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REACTION CALORIMETER - A USEFUL TOOL IN CHEMICAL ENGINEERING

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SUMMARY

For elaboration of chemical processes and construction of production plant a good number of process data is required. For this the reaction calorimetry is a sophisticated and practically orientated method. The user can investigate the reaction under realistic conditions in a small laboratory reactor. Today there are four types of instruments available on the market, which are more or less equal in terms of handling but totally different in the measuring principle. In the following report the main differences between all calorimeters will be presented. Furthermore, the special features of one measuring principle using heat flow sensors are demonstrated on a short example in the field of polymerization.

INTRODUCTION

In chemical industry the batch technique is a wide-spread working method. At the very beginning all components of reaction will be placed in the reactor and then brought to the temperature desired. In case of exothermal reaction this is done by using a part of the heat of reaction. After having achieved the temperature wanted the cooling will be activated (ref. 1). Especially for the adiabatic phase data as the specific heat and the reaction enthalpy have to be known. Furthermore, the knowledge of the main reaction with its characteristic values is needed. For an exothermal reaction the heat production rate is of big importance. This value determines mainly the maximum of cooling capacity of a reactor. For safety reasons the cooling capacity of the reactor has to be greater than the maximum of the heat production rate at any time (ref. 2). Additional data of the main reaction such as the rate constant and the activation energy should be determined before the process is transferred to a bigger scale. This can be done with systematic evaluation of the heat production rate curves (ref. 3). In case of polymerization often occurs a polymer coating on the inside reactor wall. Besides, based on the chemical conversion the

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viscosity can drastically increase. Both effects cause a lower overall heat exchange to the cooling medium. This can be critical when the cooling device of the reactor is not able to keep the reactor temperature, because it was planned with wrong data of the heat transfer (ref. 4). To determine the proper stirring motor a reliable value for the stirring power is needed.

This short description of some problems shows the importance of an early use of practically orientated methods in process development and process optimizing. By this the exact determination of the heat production rate should be in the forefront. The reaction calorimeter as a sort of mini-pilot plant allows such investigations under realistic conditions. The influence of process parameter as pressure, pH and temperature can be determined.

MEASURING PRINCIPLE OF THE DIFFERENT CALORIMETERS

Four types of reaction calorimeter are known, which use different measuring principles. In three instruments the heat production rate is determined by measuring temperature differences. The fourth unit takes into account in addition the electrical power of a compensation heater.

The determination of the heat production rate Q_r is done by the method of the heat balance (ref. 6). By this method all terms of heat flow into and out off the calorimetric system will be compared in a certain balance region. Terms of dosing, accumulation and reflux conditions can be defined only in one way. Great differences appear by defining the term of cooling resp. heating Q_k. The reasons are the use of different balance regions and various constructions of reactors.

In addition in isothermal and isoperibolic mode Q_k plays the most important rule. Therefore, in the following part only the determination of the overall heat exchange Q_k and problems of the measuring principles will be discussed.

The schematic principle of the first calorimeter (Mettler AG, RC1) is shown in Fig. 1a. An essential part is the jacket thermostated reactor of glass or metal. The balance region is equal to the inside reactor wall. The heat exchange between the content with the temperature T_r and the thermostating medium with the temperature T_k follows

$$Q_k = k_w * F * (T_r - T_k) \qquad (1)$$

$k_w * F$ is the overall heat transfer. The thermostating liquid is pumped through the jacket of the reactor so fast that for determination of Q_k the temperature at the reactor inlet can be used (ref. 5).

With constant area F of heat exchange and solutions of low viscosity $k_w * F$ will be constant and has to be determined before or after the reaction by an electrical calibration heater according to

$$k_w * F = Q_e / (T_r - T_k) \qquad (2)$$

Q_e is the electrical power of the heater. This principle is disadvantageous when using temperature sensitive components or having high changes of viscosity. The last point is often fulfilled when working with high concentrated solutions.

In addition it is difficult to determine the area F using a steel reactor. Heat losses caused by evaporation can be taken into account just overall.

The second calorimeter (Contraves AG, Contalab) considers this physical effect extensively. On one hand with an isolation jacket and mirrored lid it was tried to minimize the heat losses, see Fig. 1b. On the other hand the balance region was extended to the in- and outlet of the reactor (ref. 6). By this, the heat exchange between the reactor content and the thermostating liquid can be determined as

$$Q_k = m * c_p * (T_a - T_e) \qquad (3)$$

c_p is the specific heat of the thermostating liquid. But one has to make sure, that the mass stream m of thermostating liquid is kept constant and not to high. Otherwise, the temperatures at the inlet T_e and the outlet T_a could not be measured sufficiently.

In practice a low flow stream is used. This worsens the dynamic and the maximum of cooling capacity of the calorimeter. High exothermal reactions could not be handled in isothermal mode sufficiently. Through the combination of equation (1) and (3) the continuous course of $k_w * F$ could be obtained off-line. T_k is then calculated as the average of T_e and T_a.

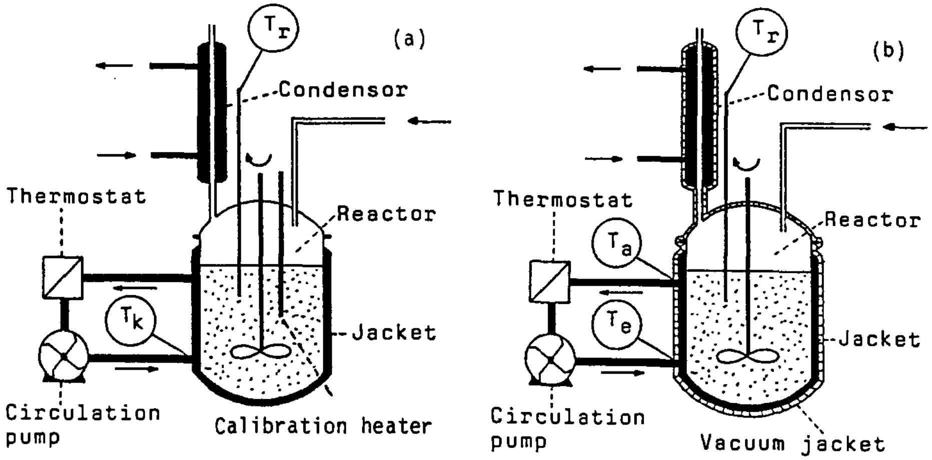


Fig. 1. Schematic principle of Mettler calorimeter (a) and Contraves calorimeter (b)

The third calorimeter (Fa. ThermoMetric AB, CPA) is totally different to the units described above. The reactor is equipped with an insulating, double-walled glass jacket to minimize the heat flow through the glass walls. The cylindrical glass vessel is capped at top and bottom with a strong chemical inert metal plate.

During the operation, the reactor is located in a fixed position in a stainless steel thermostating bath which acts as a safety shield and reference, see Fig. 2a. The temperature of this reference unit is kept always close to that of the reactor. This avoids internal reflux.

A Peltier element mounted inside the base of the reactor, serves an efficient heating and cooling device. All the power exchange between the reactor content and the reference bath occurs through the bottom flange. It is measured by a heat flow sensor that is placed between the bottom and the Peltier element (ref. 7).

The sensor is a round disk with the same area F as the bottom of the reactor. On each side are mounted hundreds of thermocouples in serial connection, which measure the average temperature T_o at the top side and T_u at the lower side of that disk.

With the well known value of the thickness D of the layer between and the heat conductivity S of the sensor material the heat exchange through the bottom is calculated on-line to

$$Q_k = S * F / D * (T_o - T_u) \qquad (4)$$

Furthermore, the reactor temperature T_r is measured. The definition of T_o is equal to T_k in the first calorimeter. That allows an on-line detection of the heat transfer $k_w * F$ using the combination of equation (1) with (4).

The area F of heat exchange is independent from the sample volume. Therefore, the heat transfer coefficient k_w can be calculated very simply. Another advantage of this principle is the very low noise level and the high sensitivity resultating from that. The reason for that is the temperature measurement over the total area of heat exchange.

The fourth calorimeter (Columbia Scientific Industries Corp.) is not very popular in Europe. The construction and working modes are in principle similar to the CPA. A metal reaction vessel is placed in a thermostating container. The container temperature is controlled by using gas instead of liquid. The heat exchange takes place only through the base of the vessel to a thermostating liquid.

Unlike the CPA in the bottom flange is no Peltier element but a compensation heater (ref. 7). This heating element compensates at all time the thermal power required to keep the content at the temperature desired while the cooling power is constant, i.e. in case of exothermal reaction the electrical power of the heating element is automatically reduced in the same way as the heat production rate Q_r increases.

The compensating electrical power Q_e is continuously registered by high precision voltage and current measurements. Q_r can be simply determined according to

$$Q_r = Q_k - Q_e \qquad (5)$$

Q_k could be calculated as described with equation (1). In practice, small variations in the heat transfer coefficient k_w, due to variations in viscosity, can be compensated by electrical calibration before and after the reaction similar to equation (2). But in case of drastic changes as described above this principle gives unsufficient results.

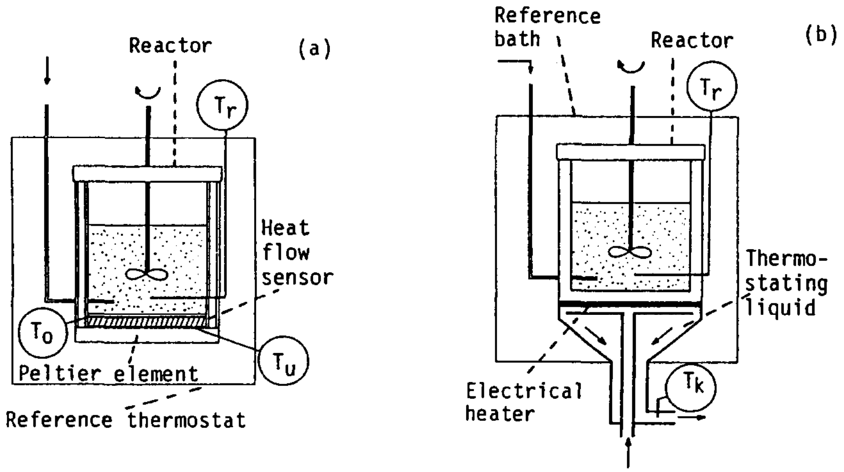
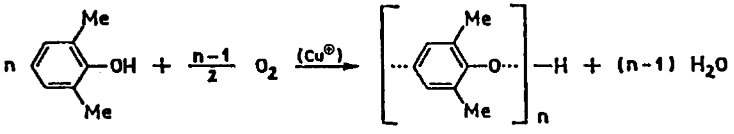


Fig. 2. Schematic principle of ThermoMetric calorimeter (a) and Columbia Scientific Industries calorimeter (b)

EXPERIMENT

Reaction

The chemical conversion described below is the heterogeneous polymerization reaction of 2.6-dimethylphenol to poly-2.6-dimethyl-1.4-phenylen ether. The main reaction is with 200 kJ/mol monomer strongly exothermic (ref. 9-10). In a side reaction phenol can be dimerised to 3.3',5.5'-tetra-methyl-4.4'diphenoquinone. In the present case this was largely suppressed by using a selective catalyst (ref. 11).



The polymerization was chosen since a large number of chemical reactions, especially those of technical importance, is running in heterogeneous phases. These reactions are often complex.

The reactive agents are present in different phases and the chemical reaction generally takes place at the phase borders or nearby. Thus, for heterogeneous reaction, the process of substance transport or the type and size of the phase borders have an additional influence on reaction rate.

The actual chemical reaction is accompanied by changes in solution viscosity and heat transfer. For the present investigation the isothermal mode was chosen in order to exclude the influence of temperature upon the reaction rate.

Experimental equipment

A schematic illustration of the experimental setup is given in Fig. 3. The air needed for the reaction was taken from a pressurized air bottle via a reducing valve and a precission needle valve. By use of the needle valve the air flow through the reactor was adjusted to a suitable value.

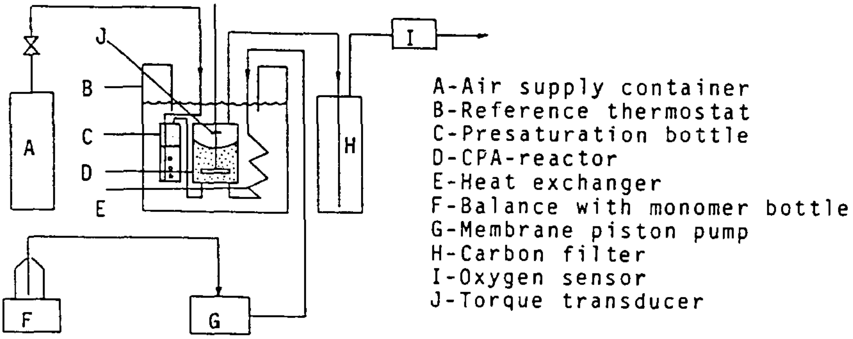


Fig. 3. Schematic arrangement of experiment

In order to minimize the thermal effect of the evaporated solvent a presaturation bottle was used. It was filled with the solvent and placed within the reference thermostat. The gas inlet to the CPA-reactor was in the bottom. So the gas stream could be fed in right below the stirrer.

To optimize the mixing a turbine stirrer was used. The gas from outlet of the reactor was passed through an active carbon filter to remove the evaporated solvent before the gas entered the oxygen sensor. The oxygen sensor was a standard Clark electrode. The monomer was pumped from the storage bottle placed on a balance into the reactor by a membrane piston pump. For controlled addition of the monomer a dosing controller was used.

The monomer flow was prethermostated in a heat exchanger before entering the reactor via the bottom. The reactor was equipped with a torque transducer to measure the stirring power during the experiment.

Experimental procedure

The reactor was filled with 104.5 g of solvent already contenting a small amount of Cu-II-catalyst. Then the reactor was placed in the reference thermostat together with the presaturation bottle and the heat exchanger. The stirring speed was set to 1000 rpm and the temperature to 30 °C.

The air flow was adjusted to a value of 146 ml/min to guarantee an excess of oxygen. The oxygen sensor was calibrated with the outlet air from the reactor and with pure nitrogen. When the reactor with the installed air flow was in thermal equilibrium the monomer was pumped from the balance with a flow of 20 g in 30 min.

Now the change in heat exchange Q_k, heat transfer $k_w * F$, stirring power and oxygen consumption V could be observed. In addition the integrated Q_k-signal resp. the total heat of reaction was continuously on-line calculated. When the reaction had declined the experiment was stopped by changing gas supply to nitrogen and a manual addition of 30 g stopping reagent.

Results and discussion

The oxygen consumption V vs. time is given in Fig. 4a. Due to the tank effect in the reactor and the back mixing effect in the carbon filter the measured oxygen concentration by the sensor is not representative for the oxygen concentration within the reactor. A back calculation was done by assuming a first order of delay.

As later shown in Fig. 5a. the temperature was nearly constant. The monomer flow was exactly prethermostated to reaction temperature. Therefore in the heat balance the terms of dosing and accumulation are negligible small. On this basis follows, that the heat production rate Q_r is equal to the on-line measured heat exchange Q_k.

The heat production rate Q_r, the integrated Q_k-signal and the oxygen consumption V are given in Fig. 4b. As one can see the heat production rate and oxygen uptake drops off when the dosage is finished. The reason is the phase separation. The area of phase border between the gas and the monomer solution changed while the water released builds up a second phase.

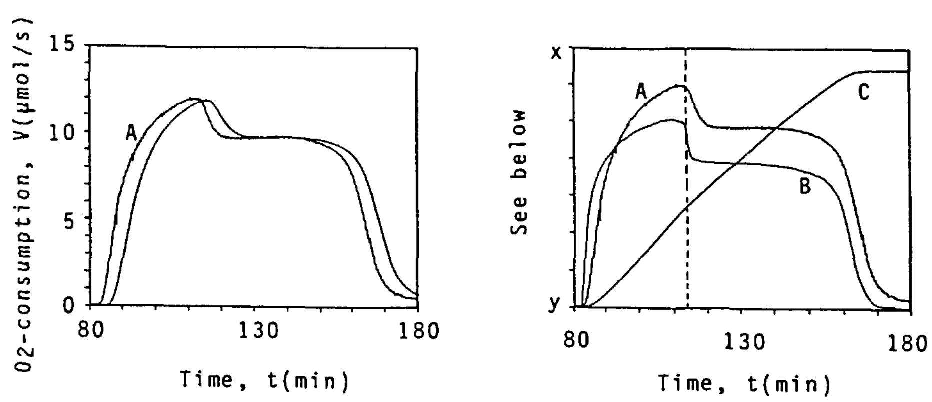
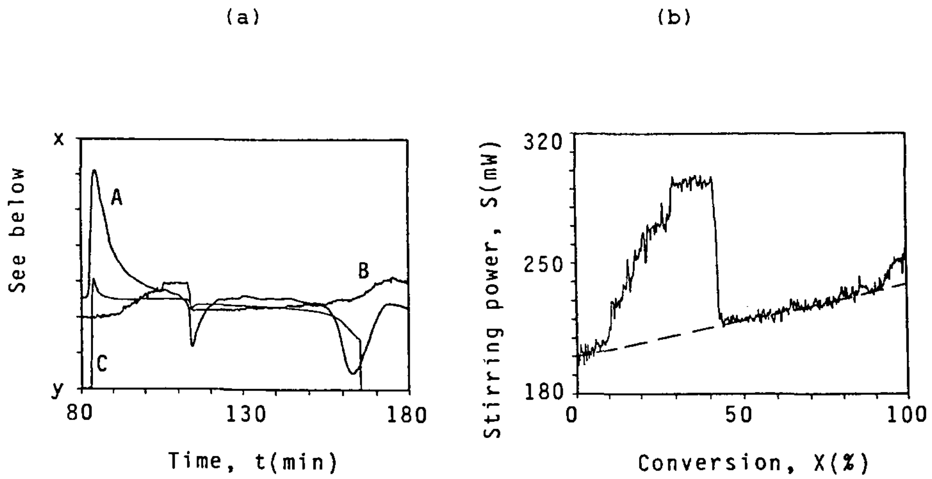


Fig. 4. Diagram (a) is showing the oxygen consumption V vs. time. Curve A is corrected using a differential equation first order. Diagram (b) is presenting the oxygen consumption V vs. time, curve A with x=14 μmol/s, the heat production rate Q_r vs.time, curve B with x=7 W and the integreted Q_k-signal vs. time, curve C with x=21 kJ, y=0. End of dosing at the dotted line.

A similar effect is obtained when the stirring speed is decreased. These results show that under the present condition the rate of polymerization is controlled only by the substance transport.

The stirring power and heat transfer $k_w * F$ are shown in Fig. 5a. Both curves correspond very well except during the addition of monomer where the heat transfer remains constant but the stirring power increases. This can be explained by a built up of a dispersed liquid.

Ignoring this peak the curve is well in accordance with Einstein's formula of appearent viscosity, as shown in Fig. 5b.


(a)

(b)

Fig. 5. Diagram (a) is showing the reaction temperature vs. time, curve A with x=30.18 °C and y=29.90 °C, the stirring power vs. time, curve B with x=700 mW, the heat transfer $k_w * F$ vs. time, curve C with x=7 W/K and y=0. Diagram (b) is presenting the stirring power vs. conversion. The dotted line is illustrating the Einstein correlation.

The on-line calculation of the heat transfer requires a certain level of thermal power. This is the reason for the stepwise change at the beginning and the end of the experiment. Heating the reactor constantly with an additional amount of thermal power by a separate heating coil could avoid the effect shown.

After the experiment the liquid loss in the reactor was determined to 1.2 g. This shows a small negligible loss of solvent during the experiment.

The total heat of reaction was determined to 19 kJ. The monomer solution was 55 Weight %. That gives a reaction enthalpy of 210 kJ/mol. The integral of the oxygen consumption gives 46 mmol. Both values have an error of +/- 5 %.

CONCLUSION

As illustrated in this paper, the reaction calorimetric technique is unique in providing information concerning the thermodynamic and kinetic of reactions under realistic conditions. This technique allows the chemical engineer to simulate a process in a bench scale instrument without renouncing the main standard unit operation. These informations are useful in many areas, such as process safety studies, process development and process optimizing. The sophisticated calorimetric system which was used for the polymerization example offers the big advantage of continuously on-line monitoring of many data. Therefore, the evaluation is easy and saves a lot of expensive operation time. As demonstrated in the experimental part, just one run leads to a vast amount of detailed information.

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