Convective Mixing and Chemical Reactions in T-shaped Micro Reactors

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Abstract
A theoretical and experimental study was performed on convective micro mixing in T-shaped micro mixers. In these devices symmetric laminar vortices are developing at low Reynolds numbers Re. The symmetry breaks up with increasing Re numbers. This leads to an enormous enhancement of the mass transfer in the mixing channel. Numerical simulations of the flow characteristics and mixing behaviour are confirmed by pH neutralisation and indication by Bromothymol Blue. The integral mixing quality in the micro mixer is measured with the iodide-iodate-reaction (Villermaux-Dushman) and shows excellent values for high Re numbers. The comparison of the characteristic numbers in the mixer and the derivation of the Damköhler numbers Da demonstrate the benefits of miniaturisation. The shortening of the diffusion length in small channels and additional convective effects are leading to outstanding mixing results.

1. Introduction and motivation

Micro reactors are belonging to the most predominant equipment in the developing area of micro process engineering. Due to their small dimensions the mass transfer and the mixing of reactants can be controlled in a very effective manner in these devices. Most of the micro reactors studied today are running in continuous operation and with laminar flow conditions, see [1]. Micro reactors are mixing two (or more) components using various principles, see e.g. [2]. One can divide between active [3] and passive mixing which are realized in many micro devices. Passive mixers are using the flow itself to combine the various streams with splitting, recombination, and at last diffusive mixing, e.g. [4]. In these mixers, laminar flow is predominant and diffusion is limiting the mixing process. A successful micro reactor, i.e. for a complete reaction with a high selectivity and product yield, is based on an efficient mixing process. More specific, the time scale of the mixing process regarding the time scale of the reaction is playing the major role. The mixing must be finished for a successful and complete reaction. Therefore a fast and complete mixing is absolutely necessary for the micro reactor. A detailed description of the processes and concerning time scales can be found in Bourne [5]. Micro structured T-mixers were often investigated in the past, but mainly with laminar flow regime [6]. An extensive investigation was performed by Wong and co-workers [7]. The authors found experimentally good mixing regimes, but their simulation results did not show the symmetry break up and mixing enhancement.

Our passive micro mixers are using convective vortices generated by curved and bended flow as well as flow instabilities with higher Re numbers ($Re > 400$). The creation and development of the vortices were investigated by numerical simulation with CFD-ACE+ of ESI Group. Additionally, the flow patterns are visualized using a test reaction of Bromothymole Blue with a dilute alkaline solution. The time scales are important in which the mixing and the chemical reactions happen. The characteristic time of the chemical reaction results from the reaction kinetics and is fixed. Characteristic time scales of our T-shaped micro mixer are determined to describe the micro mixer with the Damköhler number. The entire mixing quality is determined further by the iodide-iodate-reaction (Villermaux-Dushman reaction), a consecutive-parallel reaction, which is well documented in literature [8, 9,]. The reaction was implemented in micro mixers [10], too, but mainly the measured spectral intensity of the iodine concentration is given. In a slow mixing regime iodine is generated to a higher extend, which can easily be measured by spectroscopy [11, 12]. The generated iodine concentration is formed into a segregation index which is reverse proportional to the mixing quality.

2. Simulation of the flow regimes

The flow in the micro channels is numerically simulated by CFD-ACE+ of ESI Group and graphically analyzed [13]. In the following the mixture of two fluids (water, 20°C) is treated with a flow ratio of 1:1. The analysis of other conditions can be found in [13]. For low flow velocities, $Re < 10$, the flow is laminar and the streamlines are straight, see Fig. 1, upper left side. With increasing flow velocity the centrifugal forces of the bended flow induce symmetrical vortex pairs at the entrance of the mixing channel [14], see Fig. 1, middle left side. The vortices are damped by viscous forces and the flow is laminar again. The mass transfer between the two fluids is controlled by diffusion as can be seen at the concentration profiles in the cross section of the mixing channel, Fig. 1 middle. The symmetry of the vortex pairs is broken for higher Re numbers and fluid swaps to the opposite side. The critical Re number, where this takes place, depends on the geometry and the flow conditions and ranges from 100 to 400. This gives an additional convective part for the mass transfer and dramatically increases the mixing quality. A more detailed analysis is given by the authors in [13].
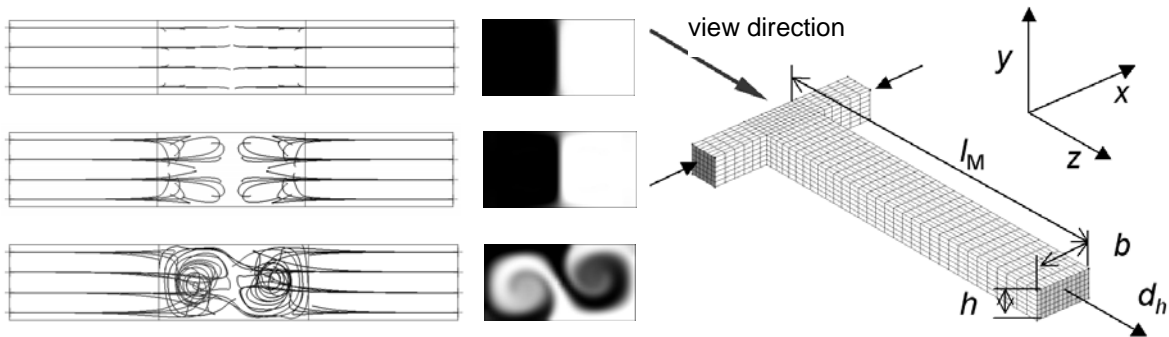

Fig. 1:   Numerical simulation of the fluid flow and mixing in a T-shaped micro mixer;
left: stream lines in a T-shaped micro mixer for three flow situations: Straight laminar, laminar vortex, and engulfment; middle: concentration distribution in the mixing channel for 1:1-mixing; right: geometry of the numerical model.

A closer look onto the flow structures of this so-called engulfment flow gives a deeper insight into the convective mixing process in a T-shaped micro mixer. The flow field at the entrance of the mixing channel can be divided into three major areas, see also Fig. 2:

- stagnation point flow at the backside of the mixing channel,
- small vortex pair with strong rotation and fast engulfment, and
- large vortex region with slow rotation.

The stagnation region and the small vortex pair are characterized by a strong stretching and folding of the fluidic elements and are therefore the key regions for the mixing enhancement.

Besides the top view of the stream lines in a T-shaped micro mixer, Fig. 2 shows the back side view and the mixer from the left and right side. The stream lines are indicating the portion of the entrance flow which is going to the opposite side of the mixing channel. This swapping area lies inside of the stream lines and includes the middle of the entrance flow with the highest velocity. The fluid with lower velocity stays on the entrance side and forms a large vortex. The swapping fluid coming from the left side goes to the top of the mixing channel and joins the large vortex, too. Only the fluid located at the sharp, outer part of the swapping area streams next to the stagnation area at the backside of the mixing channel and takes part in the small vortex which is displayed in Fig. 3.
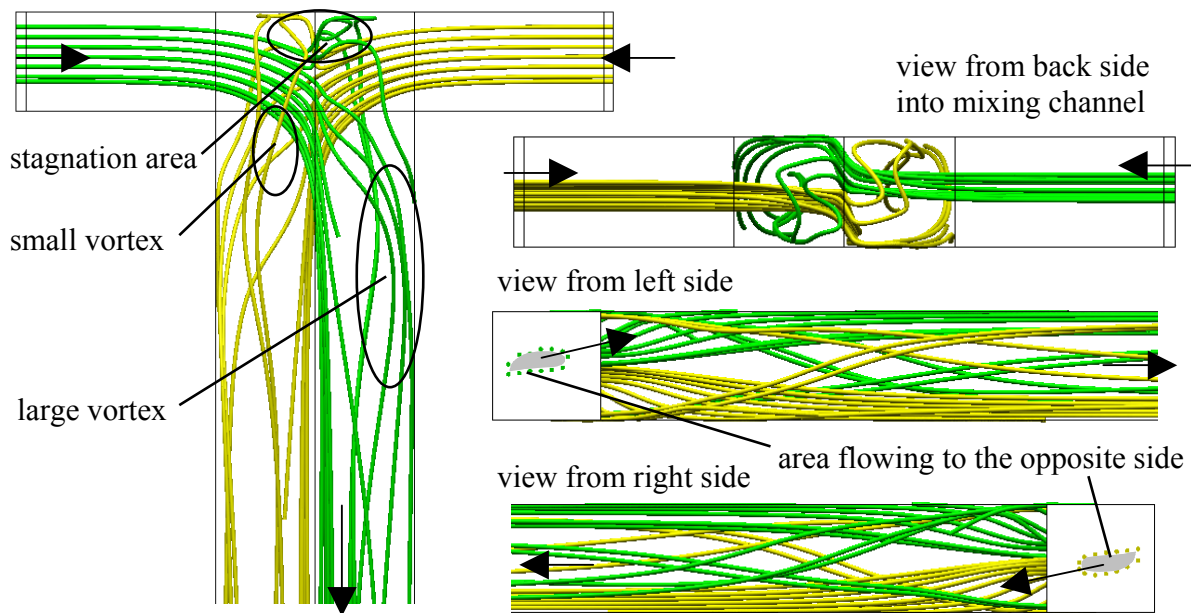
Fig. 2: Engulfment flow in a T-shaped micro mixer (200x100x100) at a mass flow of 73g/h and a corresponding Re number of about 135; the streamlines indicate the region of the entrance flow which is moving to the opposite side of the mixing channel.
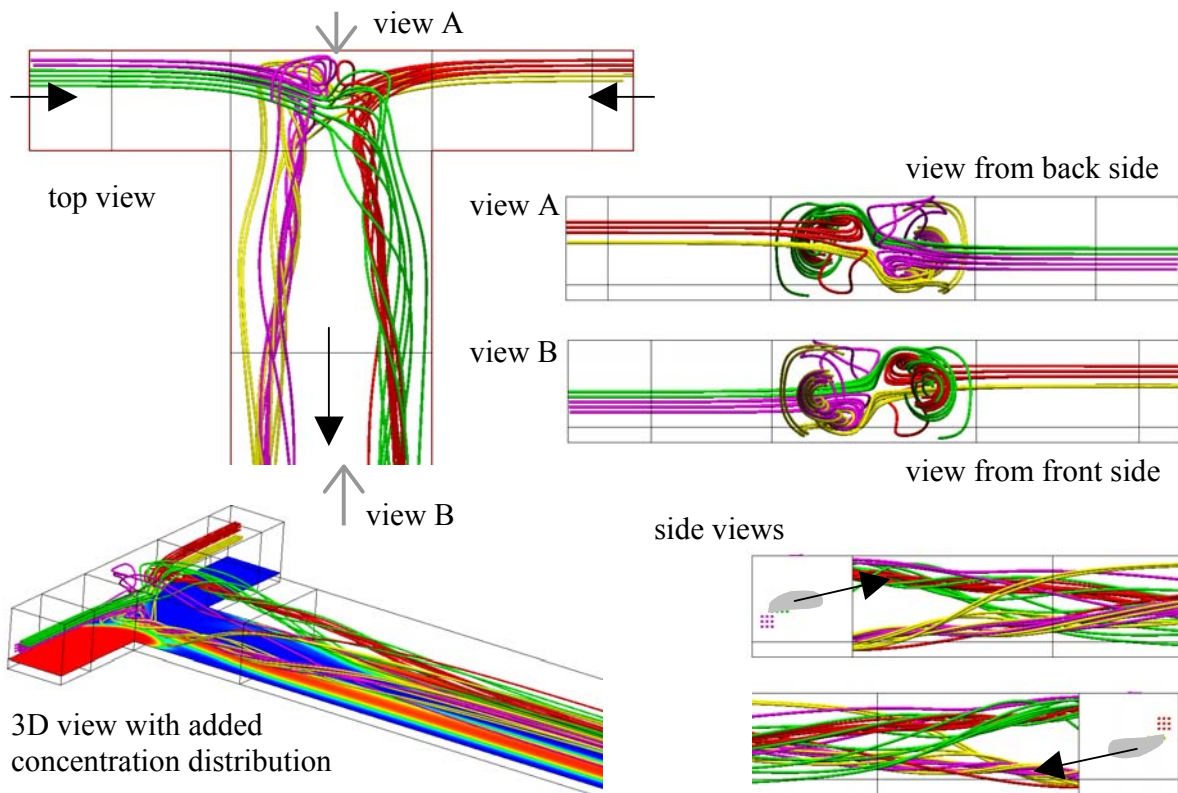

Fig. 3: Engulfment flow in a T-shaped micro mixer (200x100x100) at a mass flow of 73g/h and a corresponding Re number of about 135; stream lines for the small vortex pair which indicates the area with a high mixing intensity.

The main mixing process happens in the region of the small vortex pair which is shown in Fig. 3. This pair of small vortices starts at the corner region of the stagnation area and shows a strong laminar swirling without any turbulence, i.e. chaotic transient behaviour. With higher Re numbers the starting point of transient effects is located in this area. The fluid forming this small vortex pair comes from the sharp edge of the swapping area of the entrance flow. The investigation of this flow structures will be one of the main parts of our future research work to describe the mixing process in micro structures.

3. Experimental investigations

For the experimental observation of the flow regimes and the concentration fields, an experimental rig was set up which is described in [15]. The tested micro structures are self-fabricated by standard silicon technologies. The rectangular channels are RIE-etched on a 4 inch silicon wafer with various channel widths and the same channel depth. The fluidic connections from the back side are etched with KOH. The silicon wafer is covered by a Pyrex glass wafer and diced into twelve $20*20mm^2$ chips. The single chip is mounted in a fluidic support for the various fluidic connections and pressure measurements. The set up is described in [16].

3.1 Flow field and concentration distribution by pH-indication

To validate the results from the numerical simulations the mixing of two fluids and the existence of flow structures have to be visualized. After first tests with the fluorescent dye Rhodamin B the good optical contrast of pH indicators is used for this purpose. The equal volume flow redox reaction of an alkaline solution of di-sodium hydrogen phosphate (pH 8) with deionised water and Bromothymol Blue (pH7, green colour) results in a mixture with a pH value of 7.5 which is indicated by a blue colour. The concentration of the reactants is very low and has no remarkable influence on the fluid properties.
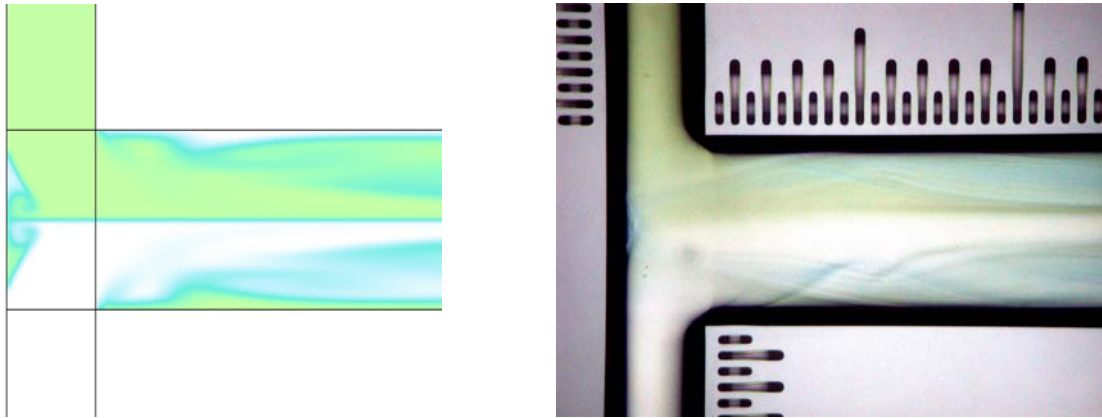

Fig. 4:   Qualitative comparison between simulation (left) and experiment (right) for a micro mixer with square cross sections (600x300x300), a mass flow of 260g/h, and a corresponding Re number of about 180.

For low flow velocities a sharp division between the two fluids can be seen. The mass transfer is controlled by diffusion in the small interface area. With increasing volume flow and Re number the interface lines first gets smaller. Suddenly the symmetry breaks up and parts of the fluid swaps to the opposite side, as described above. The fluid parts are stretched and split up which results in the filament structure as shown in Fig. 4. The comparison with the simulation shows a

similar behaviour, but the measured flow structures are much smaller. These small flow structures and their corresponding concentration field are not resolved in the simulation due to the coarse numerical grid. The error estimation and the accuracy enhancement are future research areas in our working group. This is assisted by accurate measurements from the Bremen workgroup of Prof. Räbiger which are presented in the same session.

The figures of both research groups show very fine fluidic structures with a characteristic dimension of only a few microns. These structures are decreasing the diffusion length and enhancing the mixing enormously.

With further increasing volume flow and Re number, the flow starts to get transient and the mixing quality increases further on. The transient effects occur for Re numbers over 400 to 800 which are not yet investigated by numerical simulation The optical homogeneity at the end of the mixing channel is one indicator for a good mixing, but the quantitative value is determined with the help of the iodide-iodate reaction (Villermaux-Dushman).

3.2 Description of the mixing quality with the aid of the iodide-iodate-reaction

From the literature there are some test reactions known for the determination of the mixing quality [17]. Due to safety reasons, the well known kinetics [8, 9], and the available analytical equipment (UV-spectroscopy) the iodide-iodate reaction was chosen for the determination of the mixing quality. The concurrent parallel reaction obeys the following scheme:

$$A + B \xrightarrow{k_1} R$$
$$C + \nu B \xrightarrow{k_2} S \tag{1}$$

with the first reaction being faster than the second ($k_1 \gg k_2$). Within a slow mixing process the amount of component B is sufficient to form the second reaction and the product S. This means for the mentioned reaction:

$$H_2BO_3^- + H^+ \xrightarrow{k_1} H_3BO_3$$
$$5I^- + IO_3^- + 6H^+ \xrightarrow{k_2} 3I_2 + 3H_2O \tag{2}$$
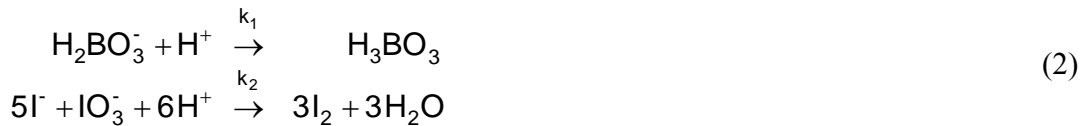
With a local surplus of H^+ ions the second reaction generates I_2. Iodine I_2 is in equilibrium with I_3^- and is spectroscopically measured in the UV range (352 nm). The measured intensity directly gives the iodine concentration and is calculated to a segregation index X_S which is inversely proportional to the mixing quality. More details of the reaction are given in [18]. In Fig. 5 the segregation index is displayed over the Re number for the mixing process in three different channel geometries. Typical values of X_S are between 0.1 and 0.01 in a stirred vessel.

The concentration of the reactants are adjusted to the Re number from 100 to 800 and corresponding volume flow in the investigated cross sections. For lower Re numbers the mixing is not fully completed inside the mixing channel and happens also outside the mixing chip. So, the results are not representative for the mixing process in the micro channels. Higher Re numbers result in a high pressure loss which was limited by the experimental set up. It is clear to see, that the mixing quality improves with increasing Re number. For a constant mean velocity in the whole mixer (600x300x300), there is a steep decrease of the segregation index X_S between Re numbers of 250 to 400. The mixing is improved in the engulfment flow and the starting transient flow. A further increase in volume flow does not increase the mixing quality. The same trend can be observed for the accelerated flow conditions (200x200x200 and 500x500x200) but at higher Re numbers, due to the stability of an accelerated flow. The smaller channel leads to a higher mixing quality, because the diffusion length between the two fluids is shorter. These results are

also in good agreement with other experiments concerning the transition from vortex flow to engulfment flow, shown in [16]. A broad mixing channel leads to a decelerated flow situation at the beginning of the mixing channel and an early transition from vortex to engulfment flow which can also be seen in Fig. 5 for the micro mixer (800x200x200). The segregation index decreases at Re numbers from 150 to 230, as expected. This decrease is followed by an increasing segregation index from Re numbers from 230 to almost 300 and then a decreasing segregation index again. This intermediate decreasing mixing quality is mainly because of the complex flow situation and will be investigated in the near future.
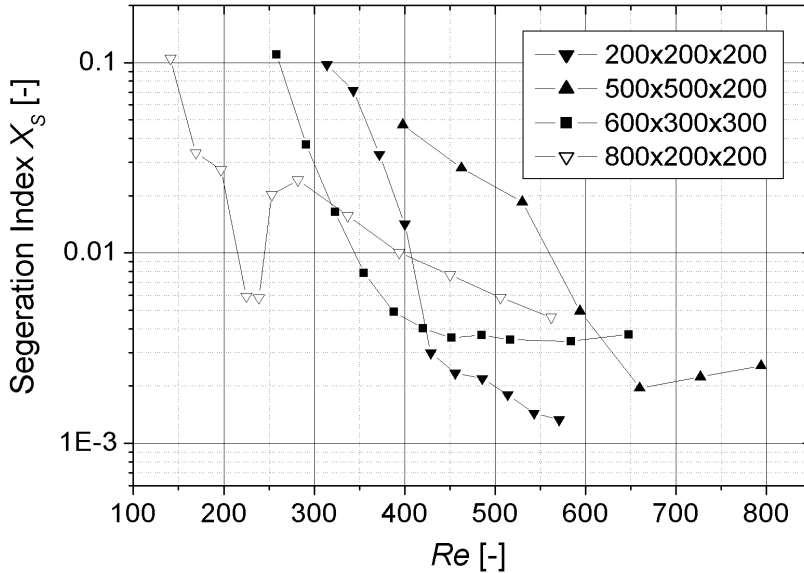

Fig. 5:   Segregation index X_S over the Re number in the mixing channel for various cross sections; The nomenclature in the legend means: width of the mixing channel x width of the entrance channel x depth of the channels, i.e. constant mean flow velocity in the T-mixer with 600x300x300, accelerated mean flow velocity in 200x200x200 and 500x500x200, and decelerated mean flow velocity in 800x200x200.

The experimental data of the concurrent parallel reactions demonstrate the good mixing characteristics in micro channels. Mainly convective effects are leading to the good mixing quality. The processes underlying these results are quite complex, so a short estimation of the characteristic times of the mixing process with chemical reactions will be given as an overview.

4. Discussion

4.1 Characteristic times for the micro reactor

The residence time of the fluid in the mixing channel is given by the channel length devided by the mean velocity

$$t_P = l_M / \overline{u}.$$ (3)

The mass transfer in radial direction, perpendicular to the flow direction, is limited by diffusion in laminar flow. The diffusion length of a molecule can be calculated by the Einstein formula

$$x^2 = 2Dt,$$ (4)

with D as the diffusion coefficient of the binary mixture. The mixing is finished, when all molecules are evenly distributed over the entire cross section which denotes a mean diffusion length of

the half of the channel width. The time for this diffusion process is calculated by

$$t_D = \frac{(b/2)^2}{2D} \propto \frac{b^2}{D}.$$ (5)

The ratio of the diffusion time to the residence time indicates the progress of diffusion at the end of the mixing channel:

$$\frac{t_D}{t_P} = \frac{b^2}{D} \frac{\bar{u}}{l_M} = Re \cdot Sc \frac{b^2}{l_M \, d_h}.$$ (6)

The ratio can be expanded with the dimensionless groups of the Re and Sc number. A ratio with a value of 1 indicates a good mixing at the end of the mixing channel. A higher ratio indicates an incomplete mixing, so the mixing quality is inversely proportional to the Re and Sc number, as also described in [14]. This is only valid for straight laminar flow. With convective effects the mixing quality is increased and almost proportional to the Re number [14].

A chemical reaction within the mixing channel brings another time scale into the process which depends on the reaction kinetics. The time variation of a species concentration is described by the reaction rate

$$\frac{dc_i}{dt} = v_i \, r = v_i \, k \, c_i^n.$$ (7)

For a first order reaction with a constant volume the half life time is calculated by:

$$t_R = \frac{c_i}{v_i \, r} = \frac{1}{k}.$$ (8)

The characteristic time of the reaction is inversely proportional to the kinetic constant k. The ratio of the characteristic process times to the reaction time are formulated in the so called Damköhler numbers:

$$Da_I = \frac{t_P}{t_R} = \frac{l_M \, k}{\bar{u}}.$$ (9)

$$Da_{II} = \frac{t_D}{t_R} = \frac{b^2 \, k}{D}.$$ (10)

For high Da_I numbers ($Da_I \gg 1$) the components have enough time to react in the mixing channel and will perform a complete reaction. This demands long mixing channels or a very low mean velocity. For low Da_{II} numbers the components are mixed very fast which leads to a complete reaction within small micro channels. A miniaturization of the mixing channel leads to a very fast mixing by diffusion ($Da_{II} \propto b^2$) which can be assisted by convective effects as shown above. A more detailed discussion of the Damköhler numbers in micro reactors can be found in [15].

4.2 Mixing time and length

With the symmetry break up of the flow and the appearance of the engulfment flow the fluidic structures are generating short diffusion paths and therefore a short mixing time. The mixing quality within the mixing channel is increased. With higher Re numbers transient flow patterns are generated which intensify the mixing process. These phenomena appear at the entrance of the mixing channel where most of the energy is dissipated (high local pressure loss). Along the mixing channel the chaotic structures are damped and laminar flow is readjusted again. In the literature mixing models can be found for developed turbulent flow, i.e. the engulfment theory in [5, 17]. These are used as a starting point for the physical modelling.

The mixing process in the investigated microstructures happens between the laminar flow and the developed turbulent flow and cannot be described with both methods either. The future research work is concentrated on the development of an adequate analytical description of the mixing process with controlled vortices, small fluidic structures and the beginning of transient flow behaviour.

5. Summary and Outlook

The mixing process is studied in T-shaped micro mixers with chemical reactions. Due to the channel bends the laminar flow is disturbed, vortices are generated, and first transient effects are observed, which dramatically enhance the mixing quality. The flow and concentration fields are investigated by numerical CFD simulation and evaluated by a pH neutralization reaction with the indicator Bromothymol Blue. A closer look on the vortex structure of the engulfment flow is given to show some mixing mechanism. The numerical diffusion is limiting the accuracy of the simulation results which necessitates the experimental investigations. The well-known iodide-iodate reaction was implemented for the measurement of the integral mixing quality. The results show the very good mixing characteristics in T-shaped micro mixers with different cross sections and accelerated and decelerated flow conditions. The comparison of the characteristic times of the mixing process and the chemical reaction also shows the good mixing characteristics in micro channels. This comparison leads to the formulation of the dimensionless Damköhler numbers.

The next steps in our research work will be the evaluation of the energy dissipation from the numerical simulations. With a refinement of the numerical grid the fine fluidic structure should be better resolved and characterized. The iodide-iodate reaction is used for the measurement of the mixing quality of further micro structures, especially for decelerated flow conditions. The mixing time will be calculated from the segregation index for the various geometries. The comparison of the various characteristic times will lead to design rules for appropriate micro mixers. These investigations will lead to the physical modelling of the mass transfer process between pure diffusion during laminar flow and pure convective mixing in fully turbulent flow in micro structures.

Nomenclature

b	width of the mixing channel	m
c_i	concentration of the component i	kg/kg
d_h	hydraulic diameter	m
D	diffusion coefficient	m^2s
Da	Damköhler number	-
k	reaction velocity	depends on the reaction, here 1/s
l_M	mixing channel length	m
n	reaction order	-
Re	Reynolds number	-
r	reaction rate	1/s

Sc	Schmidt number	-
t	characteristic time	s
$\bar{u}$	mean velocity	m/s
x	diffusion path, mean molecular mobility	m
ν_i	stoichiometric coefficient	-

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