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Characterisation of residence time and residence time distribution in chip reactors with modular arrangements by integrated optical detection

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Abstract

An experimental setup was built for the characterisation of residence time distribution (RTD) in microreactors. In order to determine the residence time distribution of those devices, the method of pulse marking with a dye tracer was used. For this method of marking, a specially constructed microstructured injection unit came to use. Detection of the tracer concentration was made by analysing the transmittance with a self-developed transmittance detection unit. The obtained residence time distributions were compared with common RTD models by means of fitting methods. The examined static micromixer showed laminar flow behaviour.

Keywords: Residence time distribution; Microreactors; Laminar flow behaviour

1. Introduction

During recent years, a growing development of microelements for biotechnological, pharmaceutical and chemical applications have taken place. Among these elements are micromixers, microreactors, pumps and valves. The volumes of microreactors are generally in the range of nanolitres to millilitres [1]. The reactors we employed in this investigation, had volumes in the microlitre range.

Microreactors possess advantages compared to conventional reactors due to their small dimensions. Additionally, larger gradients of pressure, temperature, density and concentration lead to higher reaction rates. Energy flows are highly improved due to large surface to volume ratios. Chip reactors are especially interesting for the optimisation of yield and selectivity of chemical reactions since they provide the possibility of changing reaction conditions very easily compared to conventional reactors [2,3]. Residence times and residence time distributions are important characteristics of all reactors, since they provide information about the flow and mixing behaviour of reaction components in the respective reactors [4–9]. Narrow residence time distributions and good accordance to the axial dispersion model [10] for residence time measurements in gas phase microreactors was shown by Renken and coworkers [11]. The silicon based static micromixer (Fig. 1) used in this investigation had an internal volume of approximately 8.5 μl. The measuring setup had a total volume of approximately 18 μl. This precisely reveals the difficulties of the residence time measurements in any microreactors. The reactor volume is usually smaller than the volume of the measuring unit. This means that the residence time response of a tracer is already considerably influenced by the measuring construction itself. However, in classic methods it is regarded as a requirement that the reactor volume is sufficiently larger than the volume of the measuring device. In microchannels, mainly laminar flows and the corresponding flow profile [10] are observed. For reactor modelling, however, an idealised plug flow is often assumed. In our experiments, pulse marking with a tracer [12] was used as the marking method. Thus, exit age distributions were directly obtained from the transmittance measurements in the self-developed measuring device.

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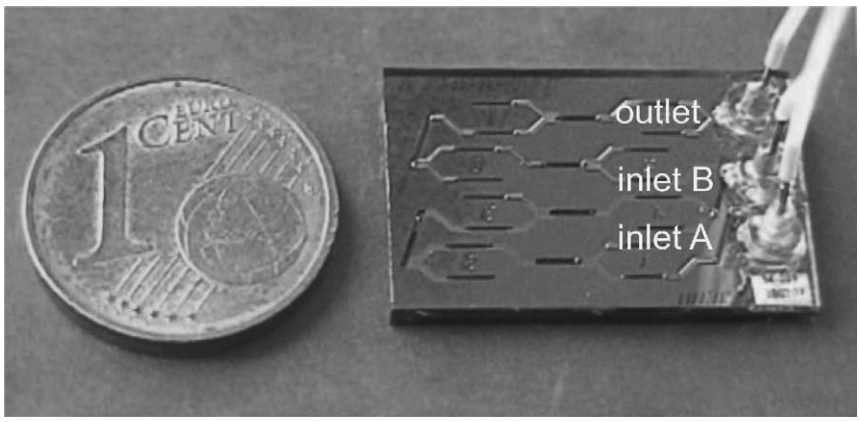

Fig. 1. Tested static micromixer with eight conversion transducers (split and recombine units), two inlets (A and B) and one outlet (C).

2. Experimental setup

2.1. Detection unit

The self-developed transmittance sensor (Fig. 2) has a total size of 1.5 cm × 1.5 cm × 1 cm. It consists either of a TELUX^{TM}-LED (TLWR 7600 red, Vishay) with an irradiation angular range $\alpha = 30^\circ$ and an emission wavelength of $\lambda = 618$ nm, or of an ordinary LED (TLHK 5100 red, Vishay Telefunken) with an irradiation angular range $\alpha = 9^\circ$ and an emission wavelength of $\lambda = 643$ nm. Opposite the LED, a photodiode (SFH 206K, Siemens, Germany) is installed at a distance of 2 mm. Between LED (TLWR 7600 or TLHK 5100) and photodiode a PTFE tube (0.3 mm i.d., 0.76 mm o.d., novodirekt, Germany or 0.5 mm i.d., 1.58 mm o.d., JASCO, Germany) is mounted. For stabilisation purposes, the complete sensor is cast in a hot-meld adhesive (GREVEN HT, Germany). The complete detection unit is arranged in a light-tight black box.

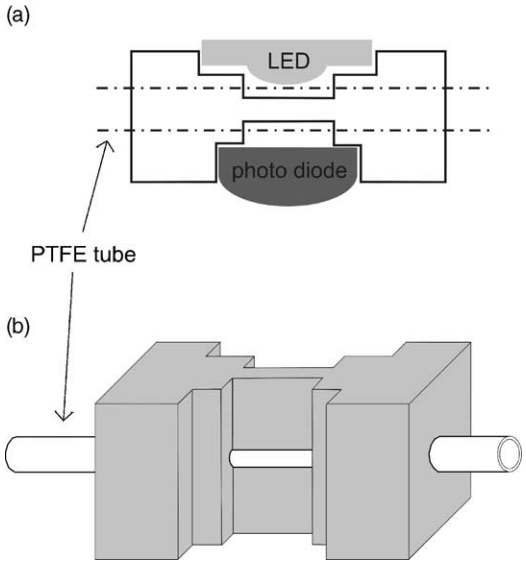

Fig. 2. (a) Sketch of the sensor unit with LED, photodiode and blind. (b) Model of the blind, which also carries the PTFE tube.

The TELUX^{TM}-LED in combination with the used dye (malachite green oxalate, Merck KG, Germany) shows the better signal-to-noise ratio than the ordinary LED, since the second absorption maximum of malachite green oxalate at 619 nm overlaps well with the emission wavelength of this LED. The detector signal is recorded as a current proportional voltage with an operation amplifier connected to a computer using commercially available software (Labview 6.1, National Instruments Germany GmbH). The transmittance measurements were made directly through the PTFE tube without a cuvette.

2.2. Injection unit

The injection unit consists of a T-junction (Fig. 3), which was manufactured at the Institute for Physical High Technology Jena, Germany. The “T-piece” is made by common silicon technologies and has three fluidic connectors. The distance between the inlets A and B is 9 mm and between B and C is 18 mm. The channels have an inner diameter of 500 μm. The length of the main channel between A and B is 68 mm. After 34 mm the side channel of the inlet C leads into the main channel through a nozzle. The length of the side channel is 8 mm. The “T-piece” is connected via standard HPLC-screw fittings. For residence time measurements, the carrier flow was pumped from A to B. The injection pulse of the tracer was carried out through port C. Because of this nozzle structure the unintentional entry of the tracers into the carrier stream could be suppressed.

2.3. Test experiments using PTFE tube

The following setup (Fig. 4) was used for determining the residence time and the residence time distribution of a tracer (dye) pulse. Water (with added detergent—20 μl of a 0.05% aqueous sodium dodecylsulphate solution) and a green dye (malachite green oxalate, $c = 63$ mmol l^{-1}) were applied by

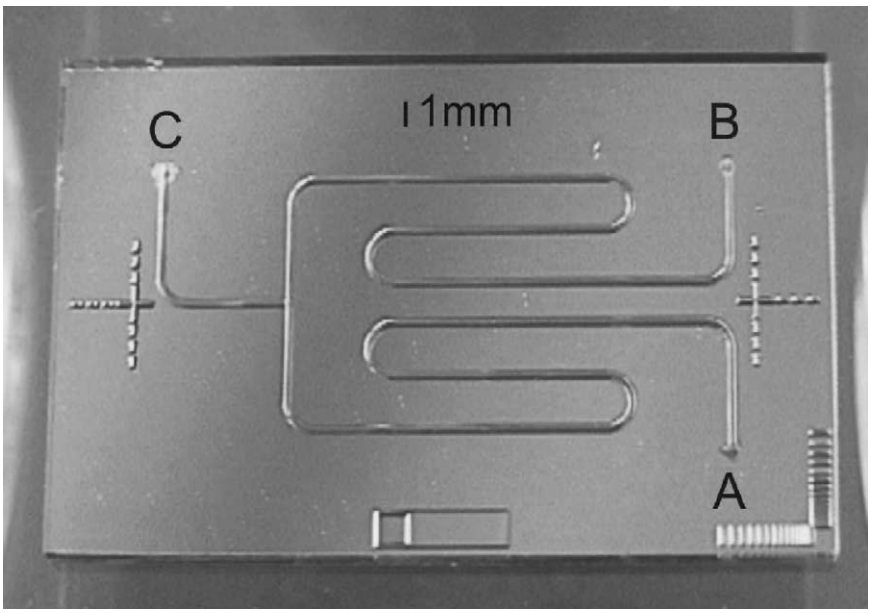

Fig. 3. T-piece like injector with an inlet for the carrier flow (A), an inlet for the tracer (C) and an outlet (B).

syringe pumps (SP100zi, World Precision Instruments Inc., USA). The pumps were equipped with polypropylene syringes (Roth, Germany) with a volume of 1 ml. The cannulae (Sterican with 0.6 mm o.d., B. Braun Petzold GmbH, Germany) were directly slid into the PTFE tube (0.5 mm i.d.).

First, the microreactor was rinsed with water (flow rates between 1.0 and 4.5 ml h^{-1}). The generation of the tracer pulse was achieved by a brief computer-controlled switch of the feed pumps. The switching time depended on the flow rate and ranged from 3.6 to 0.8 s and was selected to ensure a constant tracer volume of 1 μl. The time-dependent concentration distribution of the dye at the outlet of the reactor could be determined with the above described transmittance measuring cell. The measurement period was 240 s for all flow rates and the readout of the transmittance measuring cell took place with a sampling rate of at least 1 Hz. It was also possible to work with higher sampling rates of up to 25 Hz, in order to acquire more precise measurements.

A PTFE tube with an inner diameter of 0.5 mm in different lengths was used as test reactor. The length of the tube was varied between 2.5 and 10 cm. In further experiments the static micromixer described by Kirner et al. [13] and illustrated in Fig. 1 was used. For the determination of the appropriate residence time model, it was necessary to determine the shape of the entering signal before the reactor $x(t)$ and the shape of output signal $y^*(t)$. For this purpose, the signal was measured at a defined distance after the "T-piece" without and later with a microreactor.

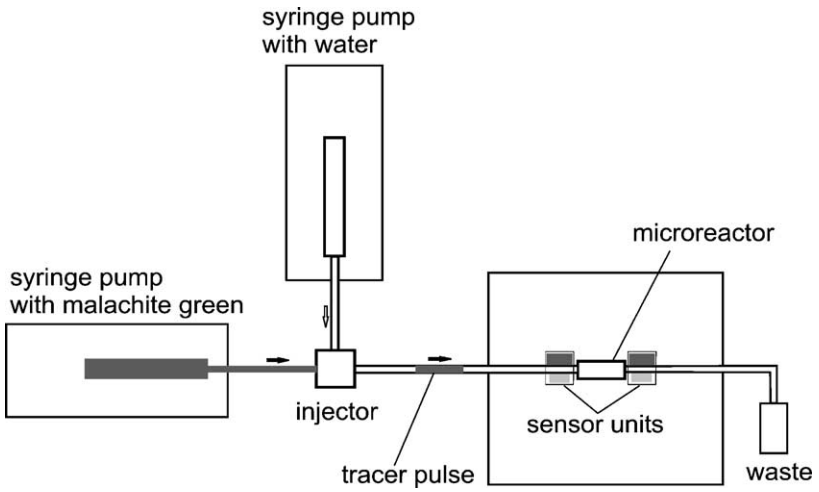

Fig. 4. Experimental setup for RTD measurement consists of two pumps, "T-piece" and two detection units.

2.4. Observation of laminar flow in the static micromixer

The setup used for the investigation of the prevailing flow conditions in the static micromixer consisted of a syringe pump (SP100zi, World Precision Instruments Inc., USA) and a microscope (Axioplan 2 imaging with UV-light source HBO 100 W and 5× objective, Zeiss, Germany) with an attached colour camera (Cohu 2252, BFi OPTiLAS, Germany). For the observation of the flow conditions, the glass-covered channels of the mixer were filled with fluorescent dyes (eosine and fluorescein sodium salt). The UV-induced fluorescence was observed with the colour camera. Addition of the dyes was performed separately through the two inlets of the mixer (Fig. 1) by two plastic syringes. The first syringe contained a 10% aqueous glycerol solution with an eosine concentration of 3.3×10^{-4} mol l^{-1}. The second syringe was filled with the same glycerol solution and fluorescein sodium salt (Demetron, Germany) at a concentration of 3.3×10^{-4} mol l^{-1}. In both cases, the flow rates for both solutions were adjusted to 20, 50 or 100 μl min^{-1}. Microscopic pictures were taken at both the first and at the last conversion transducer.

3. Results and discussion

The data interpretation was performed following a method described by Baerns et al. [6]. According to this method the time-dependent concentration of a tracer at the outlet of the reactor $y(t)$ can be described as the convolution of the concentration distribution at the inlet $x(t)$ with the theoretical residence time distribution $E(t)$

$$y(t) = \int_0^t x(t-t')E(t')\,dt' = \int_0^t x(t')E(t-t')\,dt' \quad (1)$$

If the residence time function $E(t)$ can be described by a model and the input function $x(t)$ is known, it is possible to simulate a theoretical output signal $y(t)$. The model parameters can then be determined by direct fitting (e.g. least squares algorithm) of the simulated theoretical outlet function $y(t)$ to the actually measured function $y^*(t)$. An example of this adaptation is shown in Fig. 5. In this case, the residence time element (a test reactor) is a 5 cm piece of PTFE tube with 0.5 mm i.d.

As a first model concept, the dispersion model (Eq. (2)) was employed to simulate $E(t)$

$$E\left(\frac{t}{\tau}\right) = \frac{1}{2}\left(\frac{Bo}{\pi(t/\tau)}\right)^{1/2} \exp\left(\frac{Bo(1-(t/\tau))^2}{4(t/\tau)}\right) \quad (2)$$

For adaptation the parameter Bodenstein number Bo has served as a variable for the axial dispersion model. From Fig. 5, it is obvious that the adaptation is not optimal yet. However, the measured values are qualitatively confirmed by the model. Deviations from the classic model were even greater, if the static micromixer was added to the fluidic setup (Fig. 6). The reasons are the following:

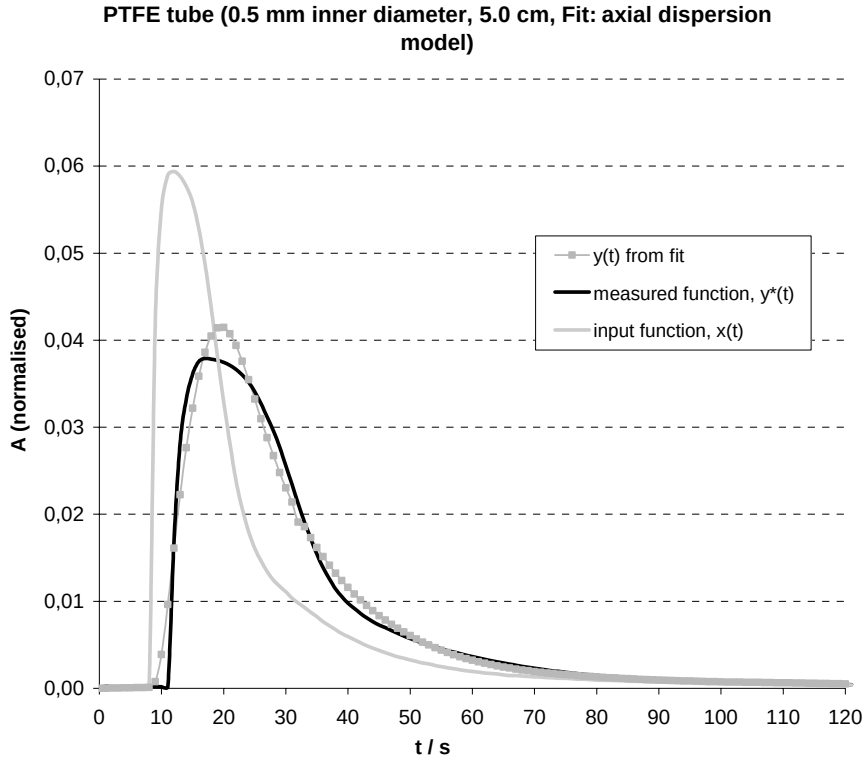

Fig. 5. Modelling of the RTD of the "test reactor" (5 cm PTFE tube with 0.5 mm i.d.). The model shown is that of the axial dispersion.

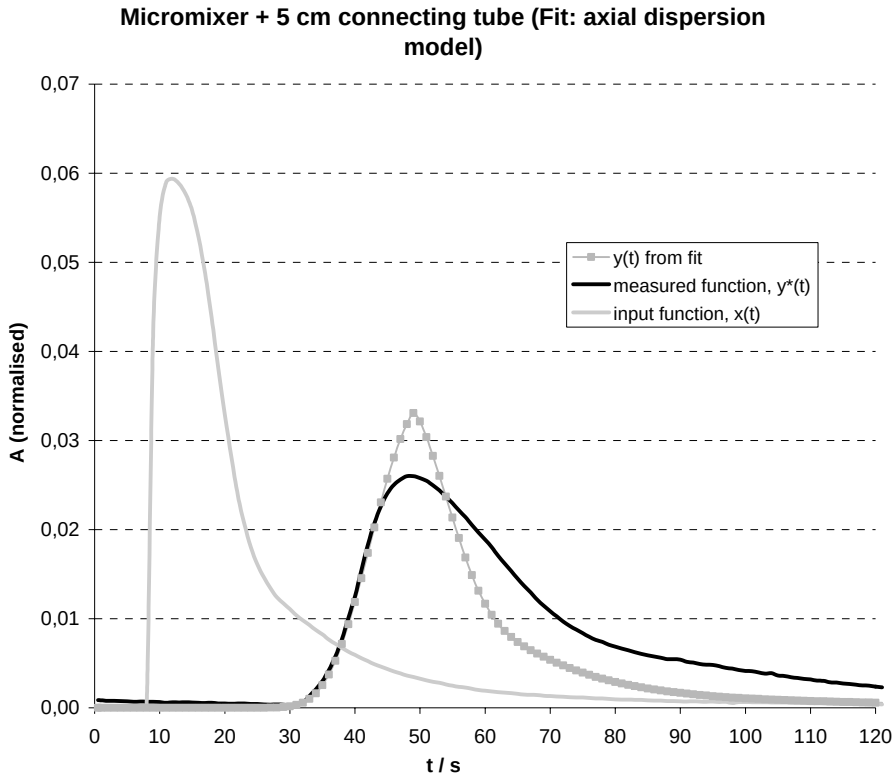

Fig. 6. Modelling of the RTD of the added micromixer after the 5 cm PTFE tube with 0.5 mm i.d. The model shown is that of the axial dispersion.

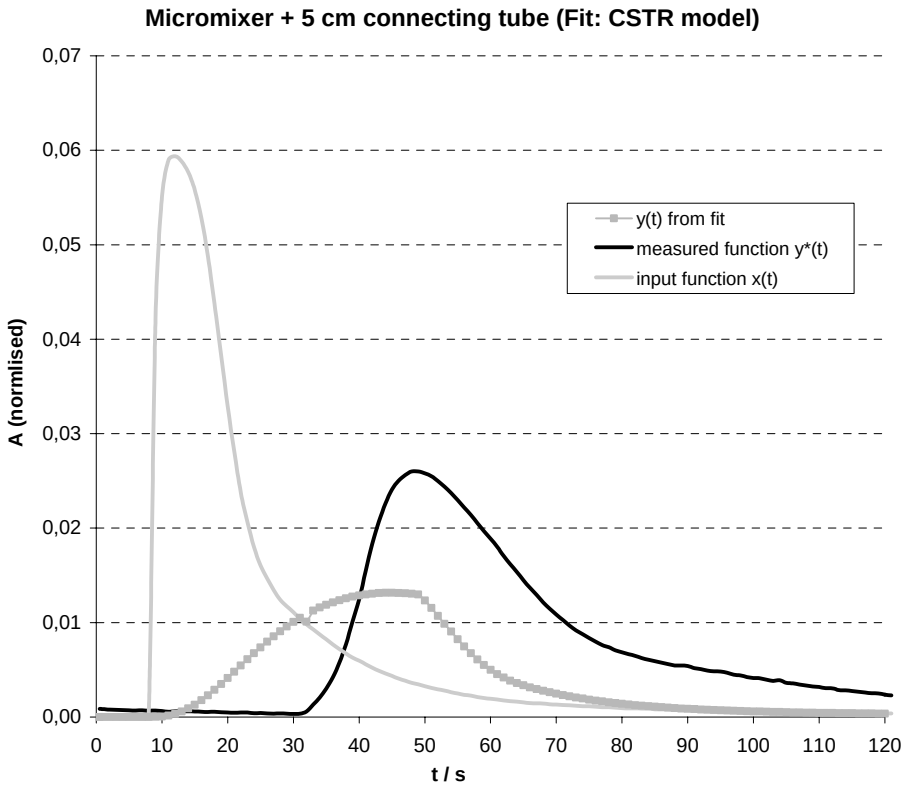

Fig. 7. Modelling of the RTD of the added micromixer after the 5 cm PTFE tube with 0.5 mm i.d. The model shown is that of the continuous stirred tank reactor (CSTR).

(1) Dead volumes which arise because one of the two inlets (Fig. 1) was blocked.
(2) Interferences due to gas bubbles in the system. The large surfaces to volume ratios have a great influence on the wettability under the experimental conditions. These effects could be reduced by the addition of a detergent.
(3) Because the input signals were not an ideal Dirac function, mathematical modelling of $E(t)$ as described in [6] became necessary. In most apparatuses commonly modelled in classic chemical engineering, turbulent flow is always anticipated, and therefore most models on residence time distributions have been developed for this particular flow type. However, microreactors always show laminar flow profiles due to their small dimensions (Reynolds number $\ll 2000$). Therefore, the adaptation of microreactors to existing reactor models is difficult (Figs. 5 and 6) and new models must be developed.

Another widely accepted model to simulate $E(t)$ is the continuous stirred tank reactor (CSTR) or the CSTR cascade (Eq. (3)). Fits to this residence time distribution model depicted in Fig. 7

$$E\left(\frac{t}{\tau}\right) = \frac{(n)^n}{(n-1)!}\left(\frac{t}{\tau}\right)^{n-1} \mathrm{e}^{-n(t/\tau)} \quad (3)$$

From the fluorescence pictures it is obvious that at a flow rate of $100\,\mu\mathrm{l\,min^{-1}}$ laminar flow behaviour prevails. This is indicated by the parallel running of the different dye solutions at the entrance as well as at the exit [13]. Due to these flow conditions, no mixing takes place by fluid-dynamic effects such as turbulences. Mixing proceeds solely by diffusion. These flow characteristics however, require further examination. The assumption of diffusion mixing is confirmed by the observation of a homogeneous solution at a smaller flow rate of $20\,\mu\mathrm{l\,min^{-1}}$ at the last conversion transducer.

4. Conclusions

For the measurement of residence time distributions in microreactors a setup was developed. The measurements were carried out in a test reactor (tube with variable lengths) and proved that the axial dispersion model is applicable approximately. This model, however, describes the static micromixer only insufficiently because of the non-ideal measuring conditions (laminar flow, influence of the measuring device on the measuring system itself). All these reasons lead to a further need to develop this equipment and particularly the method of data evaluation. Improvements of the measurement setup can already be seen in Fig. 4. In the future, measurements will be carried out simultaneously with two detection units. This arrangement will then allow to simultaneously measure the input signal function $x(t)$ and the output signal function $y^*(t)$. The detection units can be arranged directly before and after the fluidic connectors of a microreactor. With this arrangement, influences of the measuring system on measurements could be minimised.

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