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Novel multifunctional microreaction unit for chemical engineering

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Abstract

This work presents the development of a novel multifunctional microreaction unit made of silicon for application in modular microreaction systems in the chemical engineering. The main working principle of the unit is based on the combination of multilamination and chaotic advection effects. The fabrication of the microreaction unit was performed by KOH wet etching. The numerical investigations were carried out by CFD Research Corporation simulation tool. Modified Villermaux–Dushman reaction was applied to define the mixing performance of the micromixer. Additionally the microreactor unit was characterised by infrared (IR) spectroscopy. The experimental and simulation results describe well the physics of the processes taking place in the microreaction unit.

Keywords: Multifunctional microreaction unit; Villermaux–Dushman reaction; Micromixer

1. Introduction

The increasing demands of industry, for example chemical engineering, pharmacy, analytics and biochemistry, for novel and effective mixing technologies as well as the limits already achieved for execution of highly exothermic or explosive chemical reactions have led to the intensive development of the microreaction technologies. The microreaction technology is nowadays one of the most innovative and rapid developing fields in chemical engineering, synthesis and process technology. Many other expectations toward enhanced product selectivity, yield and purity, improved safety and access to new products and processes are directed to the microreaction technology. Several groups from research institutes, e.g. [1–4,12,13] as well as from industry, e.g. [2,5] are currently active in the field. The achievements of the microreaction technology (for a recent review see ref. [6] and the references there in) are however still in the dawn of their broad routine application in industry. Problems such as universal application, reliability and flexibility are still unsolved.

At present, the Fraunhofer Alliance Modular Microreaction Systems (FAMOS) is actively developing a novel versatile modular software-supported microreaction system based on a well-defined toolkit concept [7]. The FAMOS toolkit (Fig. 1) allows to set-up microreaction processes on a functionalised base-plate with suitable fluidic and electronic interfaces for the interconnection of toolkit modules, recording of measurement data and connection to the macroscopic periphery (pumps, analytics, sample handling, etc.). The basic component of the FAMOS toolkit is a special standardised multifunctional microreaction unit made of silicon offering the possibility of multiple combination of single units. The present article reports the design, fabrication, numerical and experimental characterisation of the novel multifunctional microreaction unit.

2. Design and working principle

Multifunctional microreaction unit made of silicon intended for execution of liquid chemical reactions is developed. It consists of two inlet channels for chemical educts, a micromixer, a retention zone and cooling/heating channel (Fig. 2). Up to six fluid ports are available for a flexible coupling of the microreaction unit with either similar units or peripheral devices to form one modular microreaction system. Two standard temperature sensors can be integrated into special cavities on the top surface of the unit. Microreaction units can be individually cooled or heated, either by fluids or electrically. To enable infrared (IR) reflectance spectroscopic measurements, the bottom surface of the microreactor is sputtered with a gold layer. The route of the microchannels is marked on the top surface in order to assist the correct positioning of the IR-probe. The high surface-to-volume ratios

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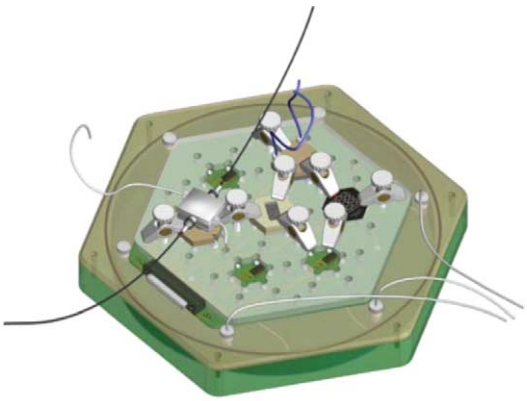

Fig. 1. FAMOS microreaction system.

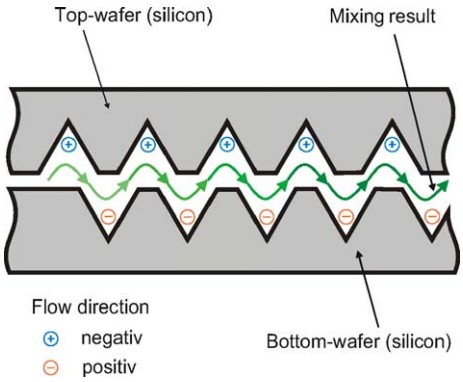

Fig. 3. Working principle of the micromixer.

and volumes in millilitre range provide the application of the unit in the microreaction engineering.

The main component of the developed microreaction unit is a micromixer where a new mixing principle is performed. The main idea is to merge chemical educts together with simultaneously multiple redirection of the common fluid flow (Fig. 3). Three different topologies of the micromixer were developed. The channels for educts supply of the first and third topology are divided into number of microrestrictions (so-called multilamination). The mixing zone is

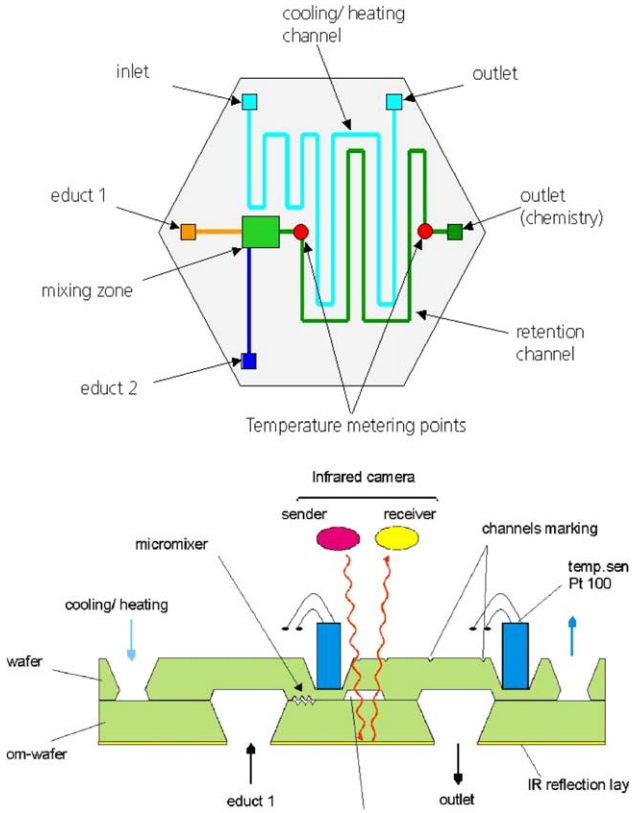

Fig. 2. Schematic of the multifunctional microreaction unit: (top) top view; (bottom) cross-section.

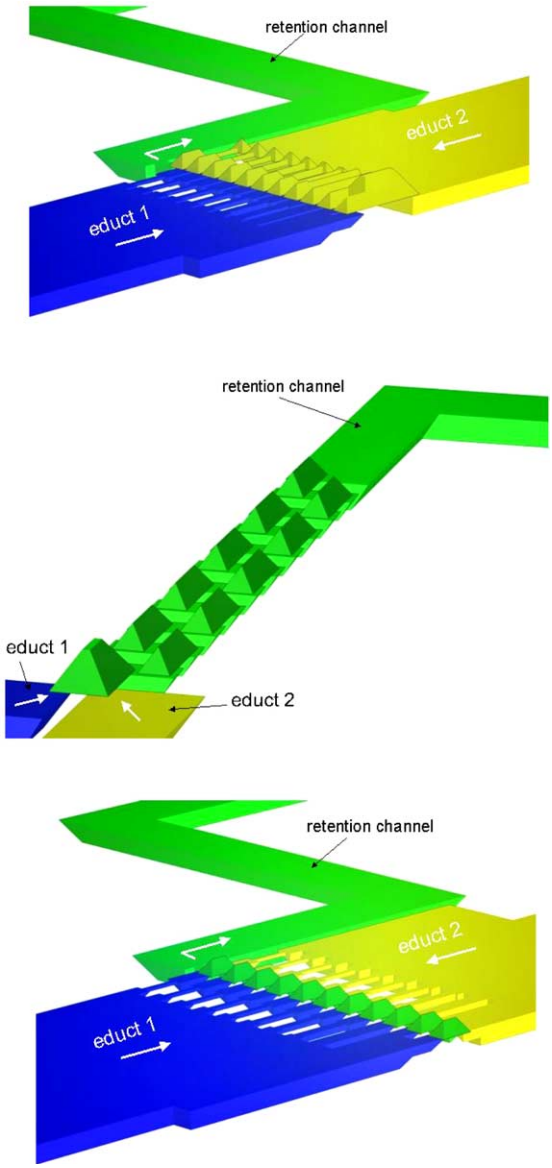

Fig. 4. Topologies of the micromixer: (top) topology no. 1; (middle) topology no. 2; and (bottom) topology no. 3.

formed through an overlap of these microrestrictions and has a 3-dimensional (3D) geometry (Fig. 4, top and bottom). The mixing zone of the second micromixer is formed through cavities in two wafer levels. The special arrangement of these cavities forms a continuous 3-dimensional channel. The geometry of this 3-dimensional channel forces the fluid to perform a complicated movement with permanent change of the flow direction (Fig. 4, middle). Effective mixing is achieved due to turbulence-like and recirculation effects at the corners of these 3-dimensional channels during the fluid flow.

To avoid the effect of dead volumes in the mixing zone of the topologies nos. 1 and 3 with multilamination it is necessary to have minimal fluid flow in the microchannels near the inlet of the retention channel and maximal flow at the beginning of the mixing zone. Therefore, the geometry, i.e. the cross-section and the length of the microchannels are analytically designed corresponding to this requirements. At this, the hydraulic model of the micromixer is described using the method of equivalent electrical circuits.

The special design of the multifunctional microreaction unit determines the following advantages:

- due to integration of the separate microfluidic components in one multifunctional unit, the dead volumes through additional fluidic couplings like tubes and pipes is avoided and better tempering conditions of the whole unit are achieved;
- the integrated temperature sensors allow an active thermal management of the chemical reactions as it is often required;
- the possibility of adaptation of infrared spectroscopy enables the performance of on-line analysis of the chemical reaction inside the microreaction unit, e.g. tuning of the reaction and metering of the process parameters are possible.

3. Fabrication

The multifunctional microreaction unit was developed and fabricated in three different design topologies from two silicon wafers using double-side KOH wet-etching technology. The encapsulation of the cavities and mixing microchannels were realised by silicon fusion bond. The general view of the microreaction unit, design and main dimensions of the micromixer topology within the unit (microstructured silicon top-wafer) are presented in Fig. 5. The first unit generation has a hexagonal shape with a size of 40 mm. The microreaction unit can be used at temperatures up to 200 °C and at maximal pressure of 20 bar. The fluidic coupling is performed by standard UPCHURCH^{TM} fittings UNF 1/4–28.

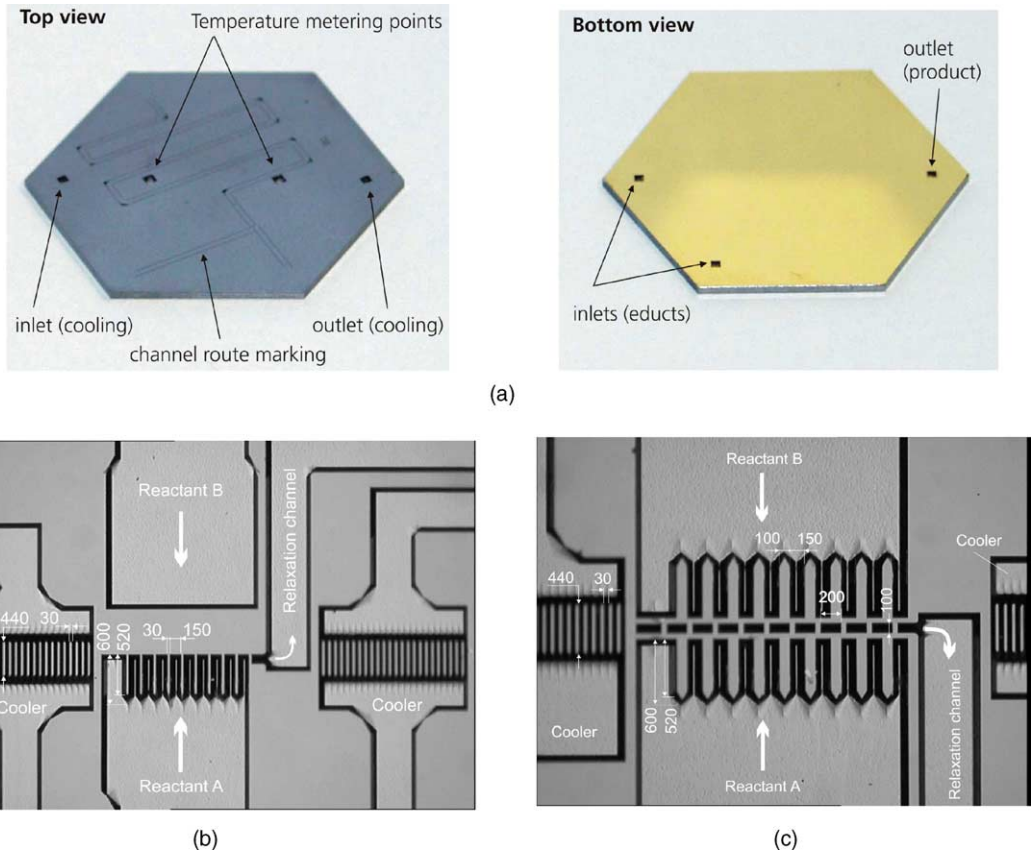

Fig. 5. General view of the microreaction unit (a) and cutout of the mixing zone (microstructured top-wafer of the unit); (b) topology no. 1; and (c) topology no. 3. All dimensions are given in μm.

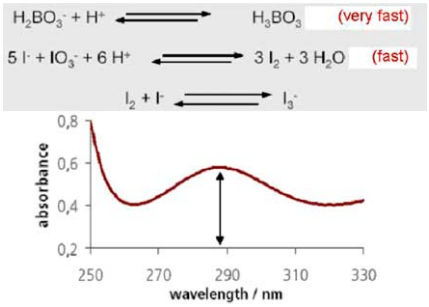

Fig. 6. Modified Villermaux–Dushman reaction used to test the microreaction unit.

4. Experimental characterisation

The excellent mixing performance of the microreaction unit in comparison to other microfluidic mixing devices was confirmed in experimental tests using modified Villermaux–Dushman reaction (Fig. 6). The test reaction was carried out inside the microreaction unit and the absorption of triiodide at 286 nm was monitored by UV-spectroscopy. Comparison of the experimentally obtained mixing quality for the micromixer developed here and other commercially available micromixers manufactured by different research institutes and companies [1,8–10] is presented in Fig. 7. In the investigated micromixers different mixing principles have been realised, for example, split and recombine [1], multilamination combined with chaotic advection [8–10]. The results show an intensified mixing performance of our microreaction unit due to the three-dimensional flow distribution. Consideration of the characteristic diagram (Fig. 8) reveals that high mixing quality is reached due to high pressure drop over the micromixer. The microreaction unit was tested up to only 4 ml/min because higher flow rates require values of the pressure drop higher than the limit for mechanical stability of the micromixer (37 bar). The recommended maximal operating pressure is 20 bar.

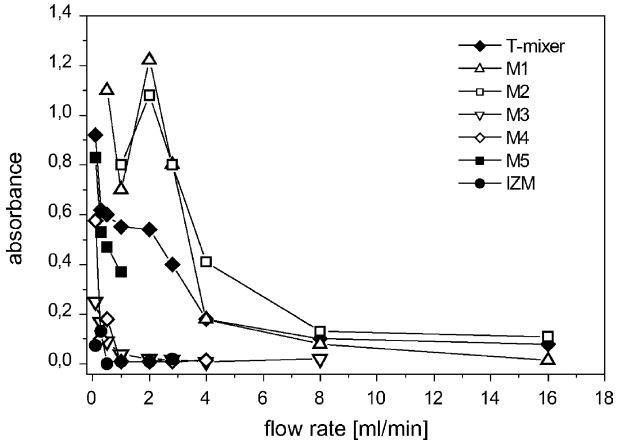

Fig. 7. Mixing quality according to Villermaux–Dushman reaction for our micromixer and other commercially available microfluidic mixing devices.

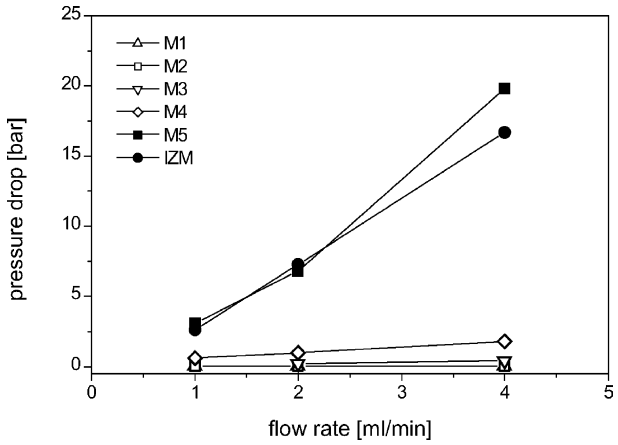

Fig. 8. Comparison of the characteristic diagrams of different micromixers.

5. Numerical simulation

The microreaction units of design topologies nos. 2 and 3 were investigated by CFD numerical simulation to determine the velocity distribution in the microchannels, the pressure drop in the micromixer and the mixing quality. The CFD simulations were carried out by program CFD-ACE v6.6.20 (CFD Research Corporation in Huntsville, USA). The CAD data of topology nos. 2 and 3 were adapted by IGES transformation program to the CFD geometry and the mesh generator tool CFD-GEOM. The original geometry of the microchannels with trapezium- or V-shapes was transferred into geometry with a rectangular shape to perform the better structured meshing. Since the mixing zone is of particular interest, the number of the microchannels in the micromixer considered in the simulations was reduced up to three. This helps to perform fine meshing and to reduce the CPU time. The flow rates at inlets of the microreaction unit were varied in the range of 0.1–10 ml/min. As a working medium, water was used.

Fig. 9 presents selective results for the velocity distribution, the pressure drop and the mixing quality in the micromixer of topology no. 3 at flow rates of 1 and 0.1 ml/min. The analysis of the simulation results has show that the mixing in the micromixer of topology no. 3 is caused by both multilamination effects and chaotic advection as expected. The mixing in the micromixer of topology no. 2 is only due to chaotic advection, which is more effective than that in topology no. 3. The pressure drop in the micromixer of topology no. 3 is about 0.001 bar at 0.1 ml/min. At higher flow rate of 1 ml/min, the pressure drop increases up to about 0.3 bar. In this case, the dependence of the pressure drop on the flow rate is not linear due to the coupled effects of multilamination and chaotic advection. The simulation results of the micromixer topology no. 2 (not presented) have shown a perfect linear dependence of the pressure drop on the flow rate. The comparison of the mixing quality of the topology no. 3 shows that it is more effective at low flow rate (0.1 ml/min,

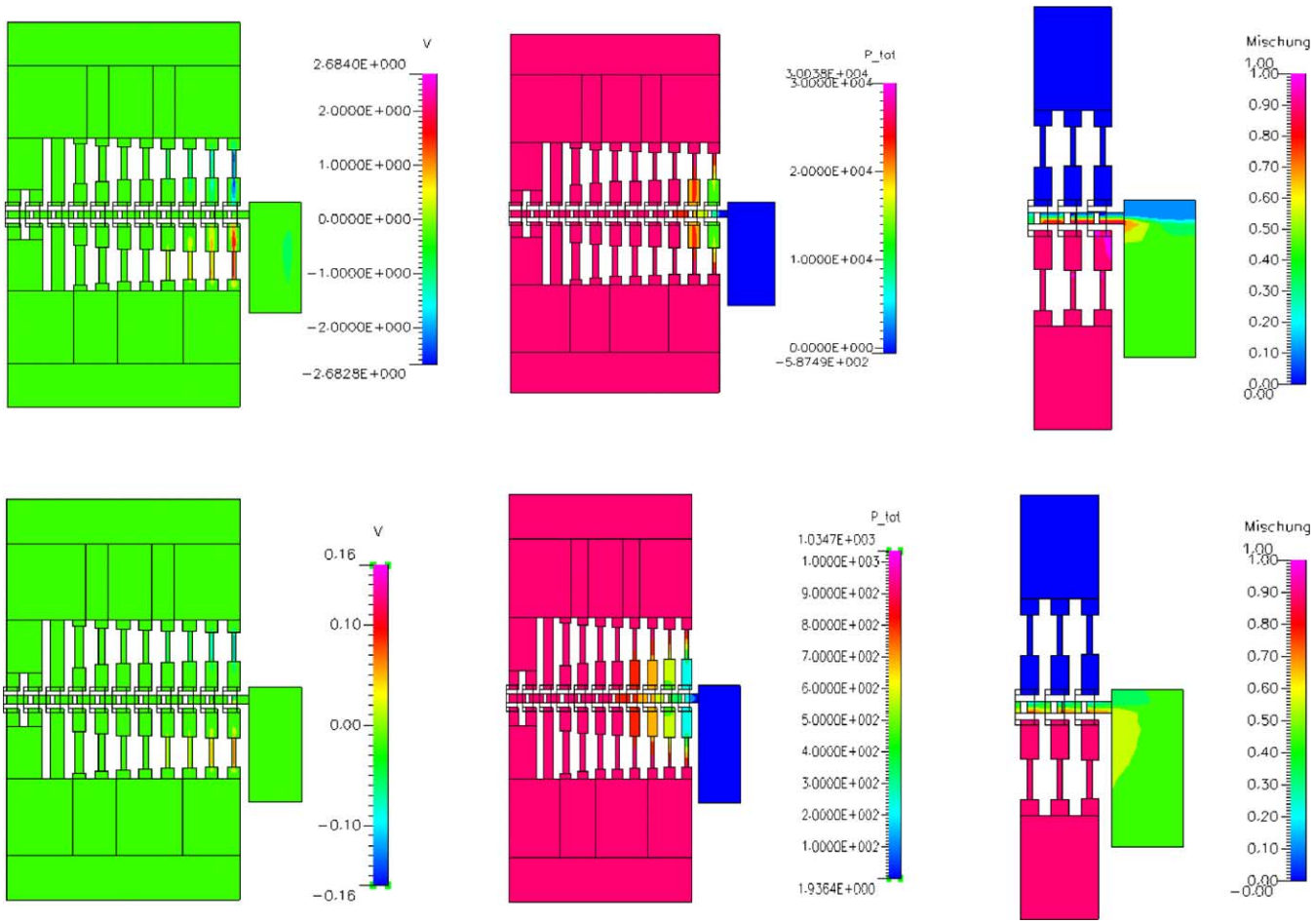

Fig. 9. Results of CFD simulations carried out with micromixer topology no. 3: (left) velocity distribution; (middle) pressure drop; and (right) mixing quality (restricted to three microchannels). Results at two different flow rates are shown: (upper row) flow rate 1 ml/min; and (lower row) flow rate 0.1 ml/min. The velocity and pressure values are given in m/s and N/m^2, respectively.

lower row in Fig. 9) than at high flow rate (1 ml/min, upper row in Fig. 9). This effect results from the short diffusion process time in the micromixer at higher flow rates.

6. Infrared analytics in the microreaction unit

The possibility to perform on-line analysis of chemical reactions directly inside the developed microreation unit is illustrated. Due to the transparency of silicon in the middle and near infrared light spectrum range, it is possible to employ IR-spectroscopy. The potential of on-line IR-spectroscopy as a method suitable for qualitative and quantitative monitoring of chemical reactions inside silicon microreactors has been demonstrated earlier on the example of novel nitration routes involving symmetric disubstituted urea [11].

Due to the specific design of the modular microreaction system, IR-reflectance spectroscopy in the middle (MIR)- and near (NIR)-range was performed. The gold deposited on the back side of the microreactor serves as a reflecting layer. The positioning of the IR-probe above the desired part of the mixing zone is facilitated by special marking that visualises the microchannel routes. Since chemical compounds absorb generally strong in the MIR-range, the depth of the microchannels was designed so small that MIR-measurements were possible.

Fig. 10 presents the IR-measurement set-ups. For the MIR-measurements, the microreactor unit is fixed on the positionable *x–y–z* stage of the FTIR-microscope. The educts are delivered by a syringe pump connected to the microreactor unit by a Teflon capillary. For the NIR-measurements, the microreactor unit is placed and fixed on the base. The NIR-reflectance fibre optic probe is fixed on special alignment unit and can be positioned over the microreactor surface. The fibre optic probe is connected directly to the spectrometer.

Using FTIR-spectroscopy in the MIR-range, the spectra of a solvent (dichloroethan) and a reagent in solution (diethyl-urea dissolved in dichloroethan) were recorded. In order to eliminate disturbances due to absorption of water vapour and carbon dioxide from the atmosphere, the background in the bulk silicon was recorded at first. Then, the entire microreactor unit was filled with the solvent and the spectrum was recorded (shown in Fig. 11,

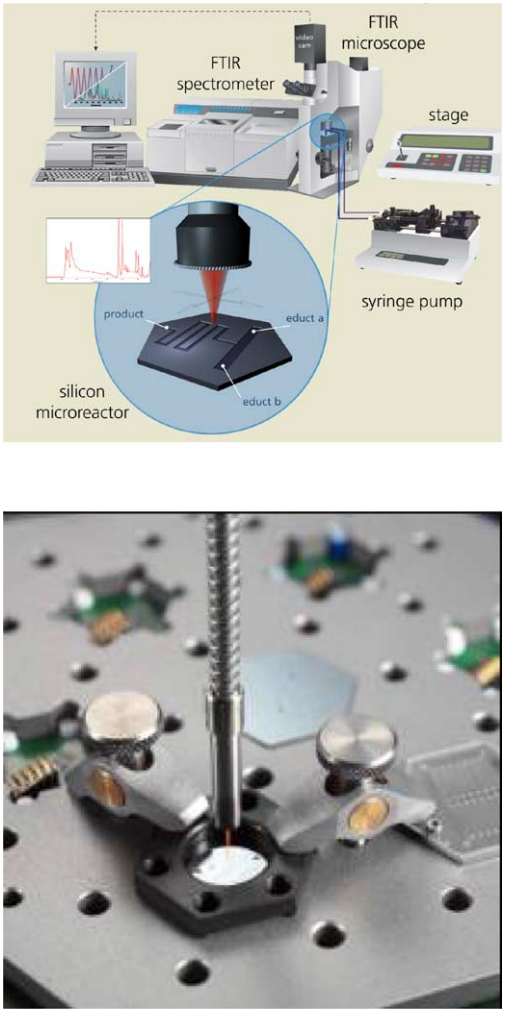

Fig. 10. Schematic of the IR-measurement set-up: (top) measurements in the MIR-range using a high resolution FTIR-microscope; and (bottom) measurements in the NIR-range using a NIR-fibre optic probe.

top). Finally, diethyl-urea was dissolved in dichloroethan, pumped through the microreactor unit and the spectrum was recorded as well (shown in Fig. 11, middle). Although the solvent shows a number of absorption bands, the characteristic bands of diethyl-urea are clearly distinguished (see Fig. 11, bottom). As marked on Fig. 11, they are:

- amid I-band at 1678 cm^{-1};
- amid II-band at 1533 cm^{-1};
- N–H band at 3435 cm^{-1}.

The key advantages of the applied MIR-spectroscopy are the high spatial resolution (about 10 μm) and the direct information on the molecular structure of the analysed substances. The combination of these features ensures identification and location of the reaction educts and products at different parts in the microreaction unit and enables investigation of the reaction mechanism. Advantages of the NIR-spectroscopy regarding the present application are the option to use optic fibre which makes the measurement

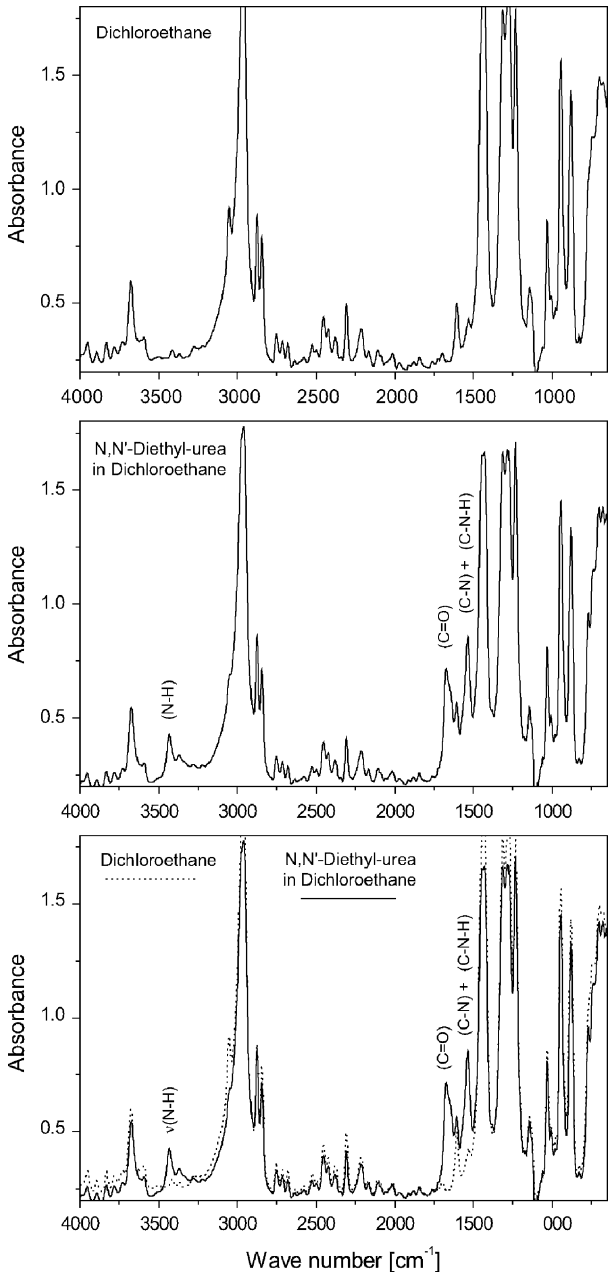

Fig. 11. MIR-spectroscopic measurements performed directly in the reaction channel: (top) spectrum of dichloroethane; (middle) spectrum of diethyl-urea dissolved in dichloroethane; (bottom) comparison of both spectra.

set-up flexible and mobile and the ability to measure spectra from highly absorbing substances.

7. Conclusions

The realization of effective mixing, temperature controlled reaction zones and infrared spectroscopic on-line analysis on one microfluidic chip makes this new microreaction unit a versatile tool for the investigation of chemical processes. The excellent mixing performance

of the microreaction unit in comparison to other microfluidic mixing devices was confirmed by experimental methods based on modified Villermaux–Dushman reaction as well as by CFD simulations. Both experiments and calculations show an intensified mixing performance due to the three-dimensional flow distribution. By using a FTIR-microscope with a high spatial resolution (about 10 μm) educts, intermediates and products of reactions can be identified and distinguished at different positions inside the microchannels. By focusing the IR-beam consecutively on different positions behind the mixing zone the progress of a reaction can be spectroscopically monitored measuring a sequence of IR-spectra.

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