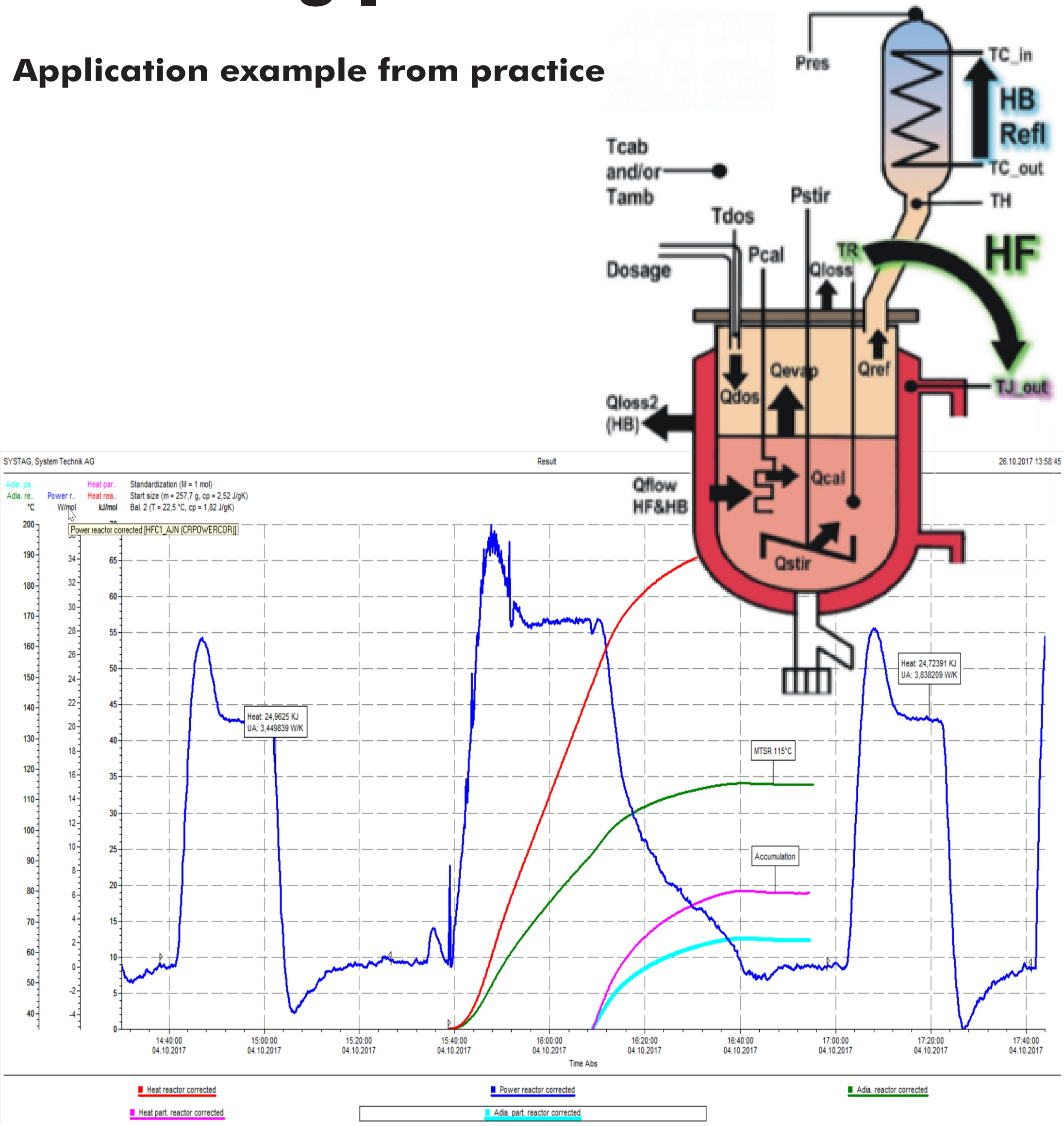
Application note

Reaction calorimetry at boiling point

Application example from practice



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Preamble

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During process development and scale-up, reliable thermal data of the enthalpy of reaction are essential. Important parameters for a safe reaction control are not only heat and power of the reaction, but also the understanding of a possible accumulation or statements about the process gas development during a reaction. With a heat flow calorimeter, the essential parameters such as

- Power of reaction
- Energy of reaction
- Adiabatic temperature rise
- Gas evolution, or
- Accumulation

can be determined reliably and reproducibly.

Safety through knowledge.

Problems at the boiling point

When reactions have to be investigated under reflux conditions, most calorimeters fail due to inadequate detection or unstable conditions.

As a result, the reaction must be adjusted to suppress evaporation.

Chart 1: FlexyPAT Heat flow calorimeter

The solution

The solution

The FlexyPAT-HFC calorimeter from SYSTAG does justice to this fact with a reflux cooler design specially developed for this purpose.

Years of experience and continuous optimization of the flow conditions result in a stable and reliable signal quality with previously unattained stability. Smaller energies or changing boiling points are therefore no longer a problem for calorimetry at the boiling point.

The advantages

- Simple reaction control
- Very stable signal acquisition
- Faster results with fewer experiments
- Reproducible results for reliable scale-up

Chart 2: Special reflux cooler for heat balance method

Reaction calorimetry

Esterification of acetic anhydride

In a conventional jacketed reactor, the esterification of acetic anhydride is carried out at 35°C. For this purpose, 1 mol acetic anhydride is added continuously for half an hour. Before and after dosing, the calibration heater is switched on for 20 minutes to determine the heat transfer coefficient.

Results

The result of the reaction power (blue curve) is determined with a maximum power of 37W/mol. The integral (red) of the power curve gives the enthalpy of 66.83kJ/mol (theory 65-67kJ).

Based on the cp values and the corresponding reaction power and reaction size, a maximum adiabatic temperature increase of 80K or an MTSR (green) of 115°C results, regardless of the boiling point of the reaction solution

The accumulation (violet) after finished dosing shows with 19kJ about 1/3 of the total energy. Thus it can already be estimated for a risk analysis whether the reaction is dosage-controlled or whether there is a potential risk with regard to accumulation. In this example, the temperature increase of the accumulation (light blue) is 29K or 64°C as MTSR of the accumulation, which corresponds approximately to the boiling point of the reaction solution.

All results are corrected with regard to the dosing temperature and its specific heat capacity. However, the evaluation would also allow this correction to be suppressed.

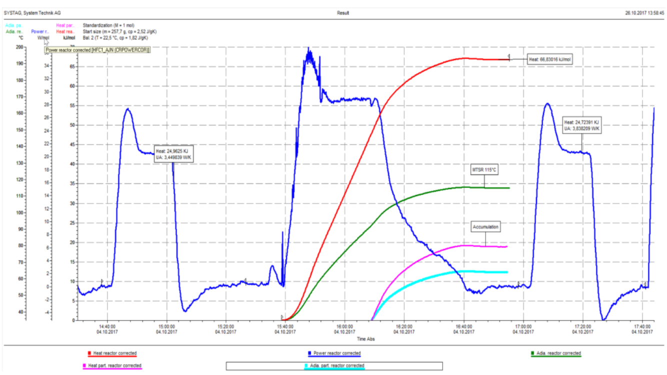

Chart 3: Evaluation by CaloGraph

At boiling point

Validation under refluxing

No calibration is actually necessary for the heat balance at the reflux. To determine the efficiency of the reflux cooler, the calibration heating (violet) can be used instead of a reaction.

When balancing at the reflux (see chart# 5; TR = red), the temperature difference between the cooler inlet and outlet (black) must be measured very accurately, and the flow through the reflux cooler must be known. If this is done with cooling water, the cp value is known (4.18J/g/K). For other media, the calibration heater can again be used once to determine the cp value of the coolant.

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Results

In the present case, the reaction solution has been heated to boiling temperature (continuous reflux). If the return flow dT is well stabilized, the calibration heating (violet) has been switched on to simulate an exothermic reaction (see Chart#5).

As a result (Chart#4) of the simulated reaction, the evaluation - based on the flow measurement at the reflux cooler - yields an energy of 24.67kJ (blue curve). To validate this result, the integral of the calibration heater is shown as a light blue curve. The maximum of this curve is 24'621Ws. This corresponds to an agreement of better than 1%.

If a cooling thermostat with a known flow or medium is used instead of water, the unknown term can be determined in the same way.

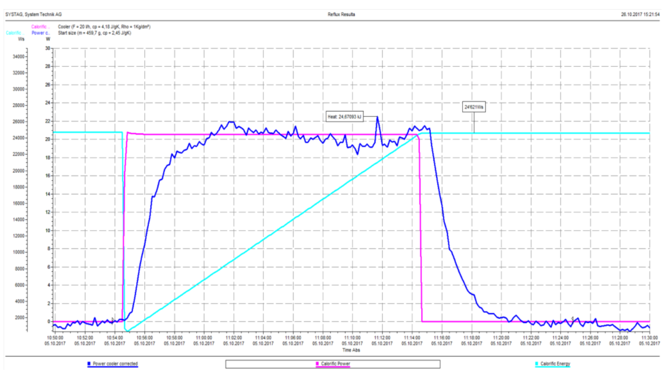

Chart 4: Validation at the poiling point

Reflux condenser

Design of the condenser

As mentioned above, the calorimetric evaluation under reflux condition often depends on the quality of the available signals. Especially the temperature difference at the reflux cooler is often an unsolvable problem.

SYSTAG has addressed this issue and developed a special reflux cooler to accommodate the very often noisy signal. The design of the reflux cooler including the arrangement of the Pt-100 sensors is sometimes very decisive. Special attention is also paid to the cooling water flow.

Different cooling media

Often water cannot be used as a cooling medium in the reflux cooler, or the flow cannot be precisely adjusted or measured..

However, for evaluation under reflux condition it is essential to know the flow rate of the cooling media and ist heat capacity. If the flow rate or the specific heat capacity of the cooling medium is not known, the reflux cooler can be calibrated by using the calibration heater.

Calibration

Calibration

As briefly explained above, a "blind experiment" can be used for this purpose. Without an exothermic reaction, the calibration heater is switched on (violet curve) and the deltaT of the reflux condenser (see chart #5) is evaluated. The integral of the calibration heater must theoretically correlate with the energy of the evaluation.

If this is not the case, the flow entered and/or the assumed cp of the cooling medium are not correct. When using water as cooling medium, the specific heat capacity is well known. In most cases the determined flow rate is not correct.

With the KaloGraph evaluation software, any number of evaluations with different cp or flow rates can be calculated. If the cp is known, the value for the flow rate can be adjusted until the energy at the reflux cooler corresponds to the energy of the calibration heater.

Strictly speaking, of course, this only applies to the current situation. Thanks to good insulation of the steam bridge, this method also leads to good results at other boiling temperatures. Alternatively, a calibration step with calibration heating can be inserted at any time before / after the reaction.

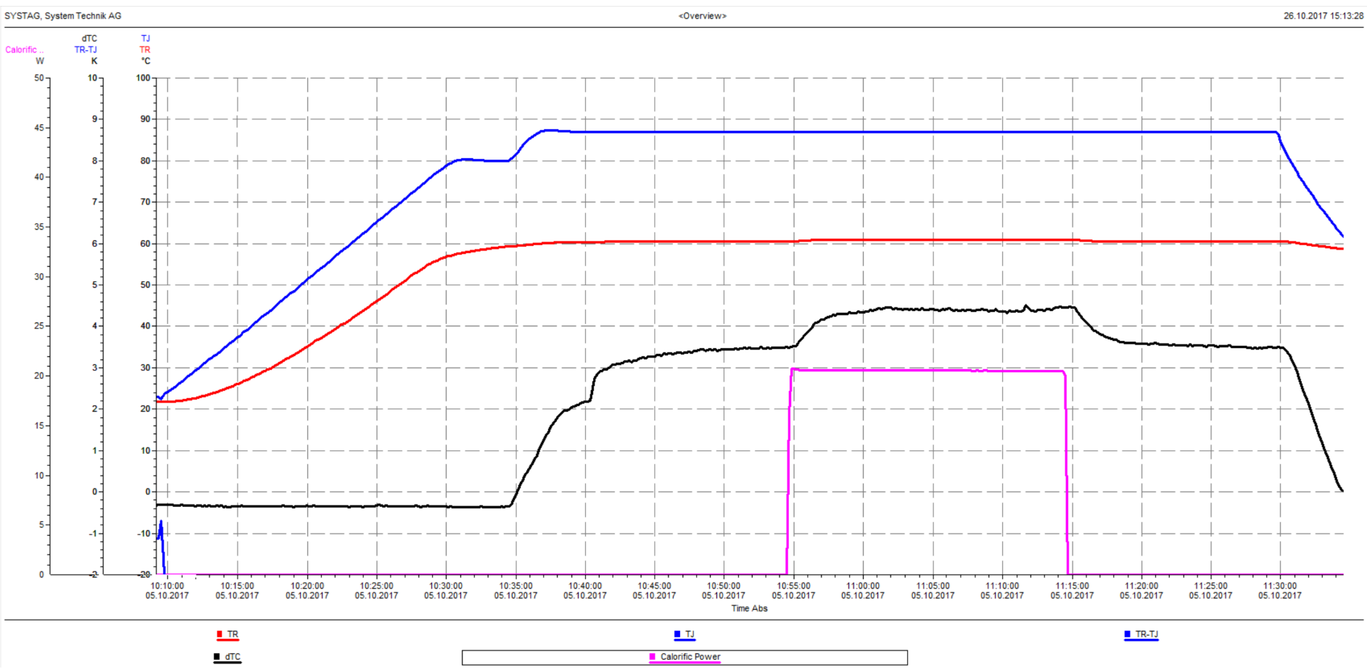

Chart 6: Reaction control at the reflux with calibration heating for validation

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