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An experimental approach to the characterisation of unstable chemical systems

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Abstract

Subject to certain external conditions, exothermically reacting chemical systems may show unstable temperature-time behaviour. Therefore, the analysis of such systems is necessary for loss prevention as well as for reconstruction of accidents caused by such instabilities, e.g. fires or explosions. It is shown that a modern DSC instrument has sufficient sensitivity for direct measurement of the heat production in lower temperature ranges. In contrast to formerly-used extrapolations from higher to lower temperature ranges, application of thermal explosion theories is now greatly simplified and leads to more reliable hazard assessment.

1. Introduction

Chemical systems, which can undergo strongly exothermic reactions, are potentially unstable. Such instability is based upon an energy feed-back mechanism: insufficient removal of reaction energy causes a temperature rise within the reacting mass which, in turn, causes an increase in heat production due to the temperature dependence of the reaction rate. This leads to an increased rate in temperature rise and so on until the system reaches a dangerous temperature with subsequent explosion or fire.

For reconstruction as well as prevention of such events an analysis of potentially unstable chemical systems is necessary. This analysis is often done by using the theory of thermal explosions, which is based on the competition between heat generation by chemical reaction and heat loss by energy transport (ref.1). Frequently the energy transport is dominated by convection and conduction, for which approximate (semi-)empirical relations are provided by the literature (ref.2,3,4).

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However, heat production by chemical reaction has to be measured and cannot be calculated in a similar manner.

Unfortunately, the range of small heat production rates (i.e. the lower temperature range) is most important. For forensic science purposes measurements with microcalorimeters are obviously more desirable than with macrocalorimeters. However, in the past we had some difficulties with such measurements in the lower temperature region because of insufficient sensitivity of our microcalorimeter. In the meantime a new generation of instruments with improved sensitivity has become available. One of the aims of this paper is to demonstrate the applicability of such an instrument for our problems. The other is to show that by direct measurement of the heat production as a function of temperature, a lot of inherent uncertainties of more complex thermal explosion theories can be avoided.

2. Theory of thermal explosions

The current theories cannot be outlined here in detail. Only some basic principals may be listed in the following.

From the first law of thermodynamics we have:

$$C_V \cdot \dot{T} = \dot{Q} - \Delta U \cdot r \cdot V \qquad (V = \text{const.}) \qquad (1a)$$

or

$$C_p \cdot \dot{T} = \dot{Q} - \Delta H \cdot r \cdot V \qquad (p = \text{const.}) \qquad (1b)$$

Here C_V, C_p: heat capacity at constant volume viz. pressure (J/K)

$\dot{T}$: rate of temperature change (K/s)

$\dot{Q}$: rate of heat exchange (W)

ΔU: reaction energy (J/kg)

ΔH: reaction enthalpy (J/kg)

r: rate of chemical reaction (kg/s·m^3)

V: volume (m^3)

From this it is clear that $\dot{T}$ and T are determined by the heat exchange ($\dot{Q}$) and heat production ($-\Delta U \cdot r$ viz. $-\Delta H \cdot r$) terms. An explicit solution of eqn.(1) would give us the complete temperature - time history of the system.

In practice, however, it is often sufficient to simplify the problem. Instead of solving the equation completely, we only look for conditions, for which

$\dot{T} > 0$ (unstable case) (2a)

or

$\dot{T} \leq 0$ (stable case) (2b)

As we are dealing only with cooling ($\dot{Q} < 0$) and with strongly exothermic reactions ($\Delta U < 0$ and $\Delta H < 0$), we set

$$\dot{q}_{loss} = |\dot{Q}/V| \qquad \dot{q}_{chem} = |\Delta U \cdot r| \text{ or } = |\Delta H \cdot r| .$$

From eqns.(1) and (2a) we now get eqn.(3) as a general condition for unstable behaviour:

$$\dot{q}_{loss} < \dot{q}_{chem} \tag{3}$$

The cooling term may be approximated by a linear function of temperature:

$$\dot{q}_{loss} = h \cdot F/V \cdot (T - T_o) \tag{4}$$

with h: effective heat transfer coefficient ($W/K \cdot m^2$)

F: effective heat exchange area (m^2)

T_o: temperature of the cooling medium (K)

The heat production term often shows an Arrhenius-type temperature dependence. In the zero-reaction-order approximation we have

$$\dot{q}_{chem} = A \cdot \exp(-B/T) \tag{5}$$

with A: constant (W/m^3)

B: characteristic temperature of chemical reaction (K)

Fig.1 shows a graphic representation of both terms as functions of temperature. Curves 2 and 3 are heat losses at different values of h · F/V and hence show different slopes. Curve 3 does not intersect the heat generation function at all. So the system is completely unstable, as eqn.(3) is fulfilled for every temperature. A more effective heat removal is represented by curve 2, which intersects the heat generation function at the "critical" temperature T_k. At operating temperatures

$T \leq T_k$,

for example at a temperature T_1 in fig.1, all heat produced by chemical reaction is removed by cooling. Unstable behaviour according to eqn.(2a) cannot occur unless the temperature of the reacting mass exceeds T_k, e.g. at T_2.

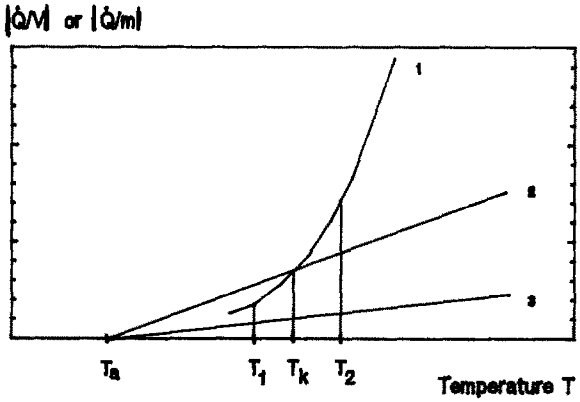

Figure 1. Stability diagram. Curve 1: heat generation, curves 2 and 3: heat loss

3. Example for an application

3.1 The problem

Cellulose filter slabs (2m x 1m x 3mm) are normally produced from a material, which has chemical properties as shown in fig. 2. When investigated by differential scanning calorimetry only one exothermic peak in the temperature range 300 - 380°C is detected.

During some test runs the manufacturer wanted to investigate how much of the cellulose could be substituted by polyethylene. However, desiccation of the new material turned out to be more difficult. So the drying temperature at the end of the production process had to be increased up to 150 - 160°C. As this was known as uncritical for the pure cellulose, the temperature was increased without hesitation. As usual, the

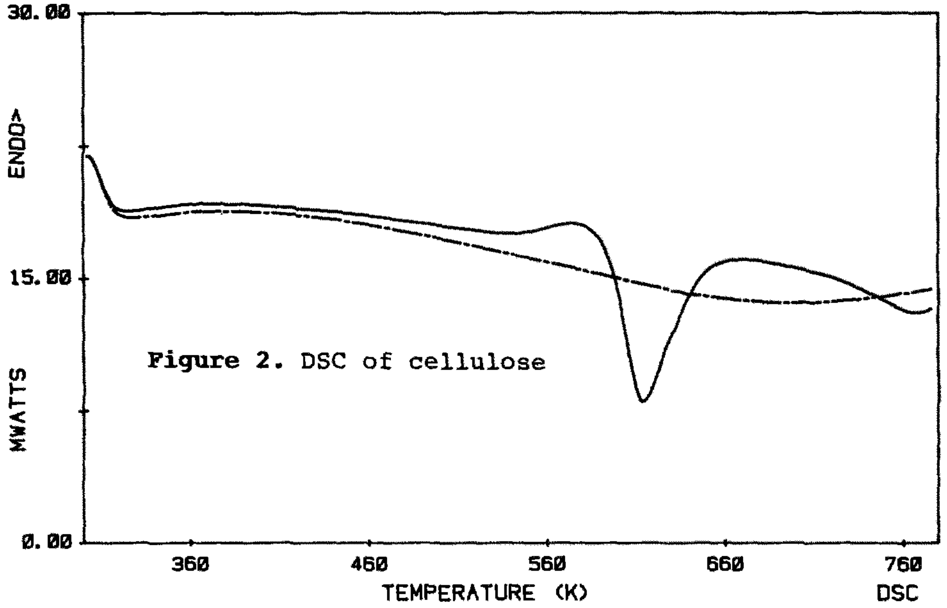

Figure 2. DSC of cellulose

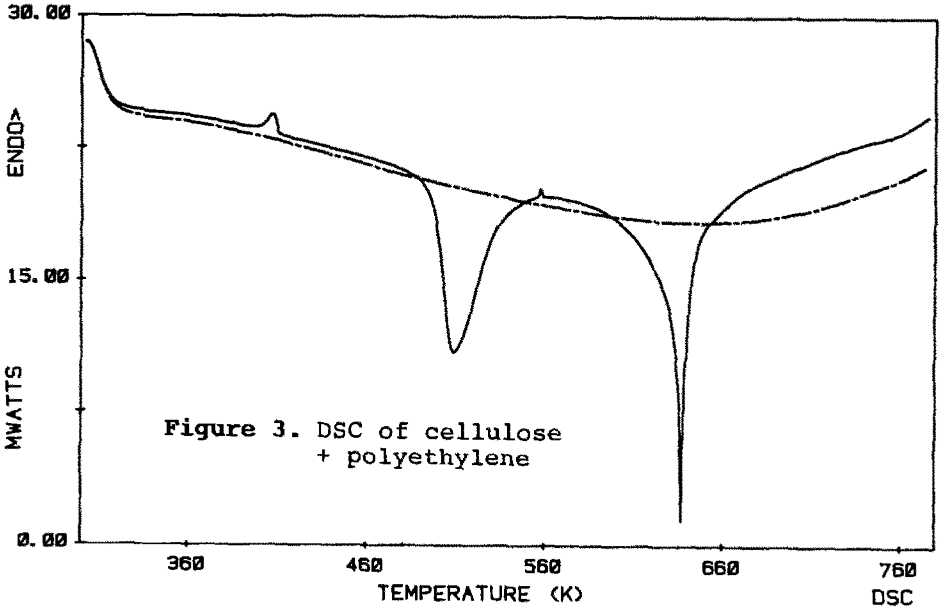

Figure 3. DSC of cellulose + polyethylene

test slabs were piled up to a height of more than one meter in a depot. Overnight, the building suffered severe damage by a fire, which obviously broke out in the pile of the freshly produced test charge.

Differential scanning calorimetry measurements of the polyethylene modified cellulose showed a second strongly exothermic peak at remarkable lower temperatures of about 200°C (fig.3). So the question arose, whether that new reaction could be responsible for the fire.

3.2 Estimation of $q_{chem}(T)$

Measurements like that of fig. 3 had been made by a Perkin Elmer DSC 2C. As that instrument was not sensitive enough, the above question could not be decided, since heat production near the temperature of 160°C could not be estimated quantitatively. Reinvestigation of the interesting temperature range (140 - 200°C) by a Perkin Elmer DSC 7 gave thermograms like fig. 4. From this, quantitative estimations of the heat production rate down to 150°C were possible.

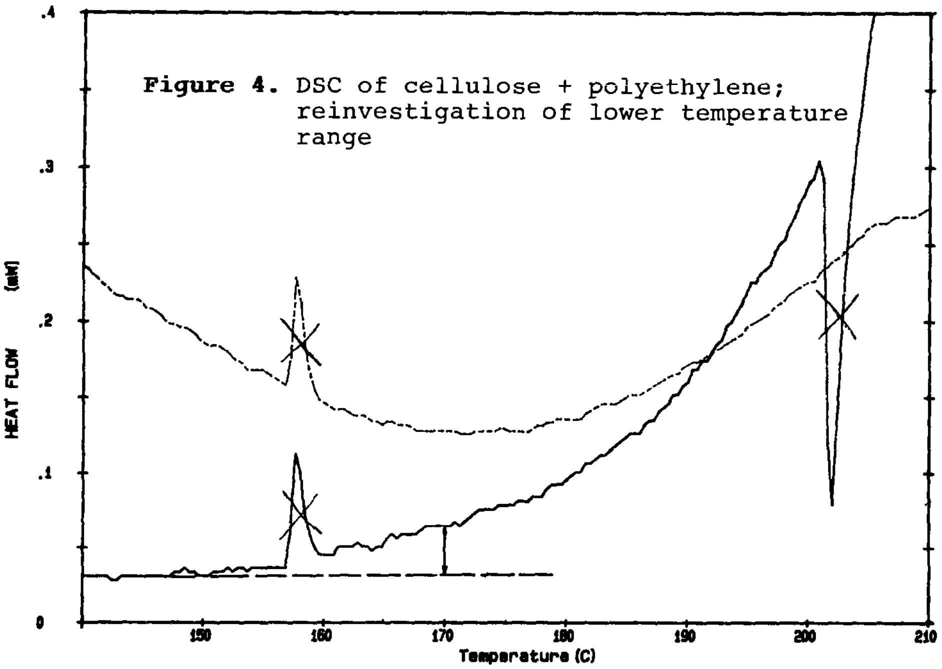

Figure 4. DSC of cellulose + polyethylene; reinvestigation of lower temperature range

At the very beginning of the reaction the zero-reaction-order approximation (eqn. 5) must hold. So an Arrhenius plot of $\dot{q}_{chem}$ vs. 1/T should give a linear function, which may serve as a consistency check and for extrapolation to (slightly) lower temperatures (fig. 5).

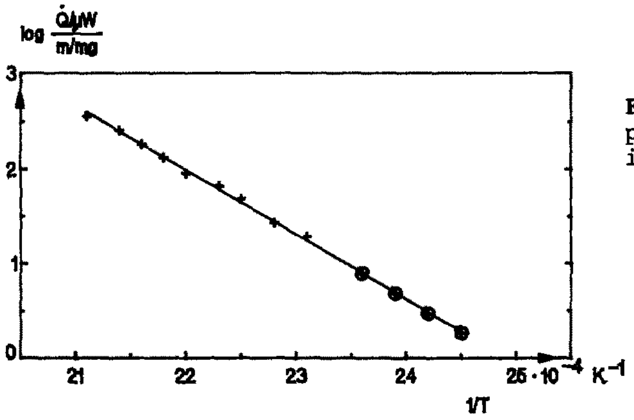

Figure 5. Arrhenius-plot of heat production from figure 4

The consistency of the data is obvious. So the normalized DSC - curve from fig. 4 and the extrapolation from fig. 5 may be used directly to construct the heat production function in an appropriate stability diagram (fig. 6).

3.3 Estimation of $\dot{q}_{loss}(T)$

For sake of simplicity the so called Semenow approximation (ref.1) only is considered here for the estimation of the heat loss function. The basic assumption is, that energy trans-port by heat conduction within the reacting mass is very efficient. So heat loss is dominated by surface heat transfer to the ambient air according to eqn.(4).

For our problem the heat transfer coefficient h depends on geometric, aerodynamic and other parameters. As we can assume free convection of air, the following relation is used to estimate h (ref.2):

$$Nu = \frac{h \cdot z}{\lambda} = 0.48 \cdot \left[\frac{g \cdot z^3 \cdot (T - T_a)}{\nu^2 \cdot T_a}\right]^{1/4} \qquad (6)$$

with z: height of the pile (m)

λ: heat conduction coefficient of ambient air (W/m·K)

g: acceleration of gravity (m/s²)

T: surface temperature of the pile (K)

T_a: temperature of the ambient air (K)

ν: kinematic viscosity of ambient air (m²/s)

Neglecting the weak temperature dependence of Nu in eqn.(6) one gets approximately linear functions $\dot{q}_{loss}(T)$ with the stock height z as parameter (fig. 6).

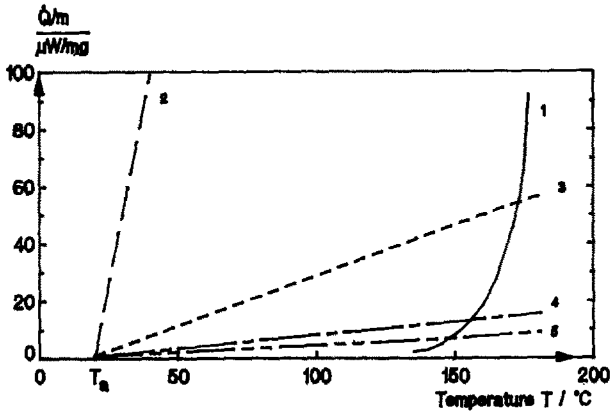

Figure 6. Stability diagram with varying stock height z;
curve 1: heat production
curve 2: z = 3mm,
curve 3: z = 6cm,
curve 4: z = 50cm,
curve 5: z = 1m

3.4 Discussion

Fig. 6 shows the variation of the critical temperature (the intercept between heat loss and heat generation functions) with varying parameter z. It is easy to see that a single filter slab (curve 2, z = 3mm) is a stable system at least up to 200°C as no critical temperature range exists. A stock of about 20 slabs (curve 3, z = 6cm) would have a critical temperature around 173°C, which is significantly higher than the maximum dryer temperature of 160°C. By increasing z to the actual value of one meter or more (curve 5), the critical temperature now decreases to values below 150°C.

So the desiccation at the end of the production process in connection with the subsequent piling of the slabs clearly brought the system into an unstable state, where internal heat production could no longer be balanced by heat loss to the surroundings. After having been started the strongly exothermic reaction obviously heated the system up to its ignition temperature with consecutive outbreak of the fire.

4. Concluding remarks

To conclude, the following should be emphasized:

a) Our heat loss problem discussed above is rather a quite general than a special one. Geometric dimensions and heat transfer conditions like ours have to be considered frequently when hazardous material is stored, and heat loss may often have a similar order of magnitude.

b) The main problem in constructing stability diagrams is not the estimation of the heat losses. In many cases a Semenow approximation and a semi-empirical engineering approach are sufficient for safety considerations.

c) On the other hand, heat production functions have to be measured as precisely as possible in the interesting temperature range to avoid erraneous extrapolations. Therefore instrumental sensitivities down to 5 or 10 μW/mg are needed. From the view of forensic science as well as under loss prevention aspects it is highly desirable to have microcalorimeters fulfilling that specification.

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