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Development of a fast sensor for the measurement of the residence time distribution of gas flow through microstructured reactors

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Abstract

Microreactor technology has developed various components in recent years—microreactors, micromixers, micro-heat exchangers and others. These components are advantageous with respect to the mixing procedure, heat transfer and also residence time distribution. However, it has hitherto not been possible to measure the residence time distribution of microstructures with gas flow with sufficient accuracy. This situation is very unsatisfactory.

In this work, a sensor system was developed for the measurement of the residence time distribution for gas flow through microstructured devices. The sensor is based on a thermal conductivity detector and fulfills the requirements for such measurements.

The sensor was tested on microreactors built by Forschungszentrum Karlsruhe. A relatively large dispersion within the microstructure was found, which could be the result of unequally distributed flow through the microreactor channels.

Keywords: Microstructure; Residence time distribution; Sensor; Gas flow

1. Introduction

Microstructured systems are expected to be advantageous in terms of thermal behaviour (good thermal control, isothermal reaction) and mixing abilities [1–4]. Furthermore, these systems are assumed to have a well defined narrow residence time distribution (RTD) as a result of the defined and small dimensions of the channels. Thus, the progress of the individual steps in complex reactions with consecutive and parallel steps can be efficiently controlled and the conversion and selectivity can be improved.

In addition, knowledge of the RTD is necessary for the simulation of the reactor behaviour by means of dispersion, cell or other substitute models. In these cases the fluid dynamics of the reactor is integrated into the model by model parameters (effective dispersion coefficient, cell number) derived from the RTD [5]. Knowledge of the RTD is therefore important for the mathematical modelling and for performance studies of the reactor. However, to date no sensor system has been available to measure the RTD of the catalytically active parts of microstructured reactors for gas flow with sufficient accuracy. Such a sensor system has to fulfil two main requirements: firstly, the sensor system must be small enough to be integrated into the reactor system and secondly, it must be fast enough (time constants in the region of milliseconds).

The integration is necessary because the RTD effects of the microstructured system are small compared with the RTD effects of capillaries to external sensors. In the case of conducts to external sensors it is not possible to measure the RTD effects of the reactor sufficiently precisely [6].

The mean residence time of molecules in the microstructured reactor is in the range of seconds. The sensor has to be at least one order of magnitude faster, thus the time constant of the sensors has to be in the range of milliseconds.

The aim of the work presented was to develop a sensor system capable of measuring the RTD of gas flows through a microstructured reactor. It is not the intention of this work to examine the RTD of microreactors in-depth. Therefore, the RTD measurements carried out in this work aimed the confirmation of function of the developed sensor.

2. Principle of RTD measurement

For the experimental determination of the RTD, a detectable property of the gas flow into the reactor is changed corresponding

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to a defined function of time; ideally this would be directly at the reactor entrance. The function of time of this property is detected at the outlet of the reactor. This function is the basis for the determination of the RTD or the residence time sum function: the fluid elements entering the reactor are marked and their fate in the fluid system is monitored [5].

Electrical conductivity, light absorption and radioactivity are generally used as detectable properties in liquid-phase systems but are not usable in gas-phase systems (except radioactivity). For gas-phase systems, preferably the thermal conductivity is used.

The fluid elements that enter the flow system are frequently marked by an impulse or a step function. As response to an ideal impulse the RTD can be measured at the reactor outlet; as a response to an ideal step function the residence time sum function can be measured at the outlet. However, in real experiments it has to be noted that real test functions can only have approximate step or impulse function shapes. In addition RTD effects already occur between the place where the functions are generated and the entrance to the fluid system. In this case the course of the real test function at the reactor entrance must be measured and taken into account when determining the RTD of the fluid system.

3. RTD measurement of gas flow through microstructured systems

3.1. Sensor

The authors had previously demonstrated experimentally that the above-mentioned requirements of the sensors can be achieved by thermal conductivity detectors (TCD). A TCD is in principle an electrically heated wire. This wire is put directly into the test fluid—in this case directly in front of and behind the channels of the microreactor.

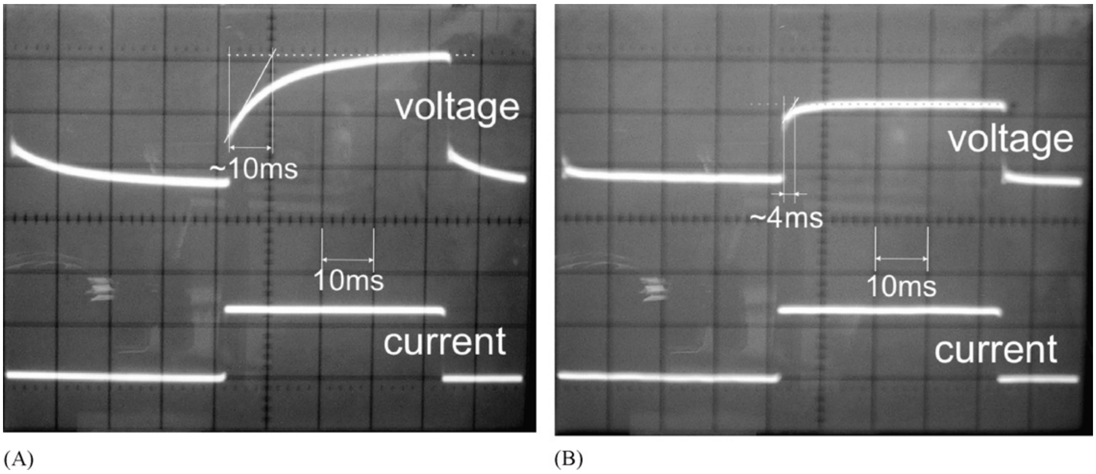
The heat transfer between the wire and the surrounding medium depends on the thermal conductivity of the medium. When it is changed the transferred heat and consequently the temperature and the electrical resistance of the wire will change. Therefore, the measurement of the thermal conductivity can be attributed to the determination of the electrical resistance of the wire.

The wire temperature chosen for the measurements was relatively low (approximately 40 K above the inlet temperature of the gases and also the temperature at which the sensor was assembled). Under these circumstances it can be assumed that the gas parameters (viscosity, molar volume) only change to a small degree, so that these changes can be neglected. On the other hand, the wires themselves are also affected by the higher temperature—they will expand slightly. But with a thermal expansion coefficient of $8.8 \times 10^{-6}\,\mathrm{K}^{-1}$ the expansion is in the area of 3–4 μm and can also be neglected.

Besides the material parameters of the wire, the time constant of the sensor depends on the diameter of the wire. Experiments showed that a platinum–iridium wire of 12 μm in diameter has a time constant in nitrogen of approximately 10 ms. In these preparing measurements, the electrical current through the wire was changed corresponding to a rectangular function; consequently the released heat and also the temperature changed and the change in the electrical resistance of the wire was measured using a Wheatstone bridge. The time constant can be taken from Fig. 1, which also shows the time constant in helium of approximately 4 ms. The determined time constant is short enough to measure the RTD.

The sensor consists of a meandric arrangement of the wire on a plastic frame. The frame dimensions are 14 mm × 14 mm × 2 mm. The wire is mounted onto the frame by hand. The combined sensor can be seen in Fig. 2. After attaching the wire, the frame is installed in the microstructure reactor with the wire aligned directly in front of and behind the microchannels.

The microchannel reactor provides 9 layers with 14 microchannels each; the dimensions of the microchannel cross-section are 400 μm × 800 μm with a length of 10 mm. The connectors for the fluids are attached to the sensor frame. The gas is led to the reactor by a diffusor system providing an opening angle of 5°, resulting in a length of 39 mm. The complete system shown in Fig. 3 is glued together.



(A) (B)

Fig. 1. Determination of time constants of the sensor. Measurements of time constant of sensor in: (A) N_2 and (B) He.

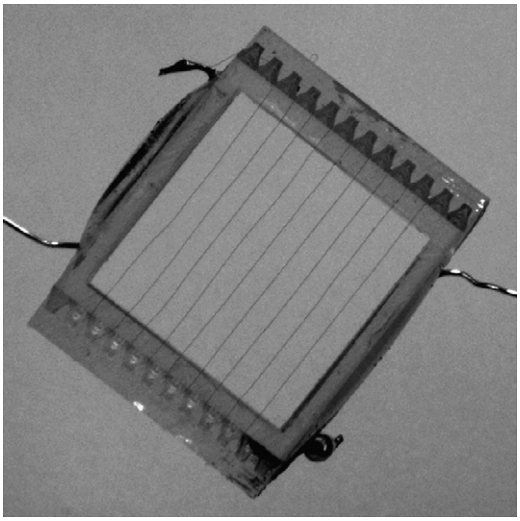


Fig. 2. Sensor.

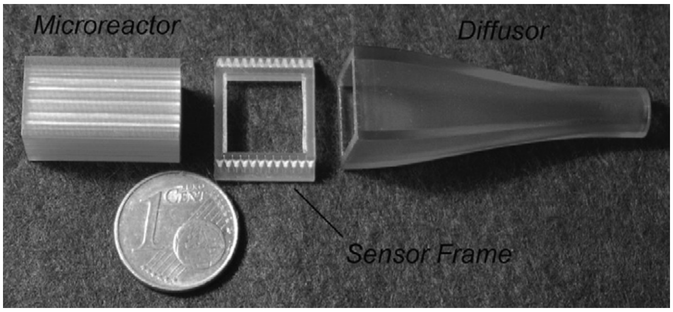


Fig. 3. Photo of the disassembled measurement system. The sensor frame (centre) has not yet been wired, and the gas outlet is not shown.

The single components of the system, fluid connectors, microchannel reactor and sensor frame, are manufactured by micro-stereo lithography, a rapid prototyping (RP) process. In general, RP is a method allowing three-dimensional devices of different materials to be generated on the basis of computer data only. The generative character of Rapid Prototyping Processes is the main difference to the more common abrasive mechanical manufacturing techniques, such as milling. Micro-stereolithography is a RP process applied at Forschungszentrum Karlsruhe/IMVT mainly for the generation of polymer microstructure devices.

The electrical resistance of the sensor wire is measured by means of a Wheatstone bridge and amplified with an adjustable amplifier (offset and amplification). The sensor signals are recorded using a computer which also controls the experimental course and set-up (offset and amplification of the amplifier, setpoint of the MFCs and the magnetic valves (see next chapter)).

With this set-up the integral RTD of the whole reactor is measured, not merely the RTD for one channel. Under these circumstances inequalities between the channels will influence the measurements.

3.2. Experimental set-up

The use of the TCD as sensor requires the change of the thermal conductivity of the flowing medium. Therefore, a marker (tracer) was used which has a significantly different thermal conductivity than the carrier used—helium as the tracer and nitrogen as the carrier ($\lambda_{\mathrm{He}}^{25\,^{\circ}\mathrm{C}} = 0.154\,\mathrm{W/(m\,K)}$, $\lambda_{\mathrm{N_2}}^{25\,^{\circ}\mathrm{C}} = 0.026\,\mathrm{W/(m\,K)}$).

The step function was used as the test function. The RTD can be calculated from the step response by differentiating. The step (concentration step of helium in nitrogen) was realized by a combination of mass flow controllers (MFC) and magnetic valves. The experimental set-up is shown in Fig. 4.

The MFCs were used to create constant flows for the tracer (MFC B2) and the carrier (MFC A1 and A2). Like all controllers, MFCs need some time to establish new constant flow values. As this time is far too long to carry out a step function successfully a magnetic valve is used additionally; this is switched between the constant carrier flow through MFC A2 and the tracer flow through MFC B2 in a sufficiently short time (<10 ms [7]). With this construction only steps between 0 and 100% tracer concentration can be obtained. To obtain smaller steps a bypass for the carrier is achieved by MFC A1.

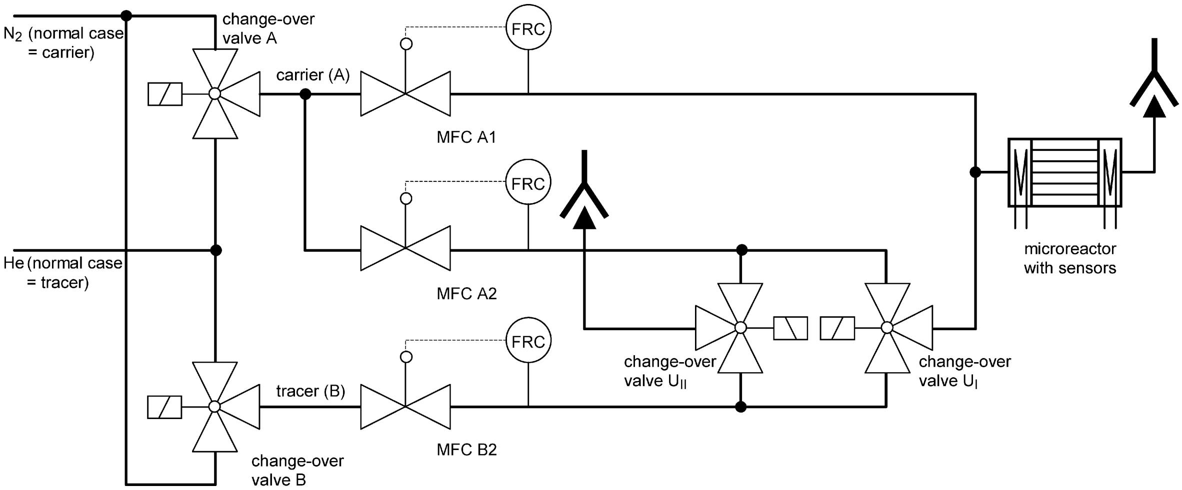


Fig. 4. Experimental set-up.

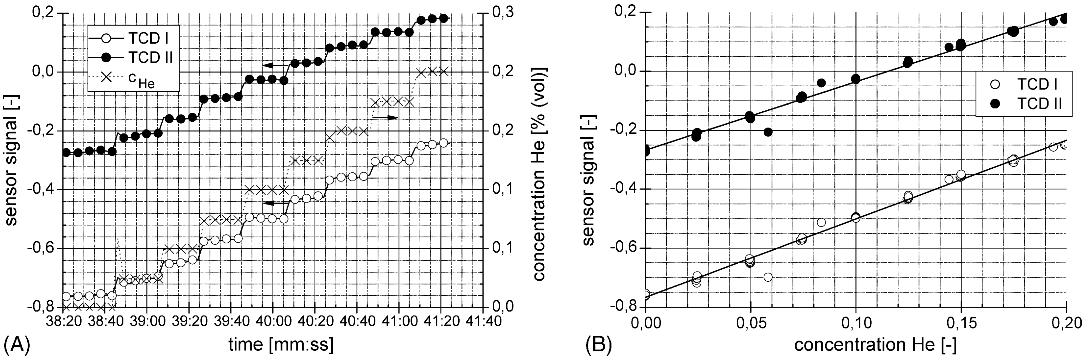


Fig. 5. Dependence of the sensor signal on the tracer concentration. (A) Measurements of sensor signal and concentration in dependence on time and (B) sensor signal in dependence on He concentration.

4. Results

4.1. Dependence of the sensor signal on the tracer concentration

The determination of RTD requires the normalized tracer concentration $c'_{\mathrm{Tracer}}(t)$ – normalized to a step between 0 and 1 – instead of an abstract value of the sensor signal S. It is, therefore, necessary to determine the dependence of the sensor signal on the tracer concentration ($S=f_{\mathrm{S}}(c_{\mathrm{Tracer}})$). If the dependence of the sensor signal on the tracer concentration is linear ($S=Ac_{\mathrm{Tracer}}+B$) it can be eliminated.

$$c'(t)=\frac{c(t)-c_0}{c(t\to\infty)-c_0}\underset{\uparrow}{=}\frac{S(t)-S_0}{S(t\to\infty)-S_0}$$

$$\text{in the case of } S=A\cdot c+B \tag{1}$$

For these measurements different tracer concentrations with a constant throughput were achieved by the MFCs A1 and B2 and the sensor signals were recorded. The time between several measurements did not exceed 20 s, so that possible changes of the reactor temperature were negligible. Fig. 5 illustrates the dependence of the sensor signal on the tracer concentration in the concentration range of 0–20 vol% He. The steps represent an increase in He concentration of 2.5 vol%. The flow was 1 L/min.

The dependence is almost linear, which can be seen in Fig. 5A and even more clearly in Fig. 5B. The deviating points can be attributed to measurements during the switching time of the MFCs, when conditions altered.

4.2. RTD measurement

Fig. 6A shows the course of the sensor signals as a function of time at the inlet and the outlet of the microstructure. The conditions were: throughput 0.5 L/min, mean residence time (τ) 99 ms, and concentration step from 0 to 10 vol% He.

If the measurements shown in Fig. 6A (smoothed by a moving average filter) are normalized (standard step von 0 to 1) and differentiated the RTDs at the inlet and the outlet, shown in Fig. 6B, are obtained. It is evident that the RTD measured at the inlet (TCD I) is broadened by the microstructure (measured by TCD II). The squared standard deviation of these curves was calculated. The squared standard deviation of the RTDs of the microstructure can then be calculated by subtracting both values [8]. Table 1 summarizes the values.

The Bodenstein number can be calculated from the squared standard deviation of the RTD of the microstructure (see Eq. (3)). The Bodenstein number is the parameter of the dispersion model which represents the ratio of convective transport to effective dispersion (see Eq. (2)). Higher values of the Bodenstein number mean smaller dispersion, lower values higher dispersion.

$$Bo=\frac{\bar{v}L_{\mathrm{R}}}{D} \tag{2}$$

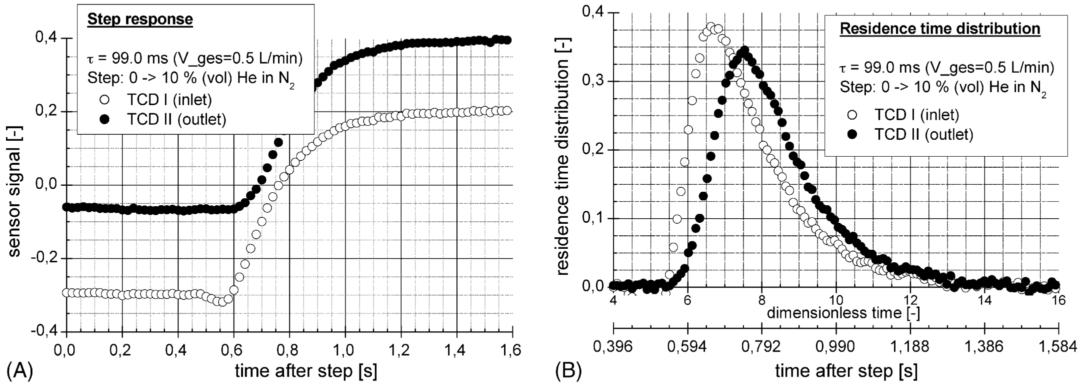


Fig. 6. Results of RTD measurements (throughput: 0.5 L/min; τ: 99 ms; step: 0 → 10 vol% He in N_2): (A) step response and (B) residence time distribution.

Table 1
Squared standard deviation and Bodenstein number

Throughput (L/min)	Mean residence time (ms)	Step (vol%)	Squared standard deviation, σ^2			Bodenstein number
			Inlet	Outlet	Reactor	
0.5	99.0	0 → 10	0.931	1.232	0.301	9.5

Eq. (3) can be used to calculate the Bodenstein number from the squared standard deviation of the RTD of the microstructure.

$$Bo = \frac{1}{\sigma^2} \pm \sqrt{\frac{1}{\sigma^4} + \frac{8}{\sigma^2}} \tag{3}$$

The Bodenstein number calculated for the above-mentioned conditions is 9.5.

In Fig. 6A, in the time region of approximately 0.5–0.6 s a negative amplitude of the measurements on the inlet can be seen. This artefact is also visible in the following experiments under modified conditions (Figs. 8A, 9A and 10A). Ultimately the reason for this artefact could not be determined; it is possibly caused by minor asymmetry on switching the valves.

4.3. Adjustment of the experimental data to the dispersion model

An attempt was made to utilize the experimental data (sensor response at the inlet and the outlet of the microstructure) by using the dispersion model and to calculate the dispersion coefficient directly. Therefore, the values measured at the inlet were used as the boundary condition for the partial differential equation (PDE) of the dispersion model (see Eq. (4)). The effective dispersion coefficient was changed by an optimisation algorithm in order to obtain the best fit between the measured and the calculated values at the outlet.

$$\frac{\partial}{\partial t}c = -v\,\frac{\partial}{\partial z}c + D\,\frac{\partial^2}{\partial z^2}c \tag{4}$$

It was found that the mere adjustment of the effective dispersion coefficient could not bring about an adequate match of the calculated and the measured data. This can be seen in Fig. 7A. The filled points show the experimental data examined at the outlet, the line denotes the model results obtained by using the experimental results on the inlet (open dots) as the boundary value. The line marks the best fit of the dispersion coefficient (D) by using the real mean flow velocity (v).

Therefore, as a second parameter of the mathematical model the mean flow velocity (at first sight difficult to justify) was chosen and adjusted by optimisation (see Fig. 7B). The fitting is clearly better with this second degree of freedom.

One possible explanation for the unsatisfactory match of the measured and calculated curves with one fitted parameter, but quite a good match with two fitted parameters could be the unequal splitting of the flow to the different channels. Measurements carried out by Forschungszentrum Karlsruhe showed that the flow velocity in the channels near the centre of the reactor body differs significantly from that in the outer region [9].

Hence, the following conclusions can be drawn:

- Due to the different flow velocities in the channels, the overall dispersion of the microstructure increases. The Taylor–Aris equation dealing with the laminar flow superposed by molecular diffusion [10,11] cannot satisfactorily describe this behaviour.
- The one-dimensional dispersion model cannot adequately describe the behaviour of the whole microstructure.

A possibility to deal with the inhomogeneous distribution of flow between different reactor channels could be a model summarizing dispersion models with different mean flow velocities for different channels.

4.4. Influence of throughput/Influence of mean residence time

To assess the influence of the mean residence time on the hydrodynamic behaviour of the flow system the throughput

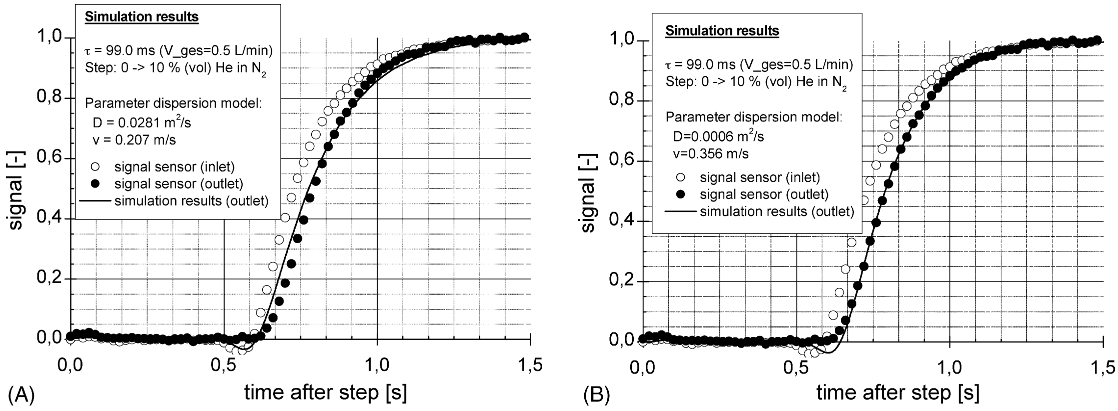


Fig. 7. Adjustment of the calculated to the experimental data using the dispersion model.

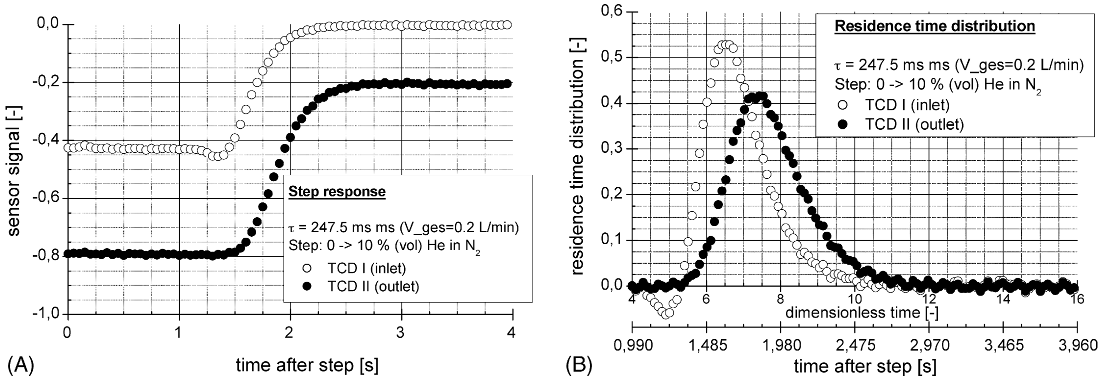


Fig. 8. Results of RTD measurements (throughput: 0.2 L/min; τ: 248 ms; step: 0 → 10 vol% He in N_2): (A) step response and (B) residence time distribution.

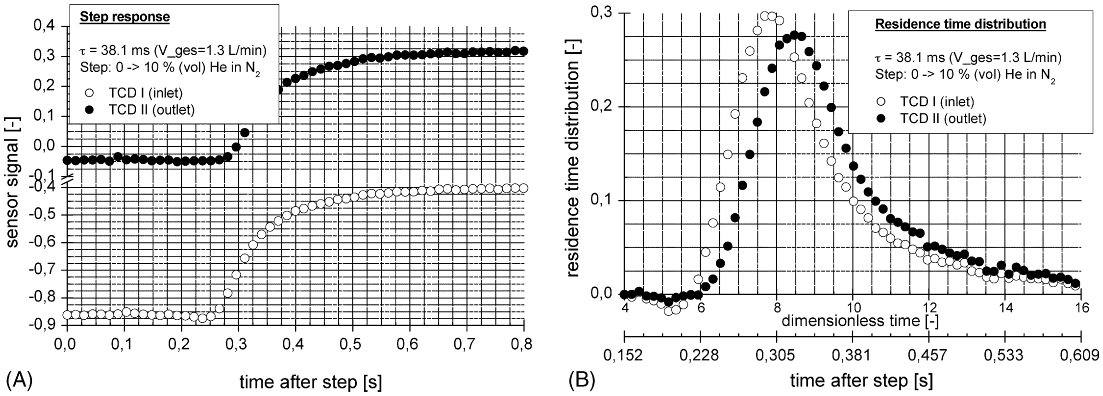


Fig. 9. Results of RTD measurements (throughput: 1.3 L/min; τ: 38 ms; step: 0 → 10 vol% He in N_2): (A) step response and (B) residence time distribution.

Table 2
Squared standard deviation and Bodenstein number depending on throughput

Throughput (L/min)	Mean residence time (ms)	Step (vol%)	Squared standard deviation, σ^2			Bodenstein number
			Inlet	Outlet	Reactor	
0.2	247.5	0 → 10	0.543	0.901	0.358	8.3
0.5	99.0	0 → 10	0.931	1.232	0.301	9.5
1.3	38.1	0 → 10	1.364	1.569	0.205	12.8

through the microstructure was changed (0.2, 0.5 and 1.3 L/min) and the RTDs were measured for a concentration step from 0 to 10 vol% He. The step responses and RTDs can be seen in Figs. 6, 8 and 9.

The Bodenstein numbers were calculated from the squared standard deviation using Eq. (3). The calculated values are shown in Table 2.

From Table 2 it can be seen that the Bodenstein number increases with increasing throughput. If the Taylor–Aris equation (see Eq. (5)) was applicable this would mean that the dispersion is determined by the molecular diffusion.

$$D = D_\mathrm{m} + \frac{1}{\kappa}\frac{\bar{v}^2 d_\mathrm{h}^2}{D_\mathrm{m}} \tag{5}$$

4.5. Influence of the step extent

The influence of the extent of the step on the RTD was investigated to confirm the assumption that such an influence does not exist. Fig. 10 shows the step responses and the RTDs for

Table 3
Squared standard deviation and Bodenstein number depending on the extent of the step

Throughput (L/min)	Mean residence time (ms)	Step (vol%)	Squared standard deviation, σ^2			Bodenstein number
			Inlet	Outlet	Reactor	
0.5	99.0	0 → 10	0.931	1.232	0.301	9.5
0.5	99.0	0 → 20	0.839	1.148	0.309	9.3

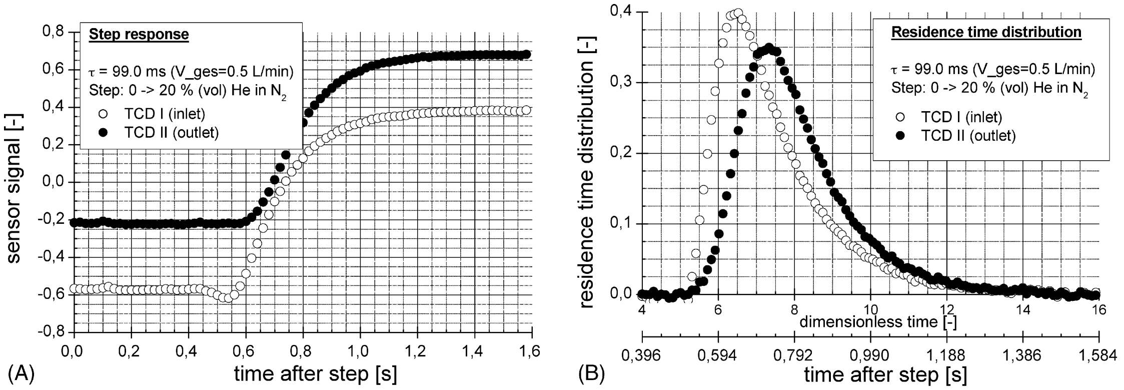


Fig. 10. Results of RTD measurements (throughput: 0.5 L/min; τ: 99 ms; step: 0 → 20 vol% He in N_2): (A) step response and (B) residence time distribution.

the throughput of 0.5 L/min and a concentration step from 0 to 20 vol% He.

If the results shown in Figs. 6 and 10 are compared with Fig. 6 it is evident that, as assumed, the RTD is not influenced by the height of the concentration step. Neither does the form of the step response indicate any influence of the extent of the step—only the extent of the step response itself, of course, is directly influenced by the extent of the step. This is also reflected by the Bodenstein numbers calculated from the RTDs and given in Table 3.

5. Summary

A sensor system was developed for the measurement of the residence time distribution for gas flow through microstructured devices. This sensor system is based on thermal conductivity detectors and was tested on microreactors constructed by Forschungszentrum Karlsruhe by stereolithography. The method used provides an integral RTD of the reactor, this means the RTD describes not the behaviour of a single channel but of the whole reactor including inhomogeneous distribution of flow between different reactor channels. In the result it gives characteristic parameter (function) which is relevant for the prediction of the chemical reaction, assuming that all channels are catalytically active.

The sensors were integrated into the microstructured device in front of and behind the channels. For the measurement of the RTDs helium in nitrogen concentration steps were used. A combination of MFCs and magnetic valves was used to create these steps.

It could be shown that the experimental set-up and the sensor system are suitable for determining the RTDs. Different throughputs and concentration step heights were applied and the behaviour of the microstructured device was measured. As a result of these experiments small Bodenstein numbers were obtained, which means a high dispersion in the fluid system. The attempt to determine the effective dispersion coefficient of a one-dimensional dispersion model directly by fitting computed and measured step responses results in an unsatisfactory match of the two curves. If the mean flow velocity was adapted additionally a good match was achievable, but a physical interpretation is difficult. These results indicated that further detailed research is necessary. The new sensor system provides an opportunity for this.

One possible explanation for the Bodenstein numbers found could be the uneven flow distribution to the different channels of the microstructure. This leads to a higher effective dispersion in the microstructure as a whole and hence to lower Bodenstein numbers. Experimental determination of the flow distribution carried out by Forschungszentrum Karlsruhe demonstrates that this uneven flow really exists.

It must be left to future studies to develop a mathematical model that can adequately describe the behaviour of the microreactor under the influence of a non-uniform flow distribution. The results of the present work indicate that the classical models cannot describe the RTD behaviour of microreactors with sufficient accuracy.

Acknowledgements

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