Simultaneous two-tracer-LASER-induced fluorescence and particle image velocimetry for the investigation of macro- and micro-mixing in a static mixer

Andreas Lehwald, Dominique Thévenin and Katharina Zähringer
Lehrstuhl für Strömungsmechanik und Strömungstechnik, Universität Magdeburg, Germany, andreas.lehwald@ovgu.de

Abstract Static mixers are important mixing tools especially for highly viscous flows (e.g., pharmaceutical products, biotechnology, food engineering, polymer production). In order to quantify the flow-induced mixing at large scales (macro-mixing), as well as mixing induced by molecular diffusion at small scales (micro-mixing), an experimental procedure has been developed in our group that is based on simultaneous Two-Tracer-PLIF (2T-PLIF) measurements. In order to check correlations between mixing and velocity fields, additional PIV measurements have been now realized simultaneously with 2T-PLIF. First raw and post-processed results are presented here for laminar conditions. In order to quantify micro-mixing by PLIF, a neutralization reaction involving the fluorescent tracer Uranine as pH-indicator has been identified as a suitable technique. Uranine and thus the pH-field are visualized simultaneously with another fluorescent tracer, Pyridine 2, which is independent from the pH and characterizes only macro-mixing. The PIV measurements are imaged simultaneously with a separate camera. After calculation of the molecular concentration fields from the LIF-images, normalized non-dimensional concentrations are determined. As an indicator for micro-mixing, the degree of deviation $\Delta$ is calculated. The repartition of macro- and micro-mixing behavior is additionally analyzed by tracing the pdf of the non-dimensional concentration and $\Delta$-values. For a quantitative analysis of the mixing efficiency, the classical segregation index is also calculated. Additionally, the PIV and 2T-PLIF results are analyzed using Fast Fourier Transformation (FFT) in order to identify the characteristic frequencies of the structures induced by the static mixer. The calculation of correlation functions between the velocity and concentration fields allows a deeper insight into the local mixing mechanisms. Thanks to these simultaneous PIV-2T-PLIF measurements, it becomes in particular possible to quantify macro-mixing and micro-mixing in mixing devices with geometrical features and dimensions similar to practical applications and to determine in a quantitative manner the connection between velocity and mixing fields. All experimental measurements are made freely available to the scientific community through a data-base accessible via Internet.

1. Introduction

Static mixers are important mixing tools especially for highly viscous flows (e.g., pharmaceutical products, biotechnology, food engineering, polymer production). They have been studied extensively in the past by different researchers in a global manner (Pahl and Muschelknautz 1982), but also more recently using non-intrusive optical diagnostics, for instance Particle Image Velocimetry (PIV) and Planar Laser-Induced Fluorescence (PLIF). PIV and PLIF have been employed separately (Lehwald et al. 2010b, Pust et al. 2006, Wadley and Dawson 2005) or simultaneously (Lehwald et al. 2008).

For a variety of applications, it is now becoming increasingly important to adjust much more precisely the mixing properties of such devices. For this purpose one distinguishes micro-mixing, which is associated with small scales down to the molecular level (Hjertager Osenbroch 2004), from macro-mixing, which refers to the flow mixing processes at large scale (up to the size of the reactor cross-section). For turbulent flows, “micro-mixing” would mean a typical length scale below the characteristic Kolmogorov scale (Baldyga and Bourne 1999) and micro-mixing is thus an important mechanism that directly influences fast chemical reactions, since the reactants locally come in contact with each other only through micro-mixing (Öncül et al. 2009). It can also be the
limiting factor e.g., for combustion reactions or biological initiation processes. Recently, mixing at the microscale has also received much attention due to the emergence of microfluidic devices and micro-reactors. In laminar systems, as ours, mixing is mainly due to diffusion and thus micro-mixing (Wheat and Posner 2009). On the other hand “macro-mixing” is controlling mean concentration and global residence time distribution (Fox 2003). Computer simulations can relatively easily describe mixing at large scales (macro-mixing) on the employed discretization grid, while mixing at small scales (micro-mixing) must usually be described by suitable models. It is therefore important to quantify both effects separately in order to develop and improve corresponding models.

This is unfortunately quite a difficult task. Most commonly, an acid-base reaction (e.g., between hydrochloric acid, HCl, and sodium hydroxide, NaOH) is used together with a pH-tracer (Koochesfahani and Dimotakis 1986). This approach is still successfully used today (Hjertager Osenbroch 2004, Lehwald et al. 2010b) since it is quite inexpensive. Concentration and pH-value are usually detected using PLIF or titration.

As an alternative, Baldyga and Bourne (1989) were the first to use consecutive competing reactions (now usually simply called Bourne reactions). In the first step, two reactants spontaneously react to a first product that, in a second, considerably slower reaction, reacts with one of the reactants to form another product. The ratio of the quantity between the first product and the second product is directly related to the ratio of mixing time to reaction time.

A third method for separating macro-mixing and micro-mixing is the simultaneous use of a fluorescent dye, produced by a fast chemical reaction (for micro-mixing) together with a second, inert laser dye (for macro-mixing). As described by Kling and Mewes (2004), it is possible to combine in a suitable manner an inert dye such as carboxySNARF and a reactive dye like FLUO-4 to simultaneously investigate macro-mixing and micro-mixing. These commercially available chemical components are unfortunately extremely expensive and can therefore only be used for small-scale installations. For more realistic installations and in particular for the case investigated in the present work, another solution had therefore to be identified.

In order to quantify the flow-induced mixing at large scales (macro-mixing), as well as mixing induced by molecular diffusion at small scales (micro-mixing), an experimental procedure has been developed in our group that is based on simultaneous Two-Tracer-PLIF (2T-PLIF) measurements (Lehwald et al. 2010b). Based on a systematic screening involving many different reaction systems and tracer dyes, we have been able to identify a suitable method for large-scale applications. This measurement procedure relies on simultaneous Two-Tracer Planar Laser-Induced Fluorescence measurements. In order to check correlations between mixing and velocity fields, additional PIV measurements have now been realized simultaneously with the Two-Tracer-PLIF. First raw and post-processed results are presented here for laminar conditions. The considered geometry is a simplified, but real-scale representation of a standard, commercially available static mixer, considering a single segment with laminar inflow conditions.

2. Method and experimental set-up

The method used for the separate characterization of macro-mixing and micro-mixing is described in detail in Lehwald et al. (2010b). Here, only the essential points necessary for the understanding of the experimental procedure are given.

After an extensive analysis of possible reaction systems, only a neutralization reaction seemed to fulfill all the required criteria. Further tests demonstrated that fluorescein disodium salt (C₂₀H₁₂Na₂O₅, also called Uranine, purchased from Acros Organics-Fisher Scientific) can be used as a tracer of the neutralization reaction. This fluorescent dye changes its fluorescence intensity.
depending on the local pH-value (Figure 1). This can be used to track the reaction progress of the acid-base reaction and thus indirectly micro-mixing. Uranine is then visualized simultaneously with another fluorescent tracer, Pyridine 2 (C_{19}H_{23}N_{2}ClO_{4}, LDS 722, purchased by Exciton, Dayton, Ohio), which is, in a certain range, independent from the pH (Figure 2) and characterizes only macro-mixing. Both tracers are excited at the same wavelength (532 nm) and their fluorescence signals can be clearly separated with two different optical filters. Quantifying simultaneously macro- and micro-mixing is thus possible using the combination of Uranine with Pyridine 2 (for details of the tracer choice see Lehwald et al. 2010b).

As it can be seen on figure 1, due to the large slope of the calibration curve around pH 6-7, we limited the measurement-range from pH 5.5 up to pH 8.5 in order to increase signal quality. Within this pH-range a water/hydrochloride acid (HCl) solution containing fluorescein disodium salt can be injected as a tracer into the main stream of an alkaline fluorescein disodium salt solution. The resulting acid-base reaction changes the local pH-value, and as a consequence the emission intensity of the fluorescein disodium salt. Using equal initial concentrations of fluorescein disodium salt in both streams, this local pH modification can be quantified by PLIF and is a direct marker of the very fast acid-base reaction, and thus indirectly of micro-mixing. Within this method only affordable tracers are employed, thus allowing the characterization of mixing properties even in large-scale installations.

The details of the optical setup and image evaluation procedure can be found in Lehwald et al. (2010b). Fluorescence of both tracers is stimulated at the outlet of the mixer by the laser sheet of a doubled Nd:YAG laser. An optimal concentration of 1 mg/l for Uranine and a range of 0 mg/l to 1.5 mg/l for Pyridine 2 have been identified as ideal for our experimental set-up, using tap water as the main fluid. The PLIF images are acquired using two identical, intensified CCD cameras (NanoStar, LaVision). These are placed side by side with an angle of respectively 75° to the measurement area, imaging the vertical center plane behind the mixer (Fig. 3). A traversing unit allows the acquisition of three consecutive image planes. To separate the macro-mixing and micro-mixing signals, the camera objectives (Nikkon AF Micro Nikkor 60mm/2.8D) are equipped with two different band-pass filters. A BP 550/10 filter is used to detect Uranine while a BP 705/30 filter is used to detect Pyridine 2.

The acquired PLIF data have been post-processed and evaluated using the program DaVis by LaVision including energy correction, background correction (reflection, diffraction and refraction) and geometrical dewarping of the acquired images. The calibration curves, used to transform the measured fluorescence light intensities to concentration and pH-fields, have been acquired.
following the calibration method described in Lehwald et al. (2010b). These curves are programmed into DaVis as a last step of the postprocessing procedure.

As for previous PIV-measurements (Lehwald et al. 2008), spherical hollow glass balls (Type 110 P8 CP00, \( d_{50} = 10.2 \mu m \)) have been seeded (25 mg/l) into the main-flow and imaged, simultaneously with 2T-PLIF, with a separate camera (Imager Intense, LaVision). It is placed with an angle of 90° to the measurement area, facing the intensified cameras (Fig. 3). Both, PIV and PLIF, use the same light-sheet of a frequency-doubled Nd:YAG-laser with a thickness of about 0.5 mm and a pulse energy of 140 mJ. The two LIF-images are captured together with the first PIV-image. The time delay between the two PIV-images is \( \Delta t = 20 \) ms. Series of 515 images have been captured in that way (limited by the main flow storage tank size, limiting the possible duration of the experiment) with a frequency of 5 Hz, which is sufficient for time resolution of the flow in this experimental set-up (see Lehwald et al. (2010b) and section 3, figure 10).

PIV images are evaluated using standard cross-correlation with an adaptive interrogation-area size from 128x128 pixels down to 32x32 pixels with an overlap of 50 % and a circular weighting window (1:1). Preprocessing includes image distortion correction, image inversion, subtracting of a sliding background (scale length 10 pixels) as well as particle intensity normalization (min-max-filter) with a scale length of 4 pixels.

The multi-pass postprocessing considers peak validation (peak ratio 1.1) and a median filter. The median filter compares the velocity components of the vector \( u \) with the velocity components of the median vector \( \bar{u}_{\text{median}} \pm \text{standard deviation} \ u_{\text{rms}} \) computed from the eight neighboring vectors. If in x- and z-direction \( \bar{u}_{\text{median}} \pm 2 \cdot u_{\text{rms}} \leq u \leq \bar{u}_{\text{median}} + 2 \cdot u_{\text{rms}} \) the vector is kept, else it is rejected. Furthermore a rejected vector will (re)inserted if in x- and z-direction \( \bar{u}_{\text{median}} \pm 3 \cdot u_{\text{rms}} \leq u \leq \bar{u}_{\text{median}} + 3 \cdot u_{\text{rms}} \). Additionally, to eliminate isolated, spurious vectors, groups with less than 5 vectors were removed. To reduce noise a 3x3 smoothing was used and x-velocity is limited to maximum 50 mm/s (about 10 times the mean velocity in the channel). If at least two neighbor vectors are available, empty spaces are filled up by interpolation. This calculation results in a vector field of 79 x 51 vectors for a window size of 14 x 9 cm², which means a resolution of almost 32 vectors/cm².

Unfortunately, a higher seeding concentration and hence smaller interrogation areas, were not possible, since otherwise too much laser-light would have been lost due to scattering and absorption, and LIF-measurements would not be possible any more with the same light sheet. This limits the minimal interrogation area size and thus the resolution of the velocity field. Very small velocity structures (< 3.5 x 3.5 mm²) can not be resolved in that way.

The flow installation used for these studies is already described in detail in Lehwald et al. (2008) and Lehwald et al. (2010b). Well-controlled, laminar flow conditions at the inlet of the mixer are obtained by using a gravity-driven flow installation (Fig. 3). Water flows down to the test section from an upper tank with a regulated, constant liquid level, which lies roughly 10 m above the axis of the channel. A 2.45 m long square inflow section leads the fluid to the static mixer. The test section has a square shape in order to increase the quality of all optical measurements by limiting refraction, laser beam divergence and image distortion.

The mixer segment consists of seven V-shaped blades with a rectangular cross-section of 13 mm x 11 mm, as illustrated in figure 4. Four blades are turned against the flow; between them, three are turned in the direction of the flow. The angle between the channel wall and the blade is 45°, the total length of the blades in flow direction is 60 mm. The straight outflow section behind the mixer also has a length of 2.45 m (Fig. 3). Inflow, outflow and mixer segment are made of acrylic glass and have a cross section of 91 x 91 mm². A flow meter is installed at the end of the test section. The required flow rates are adjusted using a precision control valve. From there, the fluid goes to a damper, so that tracers do not recirculate in the installation (open loop). The static overpressure in
the test section is 0.87 bar.

Fig. 3 Experimental set-up of the gravity-driven test channel.

The main flow, arriving from the upper tank, contains the PIV-tracer and the fluorescent micro-mixing tracer Uranine with a concentration of 1.0 mg/l at a pH-value of 8.5. Uranine with the same concentration and a pH-value of 5.5, together with the fluorescent macro-mixing tracer Pyridine 2, at a concentration of 1.5 mg/l, are injected along the centerline of the channel, 39 mm upstream of the mixer segment (Fig. 3). Both streams are co-current, laminar and have the same velocity before entering the mixer segment. The outlet of the secondary, central injection system has a square section of 169 mm². Its water/Uranine/Pyridine 2/HCl mixture flows through a thermostat (Haake Phoenix 2 P1-C25P), which is used to control the temperature (around 17°C) of this fluid and keep the difference with the main fluid temperature in the channel below 0.5 K. This very accurate temperature control was observed to be absolutely necessary in order to avoid a rapid stratification
(induced by buoyancy) between the injected mixture and the main flow.
3. Results and evaluation

Examples of postprocessed simultaneous 2T-PLIF and PIV measurement results and their evaluation as presented in Lehwald et al. (2010b) are shown in figure 5 exemplarily for one single time shot (for complete time series, see additional electronical material to Lehwald et al. 2010b). These results correspond to the previously obtained separate PIV (Lehwald et al. 2008) and 2T-PLIF (Lehwald et al. 2010b) measurements. This figure demonstrates that the combined PIV-2T-PLIF system employed in this study is also capable of providing high-quality measurement results.
The vortex structures induced by the mixer can be seen clearly on the images of figure 5. They are similar for Pyridine 2 concentration, pH and velocity. On the Pyridine 2 image, pockets can be recognized, that still contain the initially injected concentration of the tracer, thus indicating that these pockets have not yet been macro-mixed sufficiently. On the other hand, the pH-image shows that in these pockets, the pH has already increased compared to the injected pH of 5.5. This means, that micro-mixing has already started at these locations.

After calculation of the molecular concentration fields from these images, normalized non-dimensional concentrations are determined (Fig. 6, left: Pyridine 2 and right: H⁺-ions). As an indicator for micro-mixing, the degree of deviation $\Delta$ (Fig. 7) is then estimated (Lehwald et al. 2010a):

$$\Delta(\bar{x},t) = 1 \frac{c_{Pyridine_2}(\bar{x},t) - c_{H^+}(\bar{x},t)}{c_{Pyridine_2}(\bar{x},t)}$$

The aforementioned pockets can also be seen on these figures. The normalized Pyridine 2 concentration shows values near unity at these places. Simultaneously, the normalized H⁺-ion concentration has a rather high value there compared to the surroundings. Nevertheless, it is already reduced to about one third of its initial value. Micro-mixing is quantified in figure 7 through the degree of deviation. It has been already strongly reduced within these pockets.
The evolution of the probability density function for macro-mixing and micro-mixing has then been computed for each time step of the complete time series (515 images). For this purpose, the local, instantaneous, normalized non-dimensional concentration of Pyridine 2 (macro-mixing) has been plotted against the local, instantaneous degree of deviation (micro-mixing), as illustrated in Fig. 8. The colorscale for figure 8 (log-scale) indicates the number of occurrences of corresponding macro-mixing / micro-mixing combinations. Different limit combinations can be recognized:

<table>
<thead>
<tr>
<th>micro-mixing near unity</th>
<th>macro-mixing near unity</th>
<th>corresponds to initial state of central injection</th>
<th>almost not observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>micro-mixing near zero</td>
<td>macro-mixing near zero</td>
<td>almost complete mixing</td>
<td>very often observed</td>
</tr>
<tr>
<td>micro-mixing near unity</td>
<td>macro-mixing near zero</td>
<td>corresponds to initial state of main flow</td>
<td>sometimes observed</td>
</tr>
<tr>
<td>micro-mixing near zero</td>
<td>macro-mixing near unity</td>
<td>pockets of Pyridine 2 due to large-scale mixing</td>
<td>almost not observed</td>
</tr>
</tbody>
</table>

Occurrences of strong macro-mixing (low macro value) are higher for the whole range of micro-mixing. This illustrates that complete micro-mixing is only possible if macro-mixing has taken place. The temporal evolution of Fig. 8 (not shown) is rather insignificant over the 515 images of one series. The correlation between macro-mixing and micro-mixing after one mixer segment hence seems to be quite constant with time.

For a quantitative analysis of the mixing efficiency, the classical segregation index given by Danckwerts (1952) and based on the normalized concentration variance has also been calculated (Fig. 9). As it can be seen in this figure, the segregation index has already reached a rather low level after the mixer segment and is decreasing continuously further downstream. The segregation index calculated from the images representative for macro- and micro-mixing simultaneously (right) is, as expected, smaller than with macro-mixing only. It has already reached a nearly constant level, compared to the macro-mixing segregation index (left). As for the probability density function, no significant temporal evolution of the segregation index could be recognized when analyzing the complete time series.

![Fig. 9: Segregation index calculated from the Pyridine 2 images (left) for macro-mixing and from the Uranine images for macro and micro-mixing (right). Solid lines refer to the left axis for the global mean segregation index, dashed lines show the global mean average of the molar concentration on the right axis.](image)

In a first attempt to analyze the relationship between velocity field and macro and micro-mixing fields, represented by the concentration fields of Pyridine 2 and H\(^+\)-ions, Fast Fourier
Transformation (FFT) has been used in order to identify the characteristic frequencies of the structures induced by the static mixer (Fig. 10). The values for the velocity magnitude, velocity vector angle, Pyridine 2 concentration and H\(^+\)-ion concentration have been used as variables for this spectral analysis.

These spectra show nearly the same behavior for all four variables analyzed, with a main peak at 0.37 Hz (within the range of the resolution of the FFT calculation) and its harmonics. This frequency represents the frequency of the flow structures induced by the mixer and shows a clear relationship between the velocity and mixing fields.

The 2D image correlation between the velocity and concentration data has been computed for the complete time series using Matlab (Fig. 11). It can be seen from this figure that no significant temporal change can be observed for the correlation coefficient. Pyridine 2 and Uranine images can be compared directly (Fig. 11 top left), due to the same optical resolution and pixel size of the cameras. A mean correlation coefficient of 0.5 is obtained for this combination. This means that macro-mixing (Pyridine 2) and macro- plus micro-mixing (Uranine) are indeed correlated, but only in a limited manner, as can be already seen qualitatively in Fig.6.
Note that the correlation coefficients are unfortunately highly dependent on the image resolution. Since the resolution of the velocity vector fields is very different from that of the concentration images (different camera, 32 pixel x 32 pixel interrogation area), the concentration images had to be rescaled and interpolated to get the same matrix size and coordinate system for computing correlations with the velocity field. The influence of this operation on the correlation coefficient is strong, as it can be recognized in figure 11. The correlation coefficient between Pyridine 2 and Uranine goes down to a mean value of 0.2 compared to the original 0.5 when decreasing image resolution. This may be directly attributed to the loss of information, especially for micro-mixing, occurring at very small scales. As a consequence, meaningful correlations between concentrations and velocity vectors can only be obtained when both PLIF and PIV deliver flow quantities at roughly the same resolved scale.

4. Conclusions

A previously established method for the characterization of micro-mixing and macro-mixing based on Two-Tracer-PLIF has been used simultaneously with PIV for the analysis of the velocity and mixing fields induced by a static mixer element. The results have been postprocessed in order to analyze the relationship between velocity field, macro- and micro-mixing. Thanks to these calculations macro-mixing and micro-mixing can be quantified and their temporal behavior can be determined. The frequency of the induced concentration and velocity structures has been calculated and indicates the same frequency of 0.37 Hz, which means, that velocity and mixing fields are coupled. On the other hand, direct image correlation of the tracer concentrations with the velocity field shows a rather weak correlation, which may mainly be due to the limited resolution of the vector field as determined by PIV. In order to obtain meaningful correlations between velocities and concentrations, the PIV resolution must be considerably improved. This will be the purpose of future work, as well as the analysis of combinations of several mixer elements. Such experiments have already been undertaken and are now postprocessed. All results are available through an Internet look-up table, which will be updated in a continuous manner.

Acknowledgements

The authors would like to acknowledge the financial support of the German Research Foundation (DFG) through the Priority Programme “Analyse, Modellbildung und Berechnungen von..."
Strömungsmischern mit und ohne chemische Reaktion” (SPP1141). The identification of the method, the construction of the experimental set-up and the establishment of a suitable experimental procedure would not have been possible without the intensive help of our workshop and of several students. The active support of Peter Fischer, Christian Kisow, Klaus Hanke, Sascha Jenrich, Martin Kühle and Martin Zschoyan is in particular acknowledged.

References