Design and characterization of a gas-solid reaction calorimeter

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Motivation

One of the main interests of calorimetric research has always been the estimation of safety hazards in industrial scale chemical processes. Especially, the gross reaction heat, the rate of heat generation and the adiabatic increase in temperature are relevant magnitudes to determine safety parameters like required heat dissipation capacity or thermal stability of system components. Modern applications enable real time measurements of reaction heats under isothermal and isoperibolic conditions as well as the determination of thermal data and constants[1]. However, there has been no reaction calorimeter capable of measuring the heat of gas-solid reactions yet. Although, the majority of reactions are carried out in solution, there are numerous examples for gas-solid reactions of academic or industrial interest[2]. To gain access to the heats of these reaction a new type of calorimeter was designed, realized and tested.

Design of the Calorimeter

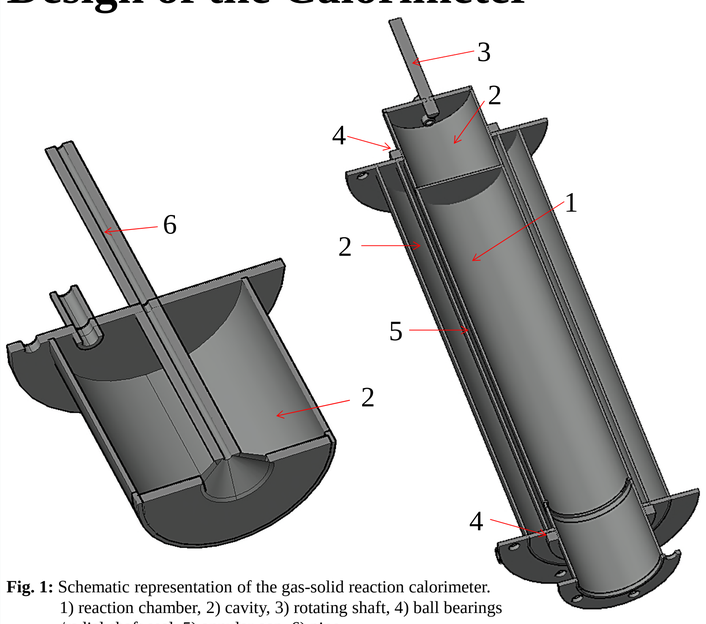


Fig. 1: Schematic representation of the gas-solid reaction calorimeter. 1) reaction chamber, 2) cavity, 3) rotating shaft, 4) ball bearings /radial shaft seal, 5) annular gap, 6) pipe

The presented gas-solid reaction calorimeter (Fig. 1 and 2) is a modified and insulated semi batch rotary pipe reactor. The heat can be measured via heat balance, solids can be mixed continuously and gas can be dosed simultaneously. The cylindrical reactor consists of a reaction chamber (1) a cavity (2) and a rotating shaft (3). A further cavity (2) is also implemented in the lid and in the jacket of the reactor. The cavities can be evacuated to minimize heat loss to the environment. The jacket forms an annular gap (5) in combination with the reactor. A tempering medium flows through the gap and transports heat out of the reactor during a reaction . The released heat can be calculated by measuring the temperature at the inlet/outlet and considering the mass flow. Furthermore, the rotation of the reactor leads to a specific flow pattern in the gap (Taylor vortices), which facilitates a uniform flow with reduced back-mixing. The jacket contains two ball bearings and two radial shaft sealings connected to a flange (4) to hold the reactor in position and to avoid leaks. Gas is dosed through a pipe in the lid (6). The end of this pipe is connected to a rotary joint.

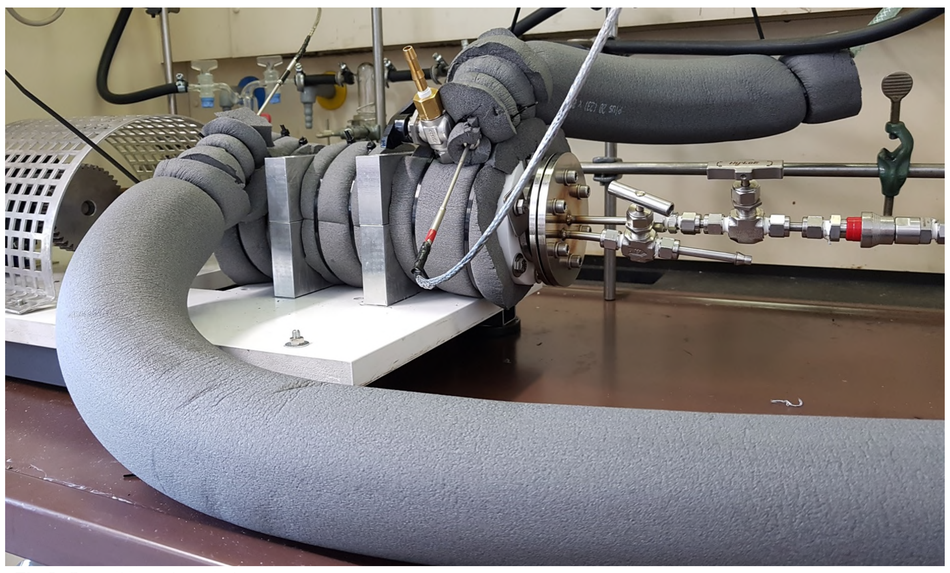


Fig. 2: Gas-solid reaction calorimeter

Characterization

It was assumed that conditions for stable Taylor vortices in the annular gap, depending on rotational speed (16.4-58.9 rpm), flow rate (200-600 ml/min) and incline (1.5-6°) could be found. Therefore, a DoE was conducted. The aim was to ensure a homogeneous flow around the reactor to reduce backmixing and to minimize the dead volume. Targeted values were the Bodenstein number, the average residence time and the dead volume.

The experiments showed that the incline does not effect the targeted values. The residence time was antiproportional to the flow rate and independent from other parameters. The Bodenstein number and therefore the degree of backmixing increased with the rotational speed and to a minor extend decreased with the flow rate (Fig. 3). The dead volume was unaffected by the variations.

Theoretically, Taylor vortices were expected at rotational frequencies of 10 rpm and more. This was experimentally confirmed with an acrylic glass model of the reactor (Fig. 4).

The study showed that favorable working conditions are found with preferably high rotational speed and a low flow rate.

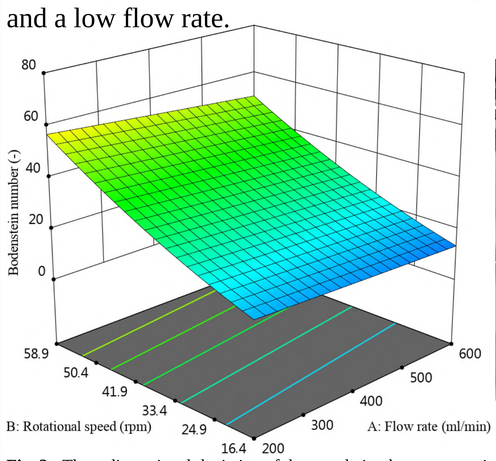


Fig. 3: Three dimensional depiction of the correlation between rotational speed, flow rate and Bodenstein number.

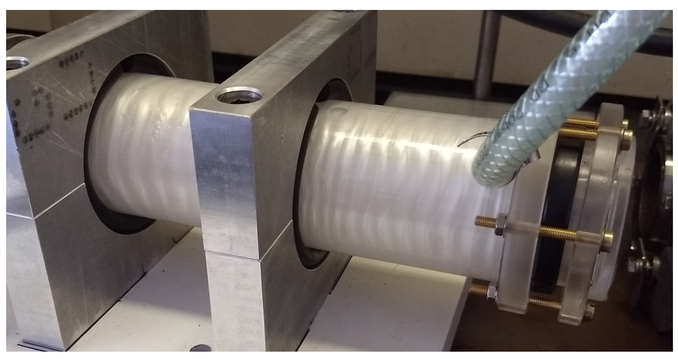


Fig. 4: Visualized Taylor vortices in the annular gap (Acrylic glass reactor model).

Conditions for optimal mixing were investigated in dependence of the rotational speed (16.4-58.9 rpm) and the filling degree (12.5-37.5 %). The aim was to have a motion behavior that ensures a continuous renewal of the solids surface. Experiments were carried out in a transparent reactor model filled with glass beads (diameter: 40-90 µm) and Zeolith 3A (diameter: 2-2.5 mm). The evaluation was undertaken visually (e.g. in Fig. 5).

The desired motion behavior was always obtained at filling degrees of 25 % and/or rotational speeds of 38 rpm or more. Further, it turned out that lower filling degrees demanded higher rotational speeds.

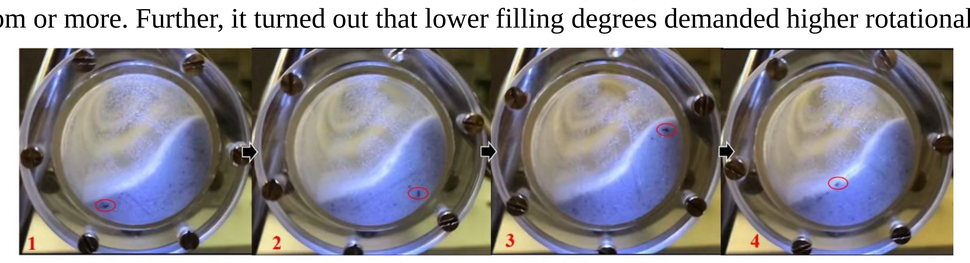


Fig. 5: Solid particle (red circle) moving through the bed in a cascading motion.

Summary

- A calorimeter based on a rotary pipe reactor was designed and realized
- Characterization of flow regime and motion behavior showed preferable working conditions
- Adsorption experiments and urotropine synthesis confirmed that the calorimeter works with adequate accuracy

Determination of precision and accuracy

Beside the heat of reaction two additional influences on the heat flux, the friction of the shaft sealings, and heat losses along the cylinder wall had to be accounted for. The first was measured, the latter was determined by simulation using COMSOL Multiphysics (Fig. 6). Both factors were considered in the following studies.

Two reactions were chosen to test the suitability of the reactor for calorimetric measurements. The first was the formation of ammonium oxalate (Fig. 7). The obtained mean enthalpies were:

-208.5 ± 3 kJ/mol (Lit.: -209.5 kJ/mol[3], 0.5 % deviation)

The second was the synthesis of urotropine from paraform-aldehyde and ammonia (Fig. 8). The obtained mean enthalpies were:

-332.6 ± 10.8 kJ/mol (Lit.: -331.7 kJ/mol[4], 0.3 % deviation)

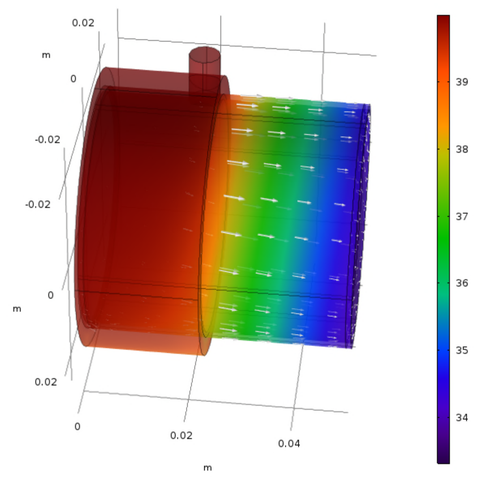


Fig. 6: Simulated temperature profile at the bottom of the reactor. For a tempering medium at 40 °C and ambient temperature of 25 °C, the conductive heat loss amounts to 0.52 W.

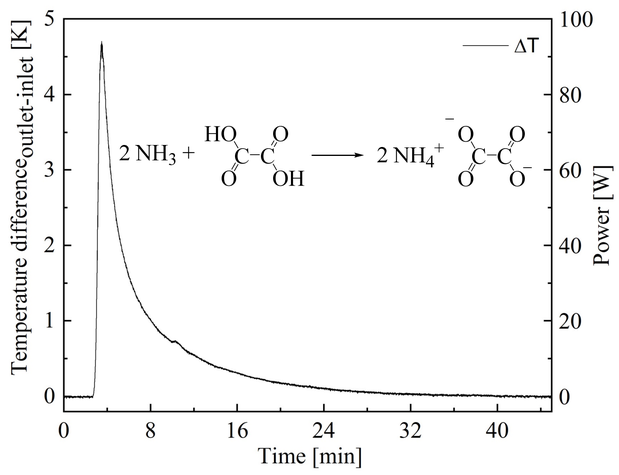


Fig. 7: Temperature/power curve of the synthesis of ammonium oxalate from ammonia and oxalic acid (13.42 g), heat: 22.07 kJ. Temperature of tempering medium: 40 °C, flow rate: 300 ml/min, rotational speed: 40.2 rpm.

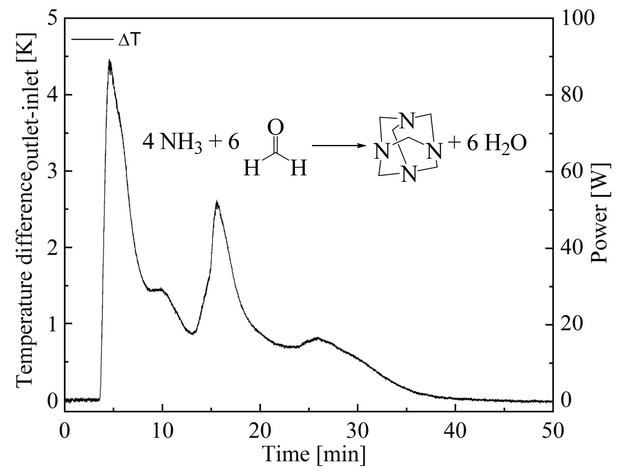
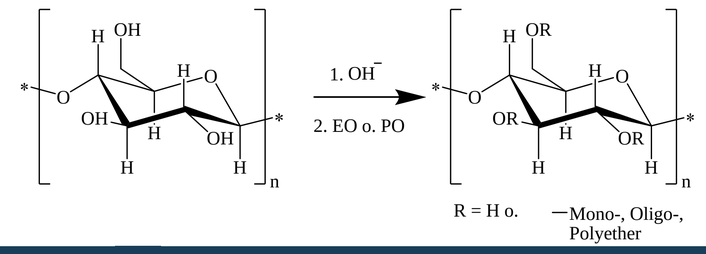


Fig. 8: Temperature/power curve of the synthesis of urotropine from ammonia and paraformaldehyde (25.58 g), heat: 46.36 kJ. Temperature of tempering medium: 40 °C, flow rate: 300 ml/min, rotational speed: 40.2 rpm.

Outlook

- Investigation of further gas solid reactions (adsorption, acid/base reaction, complexation,…)
- Investigation of the applicability for reactions with viscous reagents
- Determination of the heat of reaction for the ionic polymerization of alkali cellulose with EO



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