Residence Time Distribution of Gas Flows in Microreactors: Measurement and Model Comparison

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Abstract The optimization of microreactor designs for applications in chemical process engineering usually requires knowledge of the residence time distribution (RTD). The applicability of established models to microstructured reactors is currently under debate (Bošković et al. 2008, Günther et al. 2004, Stief et al. 2008). This work provides new experimental data on the residence time distributions of gas flows through different types of microstructured reactors and analyses the data with established RTD models. By this, the dispersion model was found to describe the RTD behavior of gas flow for a majority of the microstructured devices tested. The model could therefore be used to predict the RTD of those reactors.

Keywords: microchannel, gas, residence time distribution, dispersion model, microreactor, thermal conductivity sensor

1. Introduction

For real reactors the residence time (the time interval of a molecule between entering and exiting the reactor) is not the same. The resulting residence time distribution (RTD) of these molecules in the reactor is a characteristic feature for the chemical reactions to take place inside the reactor.
Due to the small channel dimensions of microstructured devices narrower RTDs are to expected from microreactors (Stief et al. 2008, Rouge et al. 2001). A comparison of microchannels to conventional fixed-bed reactors (Kockmann et al 2008, Hessel et al. 2004) indicates that microchannel reactors do indeed offer the potential for narrower RTDs than fixed-bed reactors.
Knowledge of the RTD is essential for the prediction of reactor behavior. Reactor modeling is very often based on simplified models (dispersion model, series of perfectly mixed cells, or other empirical models (Baerns et al. 1992)) as a substitute for time-consuming computational fluid dynamics (CFD) simulations. However, the validity of established correlations for microstructured reactors has been questioned and is the subject of ongoing scientific discussion (Bošković et al. 2008, Günther et al. 2004, Stief et al. 2008). In this publication an experimental technique, first used in the work of Stief et al. 2008 for a single test device, is refined and can now be applied to determine the RTD for gas flow for different kind of microstructured devices. It consists of sensors placed at the entrance and exit of the microreactors. Through correlation of the two signals, the residence time distribution can be determined. Measurements are compared to commonly used models.
In this work several reactor geometries and materials are investigated, some of them provided by industry partners.

2. Models for the residence time distribution in chemical reactors

The RTD is often described according to simplified models. The dispersion model is an intermediary between plug flow and a perfectly mixed cell that can be used to account for certain behaviours such as bypass or dead volumes (Baerns et al 1992). The

dispersion model is often used for tubular reactors. The model parameter D_{ax} describes deviations of the residence time from an ideal plug-flow system. D_{ax} includes diffusion effects and effects due to deviation of the local flow velocity. It is often represented in dimensionless form via the Bodenstein number:

$$Bo = \frac{u \cdot L}{D_{ax}} \tag{1}$$

Bo represents the ratio of convective transport to dispersion. An infinitely large value for *Bo* represents an ideal plug flow reactor and a value of zero indicates a perfectly mixed reactor (at the molecular level). *u* is the flow velocity, *L* the characteristic length. *Bo* is determined from the measured RTD.
D_{ax} is an adjustable parameter in the dispersion model which describes the space and time resolved concentration *c* of a tracer:

$$\frac{\partial}{\partial t} c = -u \cdot \frac{\partial}{\partial z} c + D_{ax} \cdot \frac{\partial^2}{\partial z^2} c \tag{2}$$

According to Baerns et al. 1992, the RTD for a reactor open for dispersion on both ends is given as

$$E = \frac{1}{2\ \Theta} \sqrt{\frac{Bo}{\pi\ \Theta}} \exp\left[-\frac{Bo\ (1-\Theta)^2}{4\Theta} \right] \tag{3}$$

with the dimensionless time

$$\Theta = t / \tau\ . \tag{4}$$

The convolution of the inlet signal S_{in} with the (fitted) RTD function *E* of the reactor results in the outlet signal S_{out} of that reactor:

$$S_{in} * E = S_{out} \tag{5}$$

The dispersion model is based on one single parameter. It describes the RTD for simple cases using plug flow and perfect back mixing as the two limiting cases.
More complex flow behavior of the reactor might require models with more than one parameter and/or a combination of ideal reactors (Baerns et al. 1992). For microstructures such a model could include additional parameters for the description of an uneven flow distribution to the microchannels.

3. CFD simulations on flow distribution

Stief et al. (2008) assumed that disagreement between their measurements and the dispersion model was related to an uneven distribution of the gas flow to the array of microchannels they used. Pfeiffer et al (2008) confirmed this uneven gas flow distribution experimentally using hot wire anemometry measurements for the same test reactor geometry.
To identify the factors that have a significant impact on the flow distribution and thus on the RTD, CFD simulations are performed. For gas flow through an array of microchannels of channel cross-sections smaller than *400 µm x 500 µm*, the simulation show a homogeneous flow distribution independent of the gas flow rate. This is related to the high pressure losses in the small microchannels compared to the rather small losses in the distribution areas in front and behind the microchannels.
For cross-sections lager than *400 µm x 500 µm*, however, an inhomogeneous flow distribution becomes possible. Figure 1 shows results for an array of 64 microchannels (400 µm x 500 µm) for a volumetric flow rate of Nitrogen of 1 l/min where the flow distribution to the channels is inhomogeneous. (The area presented in the figure is reduced to the upper fourth of the simulated structure.) At a lower flow rate (0.1 l/min) the CFD results show an even distribution for the same geometry. Therefore, the RTD behavior for this geometry changes significantly for higher flow rates. Resulting from those exemplary CFD simulations, a test geometry was manufactured.

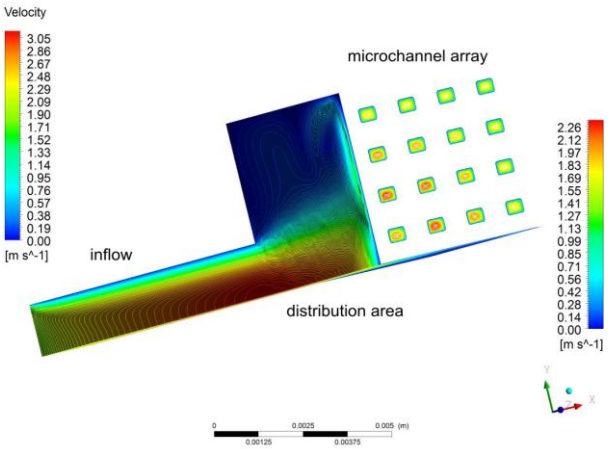

Figure 1: CFD simulation, N_2 at 1 l/min

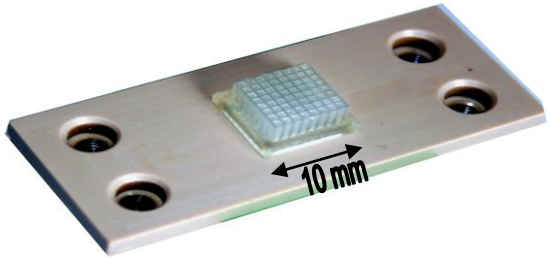

Figure 2: Test reactor made of plastic

4. Experimental setup

The RTD of gas flows in microreactors in our experiments is determined by thermal conductivity detectors (TCDs) as proposed by Stief et al. (2008). The measurement principle is similar to hot wire anemometry: a current is applied to the wire, this results in electrical heating of the wire to approximately *40 K* above the surrounding fluid temperature. Due to the temperature dependent specific resistance of the wire, its electrical resistance is a (linear) function of the temperature of the wire. When the temperature of the wire is changed due to a cooling gas flow, this results in a change of its electrical resistance. By applying two different gases of significantly different heat conductivity λ, the gas composition can be detected by the TCDs. Nitrogen ($\lambda_{N_2}^{25°C} = 0.026\,{}^{W}/_{m\cdot K}$) is used as a carrier gas and Helium ($\lambda_{He}^{25°C} = 0.154\,{}^{W}/_{m\cdot K}$) as a tracer gas.

For the experimental determination of the residence time, one TCD is put in front of and one TCD behind the test microreactor. By switching from a constant gas flow of Nitrogen (at time *t=0*) to a gas flow containing Helium and normalization of the sensor signal, the generation of a step function at the entrance of the reactor according to Eq. (6) is intended.

$$S(t) = \begin{cases} 0 & for\ t < 0 \\ 1 & t \geq 0 \end{cases} \tag{6}$$

The normalized sensor signal *S(t)* of the TCDs at the in- and outlet of the reactor is determined by Eq. (7) from the measured signal *s(t)* and the measured signal s_0 before the gas flows are switched (*t<0*).

$$S(t) = \frac{s(t) - s_0}{s(t \to \infty) - s_0} \tag{7}$$

The Helium marked gas is detected by the first TCD at the reactor inlet and subsequently by the second TCD at the reactor outlet. The usage of an inlet sensor is required as an ideal step function cannot be generated at the inlet.

The Bodenstein number *Bo* (Baerns et al, 1992) can be calculated by

$$\frac{\sigma^2{}_{out} - \sigma^2{}_{in}}{\tau^2} = \frac{2}{Bo} \tag{8}$$

using the variance values σ of the determined RTD of the sensor signal at the in- and outlet. τ is defined as the average residence time calculated from the *i* discrete measured sensor signals $S_{1..i}$ as

$$\tau \approx \sum_i (1 - S_i)\Delta t_i \tag{9}$$

The test setup is schematically shown in Figure 3. It consists of three thermal mass flow controllers (MFC) by Bürkert for setting the volumetric gas flow. MFC 1 and MFC 2 are used to control the flow rate of the carrier gas (Nitrogen), MFC 3 controls the flow rate of the tracer gas (Helium). The volumetric flows of MFC 2 (Nitrogen) and MFC 3 (Helium) are

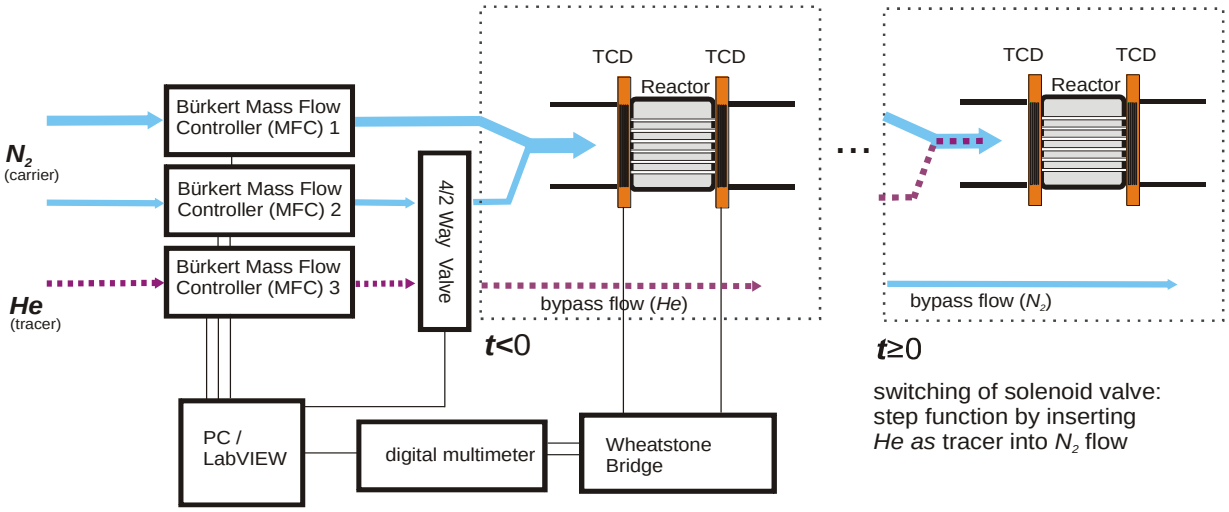

Figure 3: schematic drawing of measuring setup

set equal for the measurements. As the response time of the MFCs is too slow to generate a quick step function of the Helium tracer gas concentration, a solenoid valve is used to switch between the gas flows of MFC 2 and MFC 3. After constant flow rates of the gases are established, the solenoid valve switches (that defines time *t=0*) and the flow of MFC 2 (Nitrogen) is instantaneously replaced by the one of MCF 3 (Helium) at the same flow rate. By this a (slightly blurred) step function of the Helium tracer concentration can be generated in the Nitrogen carrier flow. This step function is detected by the TCD at the entrance to the microreactor and the response S_{out} to the inlet signal S_{in} is detected by the TCD at the exit of the reactor. The setup allows for setting the concentration of the tracer gas between 0 and 100%. The TCDs are integrated in Wheatstone bridges. The voltage of the bridge circuit is measured by a digital multimeter measuring card (National Instruments, Model NI USB-6211, precision: *0.09 mV*) connected to a PC running LabVIEW (National Instruments).

Contrary to the work of Stief (2008) this study is targeting different kinds of microreactors made of stainless steel, ceramics, plastics and also glass (not included in this publication). The microstructures do also differ whereby this paper is limited to results for parallel microchannel reactors. To enable measurements for this wide range of microreactors, a new universal TCD sensor was developed and fitting adapters (mainly for the commonly used Swagelok connections) were manufactured. Figure 4 shows a microreactor made by IMVT (Institute for Micro Process Engineering) which enables to place the sensor wires directly in front of and behind the actual microstructure. Adapters were designed enabling to connect the frame containing the TCD wire directly to the microstructure. For this setup, the RTD of the microstructure only, without connection pipes, is determined.

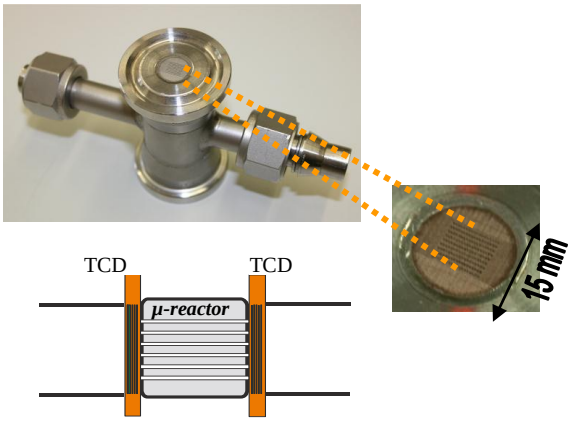

Figure 4: Microreactor by the IMVT with direct access to the microchannels

Other microreactors as the co-current heat exchanger shown in Figure 5 have a connection pipe with Swagelok fittings welded to the microstructure. For these reactors the TCDs cannot be placed directly at the microstructure. Instead the TCD is put into an adapter that fits to the Swagelok fitting, the measurement of the RTD is done as near as possible to the microstructure. However, the

RTD of the microreactor including the connection pipe is determined.

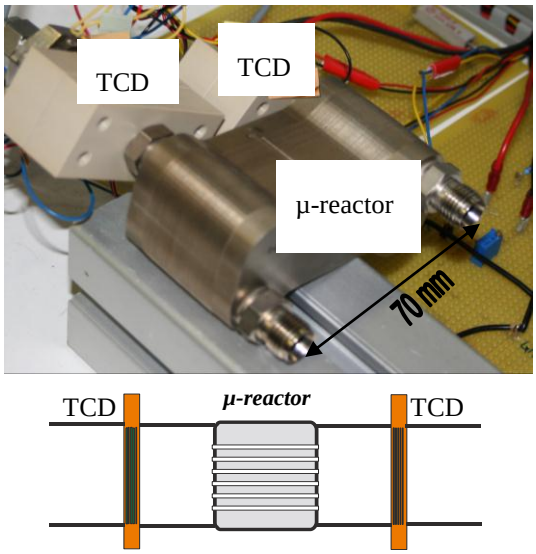

Figure 5: TCD sensors connected to the Swagelok fittings of a co-current micro heat exchanger

5. TCD Sensors

For this project improved TCD sensors were developed. This new type of sensor consists of an array of *15 µm* thick *Pt* wires and can be used for a wider range of microreactors than the ones used by Stief et al. (2008).

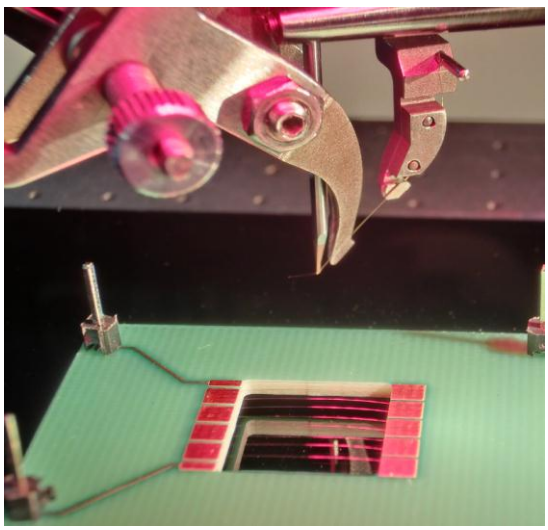

Figure 6: Wedge bonding process of a TCD

Manufacturing of TCDs

The TCD is built up on a standard PCB with bond pads. The *Pt* wires are bonded on the bond pads by an automatic wedge wedge wire bonding process (Figure 7). Force, ultrasonic energy and heat are used for the welding process. Ten wires are bonded in a chain (Figure 7) giving an overall resistance of R=72.9 Ω.

Due to the automated process the wire length is very reproducible, resulting in a resistance error less than 1% for many sensors.

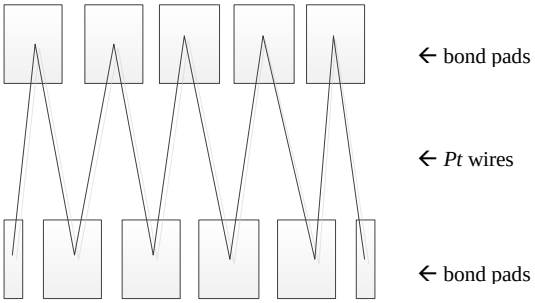

Figure 7: Schematic Drawing of TCD

Sensitivity of TCDs

The temporal resolution of the sensors is tested by a sudden increase of the electrical current (Figure 8) at a constant gas flow rate. By this, a response time of *10 ms* (Helium) respectively *34 ms* (Nitrogen) is determined.

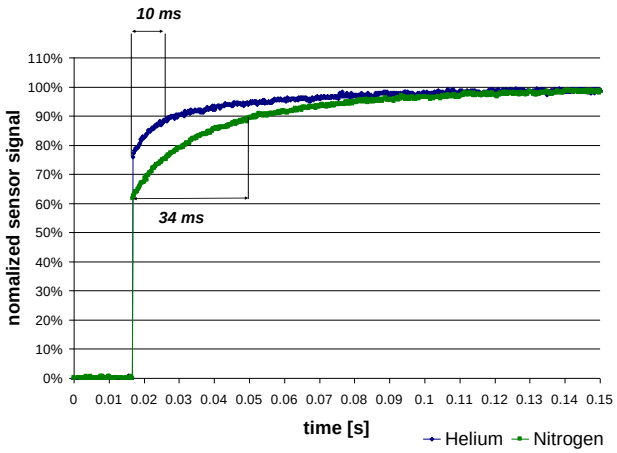

Figure 8: response time of TCD

Due to the linearity of sensor signal *s* (Figure 9) to the tracer concentration *c* the normalized sensor signal *S* (Eq. (5)) can directly be used to determine the sum function *F(t)* of the RTD for the measurements:

$$F(t)=S(t) \qquad (10)$$

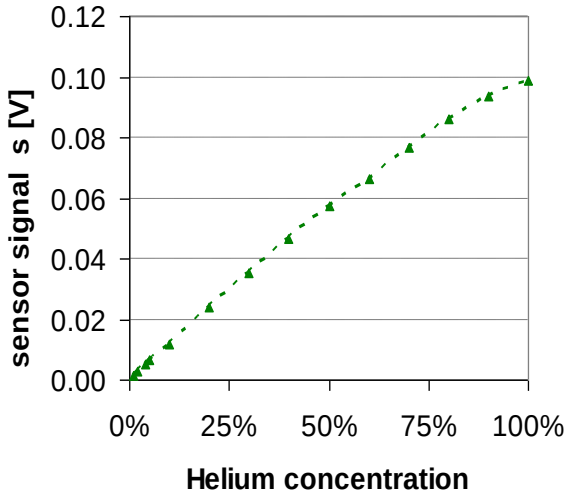

Figure 9: Sensor signal s (at 0.25 l/min)

6. Measurement results for different microreactors

The choice of RTD measurements in this presentation include the IMVT special reactor with direct access to the microstructure (Figure 4), the co-current micro heat exchanger (Figure 5), the test reactor made of plastics (Figure 2) and a test micro reactor made of ceramics provided by ESK.

Figure 10-Figure 13 plot the measured sensor signals S_{in} and S_{out} at the in- and outlet of the different reactors. Derived from those measurements, the RTD function E of the dispersion model (Eq. 3) is calculated using Matlab. The model parameter Bo is determined according to Eq. 8 and additionally calculated by a least mean square fit (s_{fit}) of the measured outlet signal S_{out} and the convolution of S_{in} and E (Eq. 5). The correspondent calculated results for the dispersion model applied to the input signal S_{in} are given as dashed lines in the figures. The calculated and characteristic RTD-curve is given by the calculated E-curve also present in the plots. This E-curve presents the RTD behaviour of the devices.

Figure 10 shows the results for the IMVT special reactor with the TCDs being installed next to the 270 microchannel array (channel cross-section: *200 µm x 200 µm*). These measurements represent the RTD of the microstructure. This is also true for the measurement for the plastic test reactor (Figure 11), but not for the co-counter flow reactor (Figure 12) consisting of 1750 microchannels (channel cross-section: *350 µm x 150 µm*) and the ceramics reactor provided by ESK (Figure 13). For these devices, the sensors are installed at the welded connection pipes to the reactor and the measurements therefore represent the RTD of the reactors plus the connection pipes.

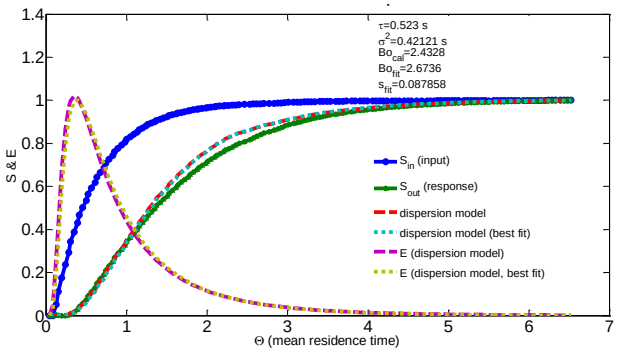

Figure 10: measurement for IMVT special reactor, mass flow 750 ml/min

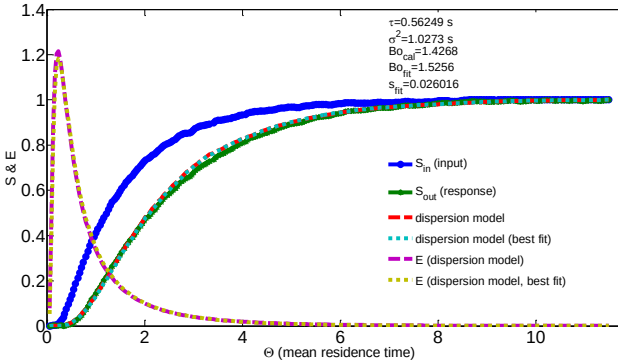

Figure 11: measurement for plastic test reactor, mass flow 100 ml/min

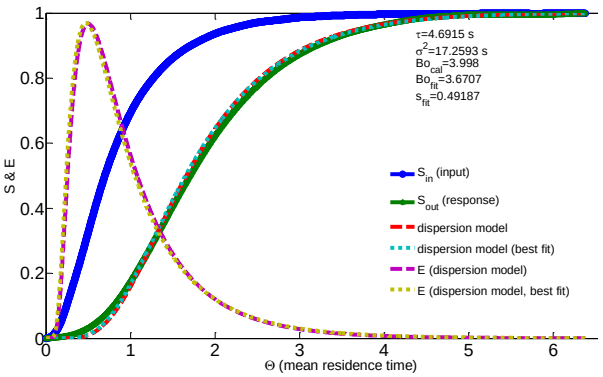

Figure 12: measurement for IMVT co-current micro heat exchanger reactor, mass flow 550 ml/min

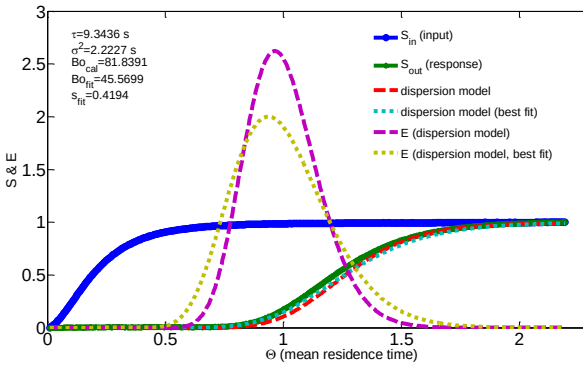

Figure 13: measurement for ceramics microreactor provided by ESK, mass flow: 100 ml/min

7. Model comparison of the measurements

An approach to determine *E* of the reactor directly by a Fourier transformation of the measured signals to the frequency domain could not be successfully applied due the intense generation of noise in the transformation. For that reason, all calculations are performed in the time domain using Matlab and parametric models for *E*.
As the intension of the project is to check the validity of the dispersion model, only results for the one parameter dispersion model are given here.
From the results given in Figure 10-Figure 13 the RTD of the devices widely agrees to the dispersion model. The most significant deviations are determined for the co-current device (Figure 12) and the reactor provided by ESK (Figure 13). This is not surprising as for these devices the TCD sensors are not installed next to the microstructure as the Swagelok connection pipes are directly connected to the reactor. Therefore, also influences of the in- and outlet pipes between TCD sensors and the reactor must be taken into account.

8. Outlook

More evaluation of the results and fitting RTD models will come. Beside the application of empirical models such as the ones proposed by Ham and Platzer (2004), we will also focus these ideas:

Considering of in- and outlet areas
An approach to determine *E* of the reactor where - beyond the microstructure - also in- and outlet sections have to be considered to convolute separate models for those regions. By this, Eq. 7 can be enhanced to

$$S_{in} * E_{inlet} * E_{microstructure} * E_{outlet} = S_{out} \quad (11)$$

Enhanced dispersion model for uneven flow distribution
When considering the applicability of the dispersion model for an array of parallel microchannels, the influence of the fluid distribution to the single channel has to be taken into account. This can be done by summing up *E*-functions for the *m* single channels by

$$E_{array} = \sum_{n=1}^{m} \frac{u_N}{\bar{u}\ m}\ E \quad (12)$$

whereby the single *E* is weighted by the velocity u_n in channel *n* and the average channel velocity $\bar{u}$ of the array.

Summary

The residence time behavior for different kind of microstructured devices has been experimentally investigated. The comparison of the experimental results to the prediction of the dispersion model showed good agreement for most of the experiments. For specific cases, however (where in- outlet effects must be considered) a satisfying model description might be possible by convolution of several models (Eq. 11). For the case of an uneven flow distribution to an array of microchannels, an “enhanced” dispersion model is proposed. For the experimental results presented here, the dispersion model could – in contrast to Stief et al (2008) - be used to predict the residence time distribution for gas flow in microstructured devices. For most experiments

in this study (only a few are presented in this paper) the dispersion model described the RTD behavior of gas flow. This model is therefore still useful to precalculate the RTD of intended microreactors, reducing time, effort and materials required for design and optimization stages.

Acknowledgements

The authors are very thankful to all colleagues who contributed by comments and suggestions.
Special thanks go to D. Spengler for providing the Wheatstone bridges and Flavio Brighenti and Thomas Geissler for the Matlab programming help.
The supply of microstructured devices for this project by BTS Ehrfeld, ESK Ceramics, Institut für Mikrotechnik Mainz, Little Things Factory, Mikroglas and Micro Mechatronic Technologies as well as the financial support by the German Federal Ministry of Economics and Technology (IGF Project 15495) is gratefully acknowledged.

Nomenclature

λ	[W/mK]	heat conductivity
σ	[s]	variance
Bo	[-]	Bodenstein number
c	[-]	tracer concentration
D_{ax}	[m^2/s]	axial dispersion coefficient
E	[-]	residence time distribution
F	[-]	sum function of RTD
i	[-]	number of measured signals
L	[m]	characteristic length
R	[Ω]	electrical resistance
Re	[-]	Reynolds number
u	[m/s]	flow velocity
$\bar{u}$	[m/s]	average velocity (array)
s	[V]	sensor signal
S	[-]	normalized sensor signal
$S_{1..i}$	[-]	signals of a measuring series of *i* discrete signals
s_{fit}	[-]	diff. of least mean square fit
t	[s]	time
τ	[s]	average residence time
Θ	[-]	dimensionless residence time
$\dot{V}$	[m^3/s]	volume flow rate
V	[m^3]	reactor volume

Abbreviations

CFD	Computional Fluid Dynamics
IMVT	Institute for Micro Process Engineering
MFC	mass flow controller
RTD	residence time distribution
TCD	thermal conductivity detector

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