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A New Multipurpose Microreactor for Process Safety Studies

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Abstract:

A new glass-lined microreactor for SETARAMs Calvet Calorimeters BT 2.15 and C 80 is described, which allows fast and simple characterization of thermal properties of chemical reactions and reaction mixtures. Application examples are presented, and the special features of this reactor are outlined.

It is well-established practice to assess the thermal risks of chemical processes systematically before introducing new or modified processes in pilot or production plants.[1] Any reliable process risk analysis must be based on thermal safety data such as the heat of reaction and the thermal stability of the reaction mass. More detailed risk evaluations require additional data such as kinetics, temperature−pressure relations, etc.[2,3]

The highly dynamic business environment in the specialty chemicals and pharmaceutical industries requires short process development times, fast process transfers between research, development, pilot plant, and production as well as between different production sites. Having the necessary data at hand is often a critical factor when it comes to the assessment of the thermal process safety.

Bench-scale lab reactors are widely used as calorimeters for the measurement of reaction energies and kinetics. They allow a close simulation of reactors in production. Samples can be taken to evaluate the thermal stability of the reaction mass using DTA/DSC instruments and for analytical process control. However, these methods are quite complex and time-consuming. In addition, quantities of starting material in the order of 100−500 g are necessary to allow for good test results. Furthermore, the pressure and temperature range of the available instruments is often limited.

Therefore a new glass-lined microreactor for SETARAMs Calvet Calorimeters BT 2.15 and C 80 has been developed, which allows fast and simple characterization of thermal properties of chemical reactions and reaction mixtures. In Figure 1, two configurations of the reactor are shown.

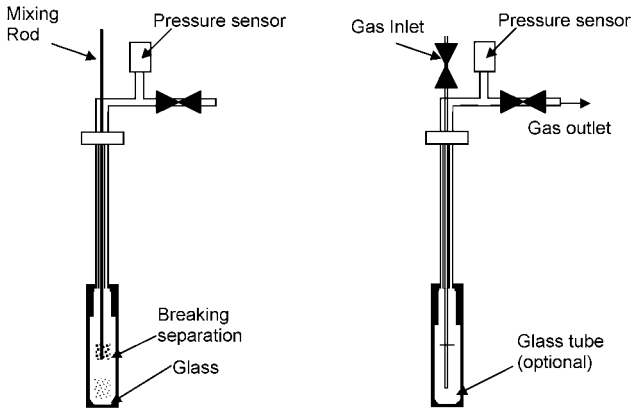

Figure 1. **Typical configurations of the reactor. (Left) mixing configuration where the two reactants are initially in two stacked glass tubes. The reaction is started by breaking the bottom of the upper tube. (Right) Configuration for controlled dosage of gas.**

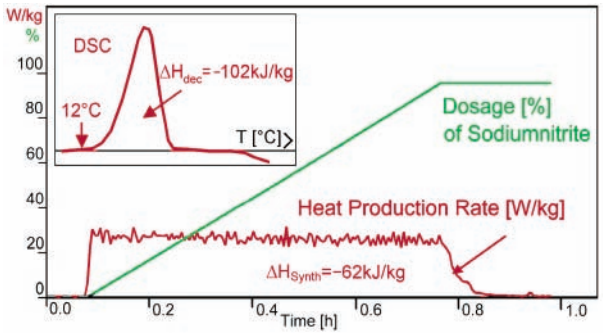

Figure 2. **Thermal analysis of the diazotation in an RC1 reaction calorimeter. (Inset) DSC plot of the decomposition of the diazo compound.**

Features of the Microreactor.

- Mixing experiments with 10−2000 mg
- Dosage of liquids under high pressure
- Dosage of gases below level, simultaneous pressure recording
- Glass-lining for corrosive media
- Pressure range: 50−200 bar
- Temperature range: −150−200 °C (SETARAM BT 2.15 calorimeter) and 25−300 °C (SETARAM C 80 calorimeter)

Example 1: Diazotation. The chemical synthesis of a diazo compound has been investigated both in the conventional way and with the new microreactor.

Figure 2 shows the results from the reaction calorimetric study in the METTLER RC1 reaction calorimeter. Sodium nitrite was added to a mixture containing an aromatic amine. During dosage, a steady heat production rate of about 20−

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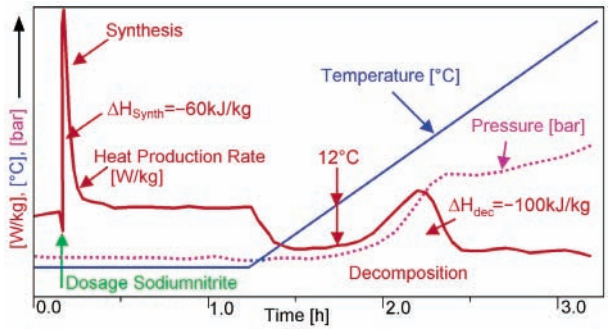

Figure 3. **Combined thermal analysis of the synthesis and the decomposition of diazoaniline. The curves have been scaled and shifted relative to each other for better visibility.**

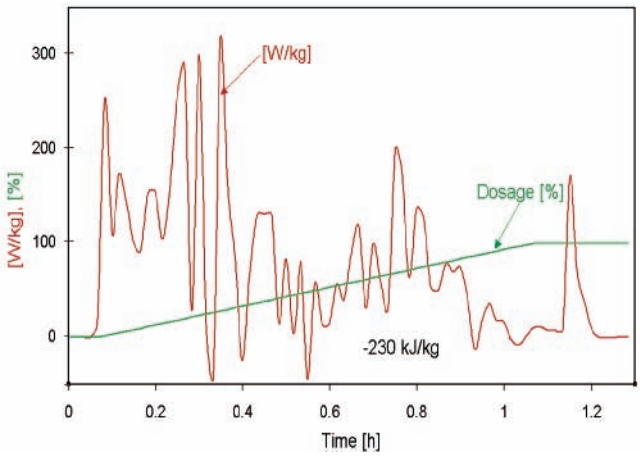

Figure 4. **Semi-batch reaction carried out in the RC1 reaction calorimeter. Dosage [0−100%] started after 2 min and was within 1 h. The heat production curve [W/kg] is very noisy due to the high viscosity of the reaction mixture.**

25 W/kg is observed. The integration of this curve yields the heat of reaction (−62 kJ/kg). After completion of the reaction differential scanning calorimetry (DSC) was carried out for the reaction mixture. The DSC plot is shown in the inset in Figure 2. The decomposition energy of the diazo was −102 kJ/kg.

In Figure 3 the test with the new microcalorimeter is shown: sodium nitrite was added at once to the amine. This resulted in a short but high heat production rate. After completion of the diazo formation, the reaction mass was heated directly in the same sample tube to obtain a dynamic DTA. Both the heat of reaction (−60 kJ/kg) and the decomposition energy (−100 kJ/kg) agree very well with the values previously obtained. In addition, pressure was monitored: the pressure curve shows clearly the release of nitrogen due to the decomposition of the diazo compound.

Example 2: Semi-batch Reaction. A reaction was carried out at 70 °C by mixing two components. The reaction mixture was quite viscous, and stirring in the bench calorimeter was difficult such that the heat production curve observed was very noisy (Figure 4). No kinetic information was obtained, but the integration yielded a total reaction heat of −230 kJ/kg. In the microcalorimeter, a simple batch

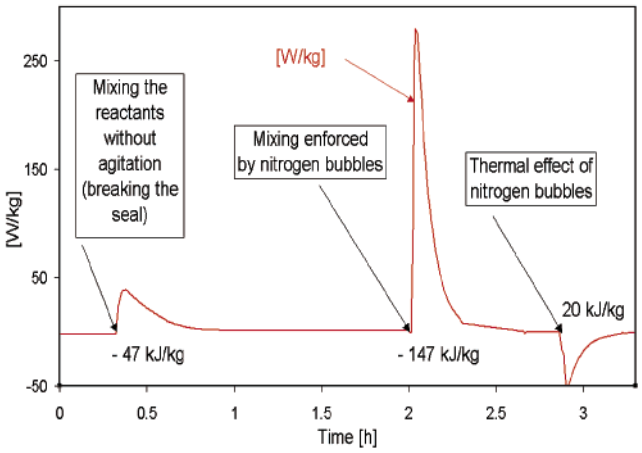

Figure 5. **Reaction of example 2 carried out in the microreactor. First the reactants were brought together without mixing, then mixing was enforced by nitrogen bubbles. After completion of the reaction, nitrogen was again blown through the mixture to evaluate the thermal effect of the gas flow.**

mixing experiment was made. The reactants were mixed by breaking the seal in the mixing cell (see Figure 1, left). Without further agitation only part of the reaction took place, releasing −47 kJ/kg. Upon enforcing mixing by bubbling nitrogen gas through the cell, the reaction was completed and another −147 kJ/kg was detected. The difference between −230 kJ/kg and −(147 + 47) = −194 kJ/kg) was due to the cooling effect of the nitrogen introduced into the cell, which was clearly shown after the test, when the same amount of nitrogen was blown through the cell again, leading to an endothermic signal of +20 kJ/kg (Figure 5).

Summary

Advantages of the Microreactor.

(1) tests possible with even less than 1 g of starting material
(2) heat of reaction and the decomposition energy in one run, no sampling
(3) wide pressure and temperature range
(4) pressure monitoring possible
(5)versatile configuration: mixing, dosage

Limitations of the Microreactor.

(1) Kinetics of two-phase reactions do not reflect the situation in production scale.
(2) Controlled dosage of solids is not possible.
(3) Reactions under reflux cannot be studied.

The new microreactor is thus ideally suited for two-component-batch and semi-batch reactions. It also allows confirming existing RC1 results after small process modifications in a short time, with small amounts of starting material and at low cost.

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