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Reaction calorimetry:
Fluitec Flow Calorimeter (FFC)

The Fluitec Flow Calorimeter (FFC) is especially suitable to obtain thermodynamic information for a scale-up of continuous processes in tubular reactors. This is useful because the released heat can strongly depend on the reaction control, especially for non-selective reactions. With the Fluitec Flow Calorimeter an axial temperature profile along the tube reactor can be recorded and the specific heat of reaction can be determined by means of heat balances and segmental dynamic parameters. The system consists of a tubular reactor, dosing systems, preheaters, temperature sensors and flow meters. Already existing ContiplantLAB PFR tube reactors can be converted easily into continuous reaction calorimeters.

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Thermodynamic properties, such as the specific heat of reaction (Q_r) are required for the design of a chemical process and are a prerequisite for high product qualities and a high safety of the plant. In P. Filipponi / B. Guélat *et al*. [1] it was shown that the Q_r determined in batch-like heat flow calorimeters (HFC) can differ greatly from the actual Q_r in the tubular reactor. For this reason, it makes sense to determine the specific heat of reaction directly in the selected reaction system, on a smaller and controlled scale.

Fluitec Flow Calorimeter
With the Milli-Conti Reaction Calorimeter from Fluitec, the chemical reaction will be investigated directly in a scalable plug flow tubular reactor (PFR) (Fig. 1). The calorimeter consists of an insulated tubular reactor with a heated double jacket and static mixers. With the axial temperature sensor inside the reactor a temperature profile along the reactor can be recorded. Two feed streams are delivered by a pulsation-free pump in a flow-controlled manner. Both feeds flow first through a preheater before entering the PFR. Further, on the heat transfer medium (HTM) side there are additional temperature sensors. One is placed at the reactor inlet and the other one at the reactor outlet. Moreover, the HTM flow rate is recorded by a Coriolis flow meter.
By means of a heat balance together with the obtained temperature profile, the heat transfer can be determined. Subsequently, the locally generated heat of reaction can be deduced using

Fig. 1: Fluitec Flow Calorimeter (first generation)

segmental dynamic parameters. The temperature profile is not only used to calculate the heat of reaction, but can also be used directly for a scale-up design in the mixer heat exchanger.

Effect of the reaction control on Q_r
In traditional heat flow calorimeters, one reactant is added continuously in small amounts, similar to a semi-batch process, in order to obtain a complete conversion of the reaction. In contrast to the tubular reactor, this leads to longer residence times, different substance concentrations and flatter temperature profiles. Thus, the selectivity of not well-defined reactions can be affected. This can lead to the formation of by-products or consecutive products which alter the measured heat of reaction, since other bonds are formed. The amount of by-product or secondary product can be found by calculating the yield of the desired product.

Difference in Q_r from HFC and PFR

If the heat of reaction measured in the HFC and PFR calorimeter differ, most probably some side reactions have occurred. They could for example be caused by different temperatures and residence times. The totally measured Q_r is composed of partially overlapped reaction enthalpies (ΔH_r) of main and side reactions, depending on their degrees of conversion (U). In the following example, the influence of an exothermic consecutive reaction on the total measured heat of reaction will be shown (Scheme 1).

$$A \longrightarrow B \longrightarrow C \qquad (1)$$
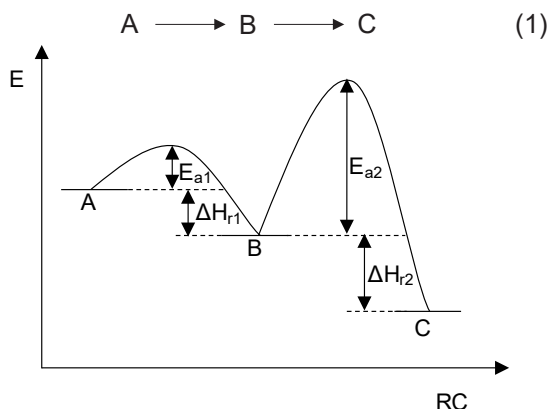
Scheme 1: Energy diagram. The consecutive reaction increases the reaction heat.

At a sufficiently high temperature at which the activation energy E_{a2} can be overcome, the subsequent reaction from B to C is initiated and a higher reaction heat (Q) is measured than for the selective conversion from A to B.

$$Q = n_{A,0}\, \Delta H_{r1} U_A + n_{A,0} U_A\, \Delta H_{r2} U_B \qquad (2)$$

The specific heat of reaction (Q_r) is obtained by dividing the heat of reaction by the mass of reaction mixture during one residence time (m_{RM}).

$$Q_r = \frac{Q}{m_{RM}} \qquad (3)$$

Fig. 2 shows $Q_{r(PFR)}$ as a function of $Q_{r(HFC)}$. The points (=reactions) are on the diagonal when $Q_{r(PFR)} = Q_{r(HFC)}$ and the reactions are selective.
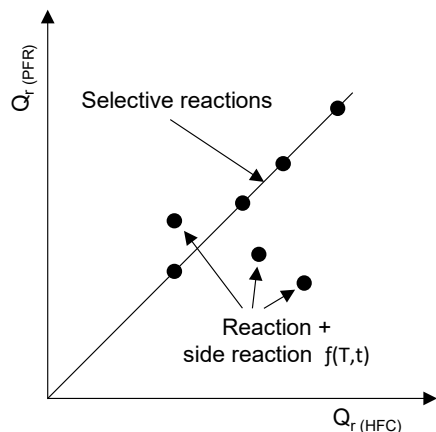

Fig. 2: $Q_{r(PFR)}$ with respect to $Q_{r(HFC)}$. Selective reactions are located on the diagonal.

If $Q_{r(PFR)} > Q_{r(HFC)}$ or $Q_{r(PFR)} < Q_{r(HFC)}$, the investigated reaction is most probably a non-selective reaction in which the residence time behaviour or temperature profile influences the by-product formation. In this case, a chemical analysis, preferably with online analytics, of the product stream provides information about the actually formed products.

Conclusion: The development of continuous processes should also be done in a continuous calorimeter.

Contiplant as Reaction Calorimeter

The ContiplantLAB PFR Ø 12.3 is not only suitable for conventional process development, in which temperature, residence time and substance concentrations are optimized, but this reactor can also be converted into a Milli-Conti Reaction Calorimeter (Fig. 3). Experiments with the scalable 12.3 Contiplant, can lead to an even more precise scale-up design, which will lead to the following advantages in a production scale plant:

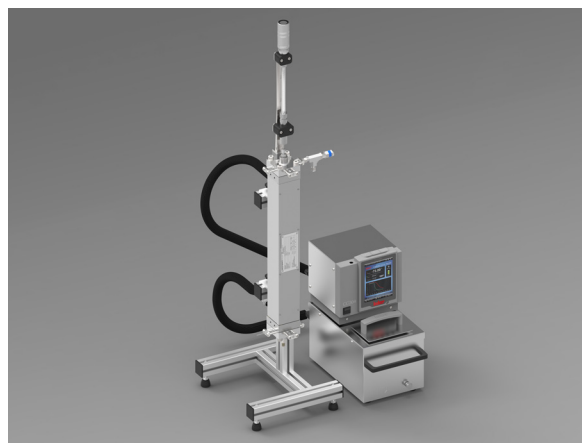- high product qualities
- high plant safety

Fig. 3: ContiplantLAB PFR.

List of symbols

ΔH_r	Enthalpy of reaction [J mol^{-1}]
E_a	Activation energy [J mol^{-1}]
m_{RM}	Mass of reaction mixture per residence time [kg]
$n_{A,0}$	Amount of substance A per residence time [mol]
Q	Heat of reaction [J]
Q_r	Specific heat of reaction [J kg^{-1}]
t	Residence time or batch-time [s]
T	Temperature [K]
U	Conversion [-]

List of abbreviations

E	Energy (free enthalpy)
HFC	Heat flow calorimeter
HTM	Heat transfer medium
PFR	Plug flow tubular reactor
RC	Reaction coordinate

Literature

[1] Mortzfeld, F., Polenk, J., Guélat, B., Venturoni, F., Schenkel, B., Filipponi, P., *Org. Process Res. Dev.* **2020**, DOI: 10.1021/acs.oprd.0c00117.