REACTION CALORIMETRY IN MICRO-REACTORS: FAST REACTION SCREENING AND PROCESS DESIGN
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ABSTRACT
The paper presents the actual status of the development of a micro structured reaction calorimeter. The small size of the micro reactor channels permits maintaining isothermal conditions as they are necessary for the kinetic characterization of highly exothermic reactions. Due to the possibility of conducting a spatial resolved calorimetric analysis of the chemical reaction, the calorimeter allows a rather quick gathering of kinetic and thermodynamic parameters.

KEYWORDS: reaction calorimetry, reaction enthalpy, thermokinetic, safety analysis

INTRODUCTION
To keep the time to market as short as possible, detailed knowledge about a chemical reaction system must be available in an early phase of process development, facilitating dependable decisions about synthesis and process management. Therefore, the analytical methods used in fast reaction screenings should offer a high volume of information combined with a short experimental period.

Based on micro reaction technology, innovative continuously-operating reaction calorimeters were developed that permit fast screening of reaction and safety parameters as well as determining the thermokinetic characteristics of chemical reactions.

EXPERIMENTAL
The new µl-calorimetric device consists of a continuous-flow micro reactor made of glass and thermoelectric modules as heat-flow sensors. The microreactors used in the new reaction calorimeters are distinguished by high surface-to-volume ratios, short residence times, and high-precision continuous process control. The high surface-to-volume ratio improves the response time, leads to efficient heat transfer and allows maintaining isothermal conditions. The main parts of the new reaction calorimeter and the measuring principle are shown in Fig. 1. The microstructured device is embedded between thermoelectric modules (Seebeck-elements) as heat-flow sensors, whereby the upper Seebeck-element is segmented into twenty miniaturized Seebeck-elements to achieve a spatial resolution of the reaction enthalpy. Hence, a first approximation of the kinetic data is possible. In Figure 2 the developed sensor-array with twenty miniaturized Seebeck-elements is shown. The sensor-array detects the absolute amount of thermal energy and generates a proportional thermoelectric voltage as a function of the local released heat-flux.
Reaction processing and data acquisition are computer-controlled by using LabVIEW-programmed automation software. Because of the modular set-up of the calorimetric system, the measurement principle can be easily adapted to other microstructured reactors. Therefore, a great variety of chemical reactions can be addressed by using different microstructured reactors; only the sensor-array must be redesigned to adjust on the respective microstructured reactor.

RESULTS AND DISCUSSION

The performance and the accuracy of this new device have been demonstrated for different exemplary reactions in the liquid and liquid/liquid regime, e.g.:

- the determination of the mixing enthalpy of acetone and water:

The results of the measurements at 298 K on acetone/ water as a function of the mole fraction of acetone are presented in Fig. 3 which shows a typical S-shaped $H^E$ curve. The minimum and the maximum in the $H^E(x_{acetone})$ curve occurred at $x_{acetone} = 0.18$ and $x_{acetone} = 0.83$, showing stronger and weaker interactions in the system, respectively, compared with the pure state. The exothermic and endothermic part of the mixing enthalpy can be determined and the results agree well within the experimental error with the results reported by Pineiro [1].
- the hydrolysis of acetic anhydride with 10m hydrochloric acid:

The hydrolysis of acetic anhydride is often used as calibration reaction for calorimetric systems [2,3]. The spatially resolved measurement of the heat flow along the flow direction permits a first approximation of the kinetic data (Fig. 4). The determined first order rate constant and the enthalpy of reaction is in good agreement with the literature data [4].

![Fig. 3: Mixing Enthalpy $H^E$ at 298 K for water + acetone.](image3)

![Fig. 4: Hydrolysis of acetic anhydride, spatial resolution of the measured heat flow.](image4)

**CONCLUSIONS**

The new µL-calorimeter has a very small time constant of about 3 s which is by a factor of 20 smaller than that of conventional calorimeters. Hence, it is ideally suited to measure fast and highly exothermic reactions at isothermal conditions.

Moreover, such a calorimetric device is of particular importance in view of process optimization at early stages of chemical process design, especially for the synthesis of new fine chemicals and pharmaceutical products, where generally only small amounts of test substance are available and time-to-market is crucial.

**REFERENCES**