microreactor. Instead of microreactors a conventional T-type mixer was installed.

The dotted lines in *Figure 3* show the extraction efficiency without contribution of the settler. Comparison of results shows a major contribution of the settler to extraction efficiency, which actually was not expected in the recorded extent.

3.2. Extraction at a constant total flow rate and varying phase ratio

The effect of the phase ratio of feed and solvent on the overall extraction efficiency was determined in the second series of experiments. All experiments were carried out at constant temperature of 293 K.

The efficiency dependence on the phase ratio was analyzed for constant total flow rate of 22 g/min. The investigated range of operation is summarized in *Table 2*.

Feed [g/min]	**Solvent [g/min]**	**Total flow rate [g/min]**
2	20	22
4	18	22
6	16	22
8	14	22
10	12	22
12	10	22
14	8	22
16	6	22
18	4	22
20	2	22

Table 2: Flow conditions for the series of experiments at constant total flow rate of 22 g/min

After an increase of extraction efficiency at low phase ratio extraction efficiency passes a maximum at a phase ratio of 18 g/min of solvent and 4 g/min of feed, to finally drop again when exceeding the optimum range of the phase ratio shown in *Figure 4*.

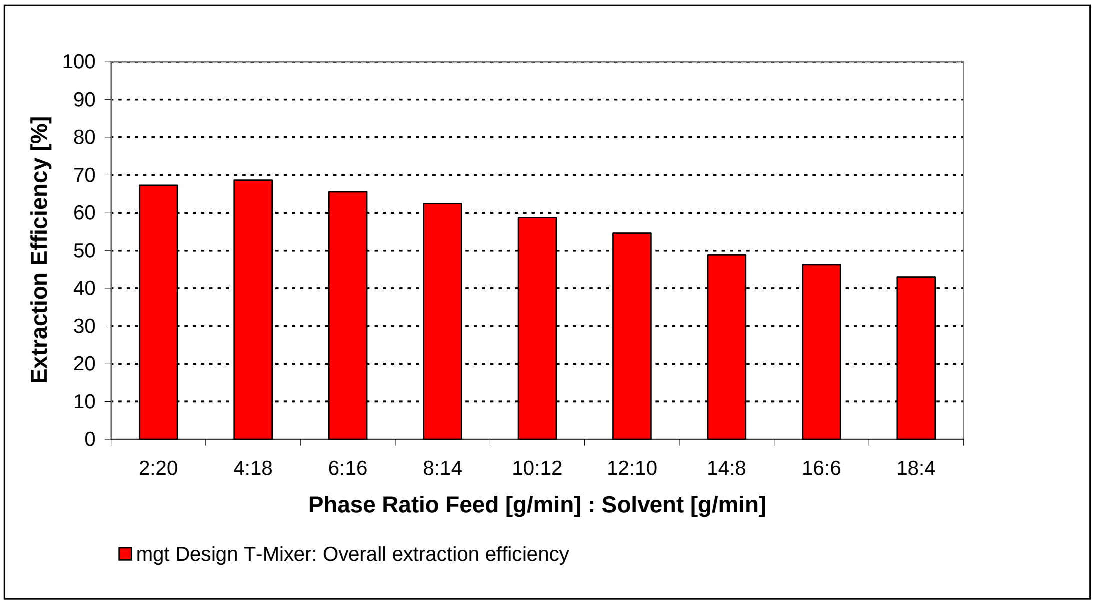

Figure 4: Dependence of varying phase ratio of feed and solvent on the overall extraction efficiency at constant total flow rate of 22 g/min for the *mgt Design T.Mixer* microreactor; T=293 K

4. CFD Simulation

Simulation of flow field has two main merits. On one hand simulation allows to get a deeper insight into the physical mechanisms of a specific process and thus foster the understanding of the liquid-liquid two-phase flow in the observed microchannel geometry. On the other hand simulation can provide a unique database of the three-dimensional velocity field and pressure field and phase distribution with high spatial and temporal resolution which can not be obtained by today’s most advanced experimental techniques. Such a database can be used to develop and improve apparatus.

To determine the flow of the two phase system (water/n-hexane) the “Volume of Fluid” multiphase approach has to be utilized. The VOF model can handle two or more immiscible fluids by solving a single set of momentum equations and tracking the volume fraction of each of the fluids throughout the domain. Typical applications include the prediction of jet break-up, the motion of large bubbles in a liquid, and the steady or transient tracking of any liquid-gas or liquid-liquid interface. The VOF formulation relies on the fact that two or more phases are not interpenetrating. In each control volume, the volume fractions of all phases sum up to unity.

The tracking of the interface(s) is accomplished by the solution of a continuity equation for the volume fraction of one (or more) of the phases. For the n^{th} phase, this equation has the following form, shown in *equation 5*.

$$\frac{\partial \alpha_n}{\partial t} + \vec{u}\nabla \alpha_n = \frac{S_{\alpha_n}}{\rho} \qquad (5)$$

with α_n fluid fraction of phase *n*

A single momentum equation with mixture properties (indices m) is solved throughout the domain of *equation 6*.

$$\frac{\partial}{\partial t}(\rho_m \vec{u}_m) + \nabla \cdot (\rho_m \vec{u}_m \vec{u}_m) = -\nabla p + \nabla \cdot \left[\mu_m \left(\nabla \vec{u}_m + \nabla \vec{u}_m{}^T\right)\right] + \rho_m \vec{g} + \vec{F} \tag{6}$$

The VOF model can also include the effects of interfacial tension along the interface between each pair of phases which is very important in this simulation. The model can be augmented by the additional specification of the contact angles between the phases and the walls. Especially at channels in the range of some microns the effect of interfacial tension is significant.

Interfacial tension between n-hexane and water was determined with a drop volume tensiometer of LAUDA, type TVT 2. In the drop volume method, the dynamic surface or interfacial tension is determined from the volume of a falling drop (*Figure 5*).

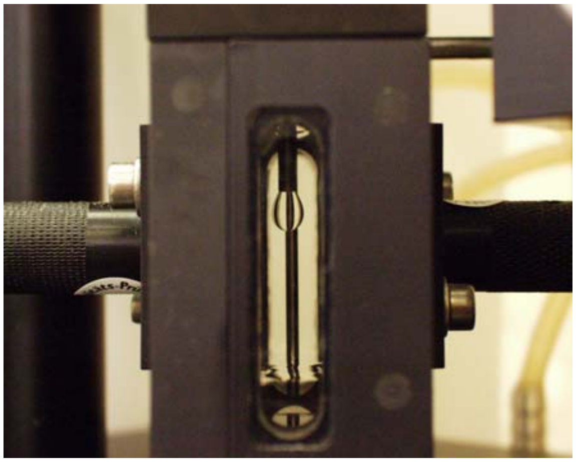

Figure 5: Interfacial tension measurement system (growing water droplet)

Drops of a liquid with high density, e.g. water, are generated in a liquid with low density, e.g. oil. Both fluids are immiscible (water/n-hexane). As soon as the weight, minus buoyancy reaches the magnitude of the holding force, the drop will split from the capillary. The volume of the falling drop is measured and the interfacial tension can be calculated with *equation 7*.

$$\sigma = \frac{g\left(\rho_{water} - \rho_{n-hexane}\right)V}{2\pi r f_{HB}} \tag{7}$$

The main interest of this project is the calculation of the interface between the two phases to identify the real mass transfer area. Other important points are the visualization of the free surface in dependency of the channel length, and the development of the free surface at different channel heights to ascertain best geometry conditions for real micro apparatus.

4.1. CFD Simulation of a single 700 x 200µm microchannel

In first simulation runs the flow rate of organic feed and solvent of 10 ml/min each was inserted at the generated phase inlets. The simulation geometry was limited to one channel to reduce the numerical effort of calculation. To obtain physically accurate solutions of flow pattern and interface a proper grid file had to be prepared. The challenge in preparing grids is to find the correct ratio of channel length to height and width of the micro structured geometry. In CFD simulation a length to height ratio of the grid cells of 5:1 at maximum ensures proper results. To obtain reliable results for the developed interface a total length of the microchannel of about 4 cm would require at least 2 Mio cells. Therefore the simulation was executed with a channel length of 1 cm resulting in a number of 220.000 grid cells. The grid construction is shown in *Figure 6*.

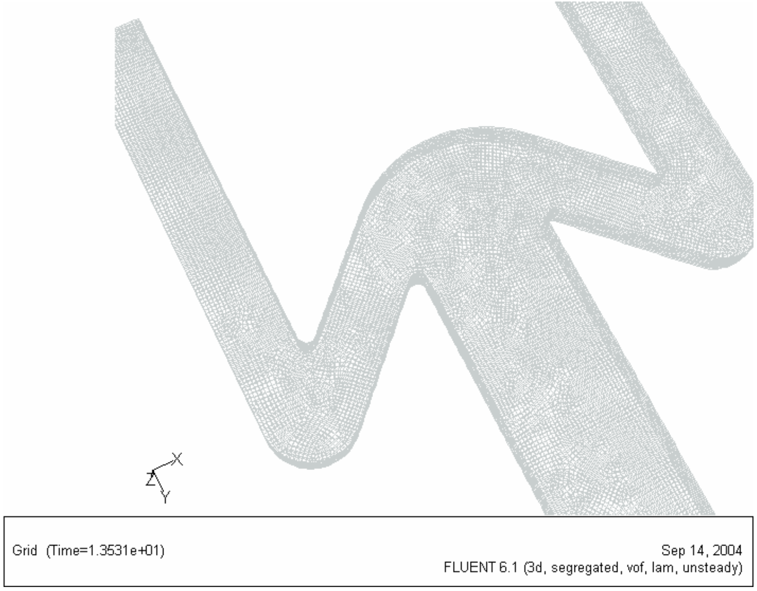

Figure 6: Grid construction of the microchannel with feed channels (700x200µm)

In first simulation runs the calculations were executed by creating a time step method to describe the formation of the interface between the two phases. At the inlet n-hexane (10 ml/min) was fed to the calculation area in positive x-direction and water (10 ml/min) was fed in negative x-direction. The time step was set to 0.005 sec and calculation were started without implementation of a turbulence model.

The simulated interface (green) between water phase and n-hexane phase after a flow time of 13.51 sec is shown in *Figure 7*. The water phase is coloured red and the n-hexane phase is coloured blue. As shown in *Figure 7* the interface is not yet fully developed and further simulation runs are needed to obtain steady state conditions at the interface. It is also displayed, that the formation of the interface is comparable with the real process. At the beginning droplets develop which slowly vanish by forming a continuous interface.

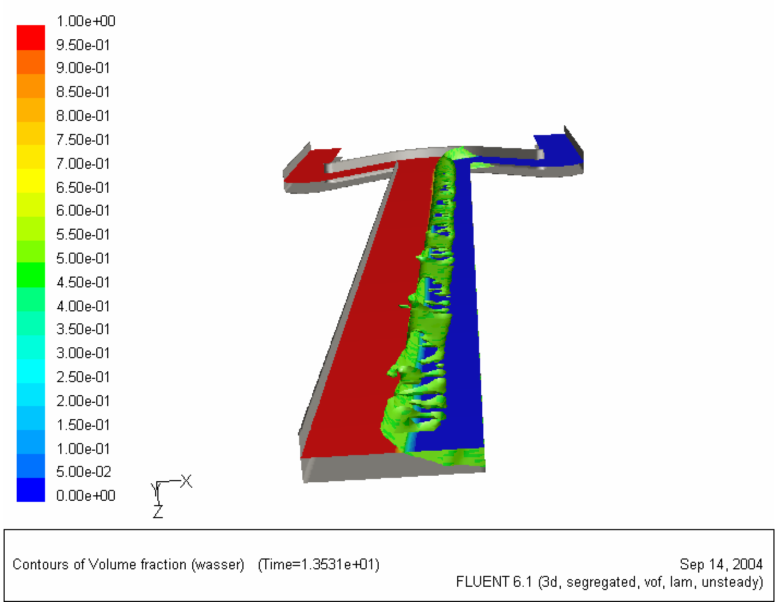

Figure 7: Calculated interface after 13.51 sec (700 x 200 µm)

Calculations were executed with a single processor Pentium III 1000MHz computer system and lasted 2.5 months to calculate the solution at 13.51 seconds. Therefore the steady simulation procedure was used to calculate the steady state interface (*Figure 8*).

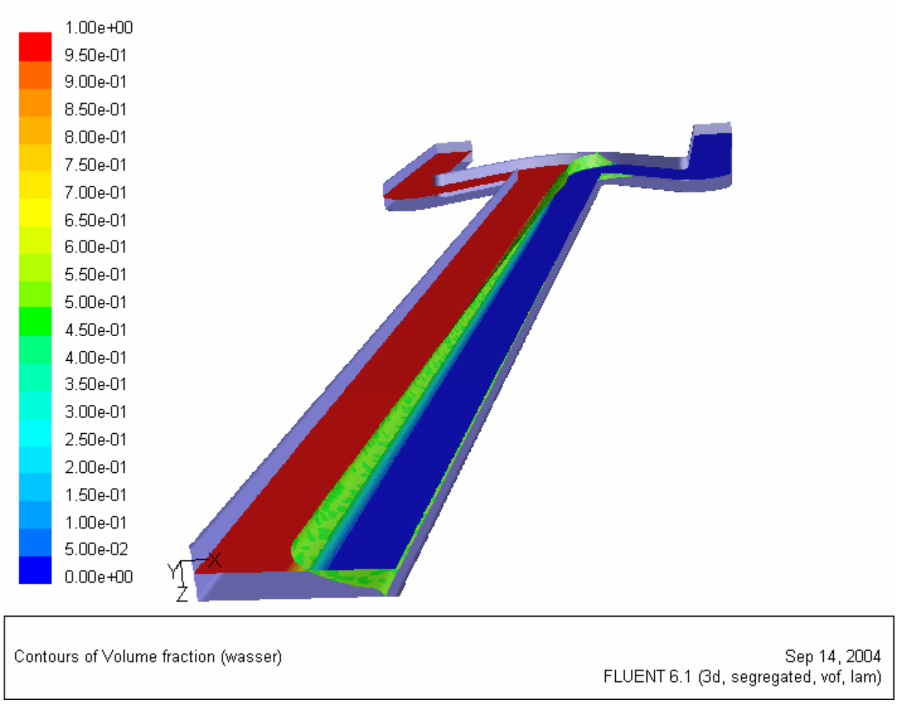

Figure 8: Calculated steady state interface for700 x 200 µm channel width

Determination of the stationary solution of the flow with the implicit VOF formulation, offered in Fluent 6.1, decreases the computational demand. With this simulation procedure a continuous interface is calculated as expected for laminar flow conditions, and the interface area can be computed with the integration function offered in the post-processing functions.

The computed interface area was $A_{interface,I} = 3.542\ 10^{-06}\ m^2$ for 700x200 µm cross-section in steady state and $A_{interface,II} = 4.694\ 10^{-06}\ m^2$ for 700x200µm in unsteady state (after 13.51 seconds run time).

As mentioned, mass transfer can be enhanced by increasing the interface area. Therefore CFD calculations were executed to prepare the influence of the geometry on interface formation by increasing the channel height from 200 µm to 700 µm.

For simulating the formation of the interface of a 700 x 700 µm microchannel a grid with 450.000 cells was created. The channel length was limited to 1 cm again and the throughput of water as well as n-hexane was again fixed with 10 ml/min. The phase velocity reduces due to the increased channel height and the interface is formed after 2.93 sec run time.

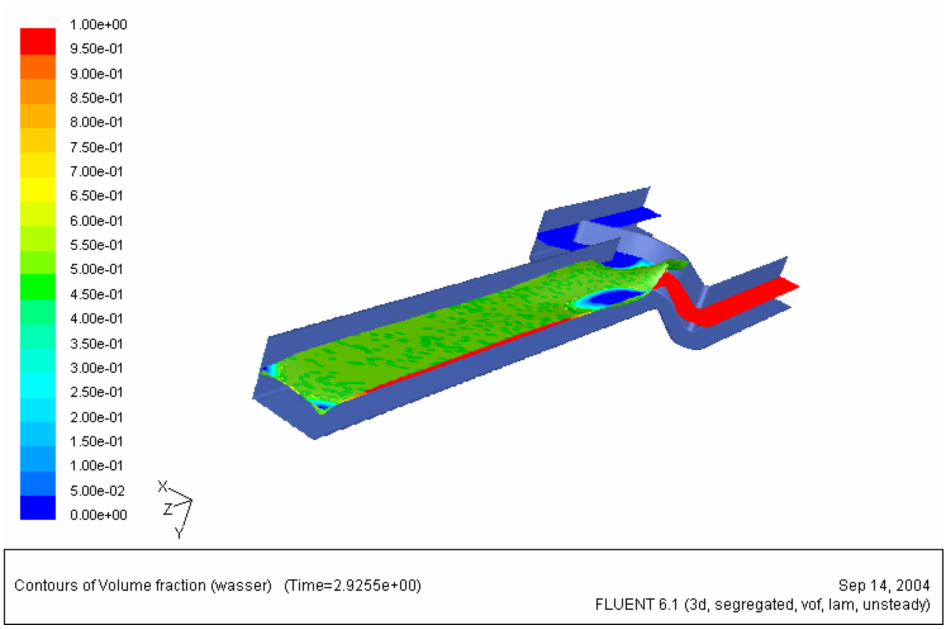

Figure 9: Calculated unsteady state interface for700 x 700 µm cross section of the micro channel

In *Figure 9* the interface is shown as horizontal surface at median channel height indicating the same volume for both phases. This result differs completely from the simulation results of the 700 x 200 µm microchannel. An interface area of $A_{interface,III} = 6.604\ 10^{-06}\ m^2$ was computed for unsteady state conditions (2.93 sec).

5. Summary

Extraction of acetone from n-hexane into water in the *mgt Design T-Mixer* yielded a net extraction efficiency of 25% at a flow rate of 8 g/min and a pressure drop of 2 bar. The decreasing tendency of net extraction efficiency with increasing flow rate results in an net efficiency of 9% at maximum flow rate of 24 g/min. Limitation of extraction efficiency was assumed to originate in the unfavorable size of 700 x 200µm channel cross section for mass transfer applications, caused by the small height of 200µm.

From CFD simulation an interface area of $A_{interface,II} = 4.7\ 10^{-06}\ m^2$ was calculated for steady state process conditions and 200 µm channel height. For comparison the simulation of the interfacial area was repeated for a channel height of 700µm, resulting in an interfacial area of $A_{interface,III} = 6.6\ 10^{-06}\ m^2$. From the comparison of the interfacial area of both simulation runs an improvement in mass transfer efficiency is concluded from enlarged channel height.

6. References

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1 Loewe, H.: Ehrfeld, W.; Hessel, V.; Richter, T.; Schiewe, J.: Micromixing Technology, Proc. Int. Conf. On Microreaction Technol., IMRET 4, Atlanta, Omnipress, Madison, WI, 31 (Mar. 5-9, 2000)

2 Benz, K.; Jaeckel, K.-P.; Regenauer, K.-J.; Schiewe, J.; Drese, K.; Ehrfeld, W.; Hessel, V.; Loewe H.: Utilization of Micromixers for Extraction Processes, Chem. Eng. Technol., 24(1), (p 11-17), (2001)

3 W. Ehrfeld, V. Hessel, H. Löwe: “Microreactors: New Technology for Modern Chemistry”, 1st ed., WILEY-VCH Verlag GmbH, 2000