Journal of Thermal Analysis, Vol. 37 (1991) 1965-1971

THE USE OF HIGH PRESSURE DTA, HEAT FLOW AND ADIABATIC CALORIMETRY TO STUDY EXOTHERMIC REACTIONS

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Cellulose, a commonly found carbohydrate, exhibits exothermic decomposition, when heated above 180°C. These reactions have been detected and quantified by a range of thermal analysis and calorimetric techniques giving complementary information. The presented results are of interest for process safety.

Introduction

Different thermal analysis and calorimetric techniques have proved to be useful for studying exothermic reactions. The obtained thermodynamic information helps in particular to provide for greater safety in industrial operations.

This paper presents a comparison of three techniques, high pressure differential thermal analysis (DTA), heat flow differential scanning calorimetry and adiabatic calorimetry. The example outlined in detail is a calorimetric investigation on the decomposition of cellulose.

Experimental

The instruments we used to study the calorimetric decomposition of carbohydrates (in particular of cellulose) were the high pressure DTA apparatus Netzsch 404 H [1], the heat flow calorimeter C80 from Setaram [2] and the accelerating rate calorimeter or ARC from Columbia Scientific Industries [3].

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The DTA apparatus and the heat flow calorimeter were used in the scanning mode at relatively high heating rates, i.e. 2.5 deg/min for the DTA measurements and 1 deg/min for the calorimetric ones. The ARC instrument was used according to the standard heat-wait-search procedure. This method consists of increasing the temperature from a chosen level by steps (generally of 5°), waiting until thermal equilibrium is reached and searching for a temperature rise due to the heat released by exothermic reactions.

The product studied, cellulose, is a finely divided powder of commercial origin (Fluka AG, Buchs, Switzerland; No 22 197): it is a commonly found carbohydrate.

In the DTA apparatus the sample cells are open so that the product is in contact with the surrounding gas atmosphere. In this study, 25 bar of nitrogen were used to observe cellulose decomposition and the same pressure of oxygen to demonstrate that exothermic decomposition can lead to self-ignition. In both calorimeters sealed cells were used for these experiments.

Results

The DTA curves obtained show ΔT between sample and reference as a function of time or temperature; the heat flow calorimeter gives the differential heat flux (from thermopiles) as a function of time or temperature. With the ARC, the data recorded versus time during the exothermic phenomena are the measured adiabatic temperature (see Fig. 1), the calculated sample self-heating rate, the observed pressure and the calculated pressure rate.

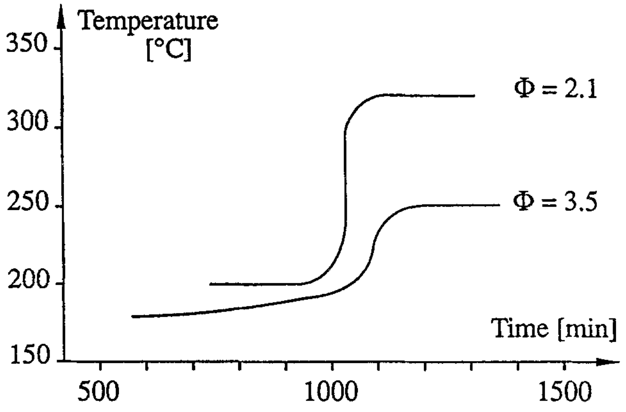

Fig. 1 Temperature *vs.* time recordings of cellulose decomposition. ARC system; PHI is the thermal inertia factor of the experiment

With cellulose, the main result is that these three techniques enable to detect the beginning of exothermic decomposition phenomena in the temperature range near 200° (see Fig. 2). When studied in open crucibles with conventional DTA instruments or differential scanning calorimeters (DSC) cellulose is often presented to be stable up to 300° or more [4, 5].

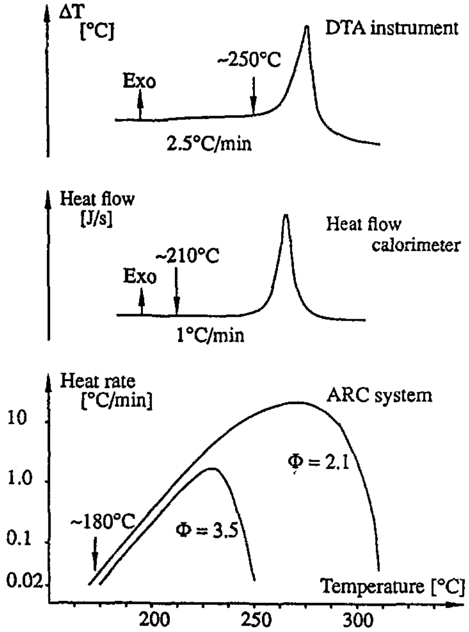

Fig. 2 Comparison of the thermal behavior of cellulose observed with three different thermal analysis techniques

High pressure DTA and heat flow calorimetry are useful techniques for screening of materials and for detecting the phenomena involved. For safety studies however the onset temperatures obtained with these techniques in the scanning mode should be treated with caution and used as a guide to determine if further testing is desirable. In such case, one can have recourse to adiabatic calorimetry, as the ARC was designed to simulate large scale industrial operations and to obtain safety data. In this technique a self-heating rate of 0.02 deg/min is often used as the threshold level for significant heat release and the corresponding temperature quoted as an onset temperature. In all cases, the concept of extrapolated onset should be avoided when studying exothermic reactions in relation to safety [6].

The calorimetric curves of cellulose decomposition presented in Fig. 2 illustrate these points, the determined onset temperatures corresponding to a significative ΔT, heat flow or heat rate on the recorded curves.

Enthalpies are not easily determined from the DTA curves obtained with the mentioned instrument. With the heat flow calorimeter, this parameter can however be calculated directly by integrating the area under the peak (corresponding to the exotherm), in the same way as for an endothermic phenomenon. The value obtained here for cellulose decomposition is approximately 650 $J \cdot g^{-1}$ [8]. With the ARC system, the reaction enthalpy can be determined by using following formula:

$$\Delta H = \Phi C_p \Delta T$$

where Φ is the thermal inertia factor, a correction factor to compensate for the heat lost into the bomb. For cellulose decomposition, the enthalpy determined this way is found to be between 500 $J \cdot g^{-1}$ and 650 $J \cdot g^{-1}$ depending on the Φ factor and on the adopted specific heat value.

Kinetic parameters such as activation energies can also be obtained from calorimetric curves [9,10].

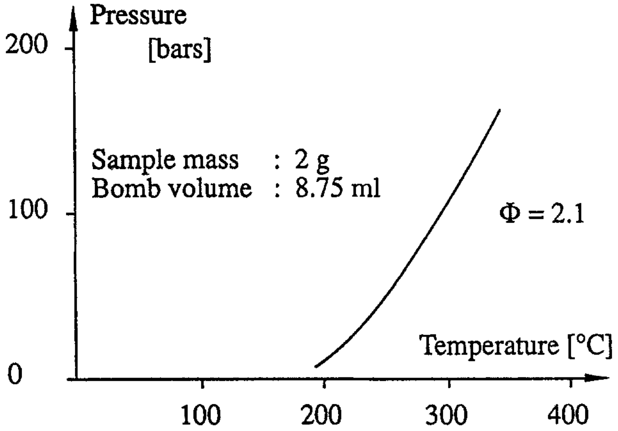

Fig. 3 Pressure *vs.* temperature plot corresponding to cellulose decomposition. ARC system

In addition to these thermodynamic data, relevant thermomanometric information is obtained with the heat flow and adiabatic calorimeters, if the pressure in the sealed cell is recorded by a sensor. Figure 3 presents the pressure curve obtained in the ARC experiments, with the cellulose heated in a sealed titanium bomb of 8.75 ml volume, as a function of temperature. The pressure rise observed is caused by the decomposition products formed above 180°.

The Φ factor (in accelerating rate calorimetry)

The thermal inertia factor or Φ factor is calculated with the following formula:

$$\Phi = 1 + \frac{M_b C_{pb} + M_{cl} C_{cl}}{M_s C_{ps}}$$

C_{ps} = sample specific heat M_s = sample mass

C_{pb} = bomb specific heat ($0.54\ \mathrm{J \cdot g^{-1} \cdot deg^{-1}}$) M_b = bomb mass (8.5 g)

C_{cl} = clip specific heat ($0.42\ \mathrm{J \cdot g^{-1} \cdot deg^{-1}}$) M_{cl} = clip mass (2 g)

The specific heat of the sample is an estimated average over the temperature range of reactions: thus if for cellulose at 20° $C_{ps} = 1.25\ \mathrm{J \cdot g^{-1} \cdot deg^{-1}}$, around 200° this value will lie between 1.9 and 2.3 $\mathrm{J \cdot g^{-1} \cdot deg^{-1}}$. From the experiments performed with the ARC a temperature rise of 135° was obtained when $\Phi = 2.1$ (sample mass: 2 g) and of 70° when $\Phi = 3.5$ (sample mass: 1 g); so the previously indicated range of ΔH values can be found.

In ARC tests, to get reliable thermodynamic data, it is preferable to impose the Φ value (by adapting the sample mass) such that the measured maximum of self-heating rate lies between 5 and 20 deg/min. Thus for very reactive materials a high Φ factor and a low sample mass are favourable. In this way, the temperature of the calorimeter will 'follow' that of the sample without error, i.e. there will be no deviation from adiabaticity, no heat lost from the sample. For materials of low reactivities, a low Φ factor and a high sample mass are to be preferred. In this way, the loss of accuracy due to a weak thermal effect and a large correction factor will be avoided.

Self-ignition

Exothermic reactions can lead to self-ignition when sufficient oxygen is available. As previously reported [11, 13], DTA and particularly high pressure DTA are useful tools to study such phenomena and to determine self-ignition temperatures under specific well-defined conditions.

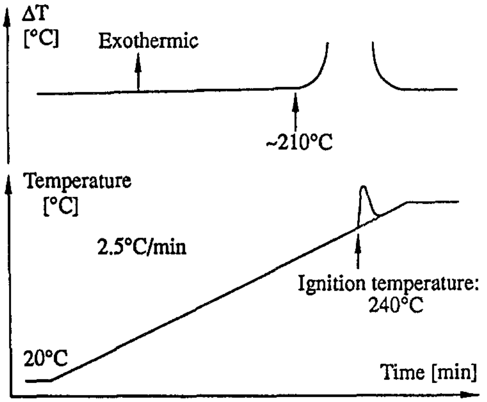

Fig. 4 DTA curves of cellulose heated and burnt under 25 bar of oxygen. High pressure DTA Netzsch instrument

Figure 4 presents the cellulose sample heated and burnt under 25 bar of oxygen. The self-ignition temperature (240°) of cellulose found under these severe conditions corresponds well with the lowest value found in the literature 254° [11]. The highest value given in literature is 400° [11], a value which should not be considered within a risk analysis.

Conclusion

High pressure DTA techniques give relevant qualitative information on exothermic reactions and on self-ignition.

Heat flow calorimetry provides the most precise quantitative thermal data, as the obtained enthalpies depend only on the calibration curve which is determined by the Joule effect.

Adiabatic calorimetry, specifically the ARC system, simulates the most severe thermal conditions: thus its thermal information is of great importance when safety parameters have to be found for storing or processing unstable materials in large scale industrial operations, especially when it is a question of larger quantities of bulk material [14].

In consequence, these three techniques must be considered as complementary, as illustrated here in this study of cellulose decomposition.

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The authors gratefully acknowledge many discussions with C. Foetisch (Linor, Orbe, CH), Prof. R. C. Reid (Lexington, Massachusetts, USA) and I. Horman (Nestlé Research Centre, Vers-chez-les-Blanc, CH).

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Zusammenfassung — Cellulose, ein weit verbreitetes Kohlenhydrat, zeigt beim Erwärmen auf Temperaturen oberhalb 180°C exotherme Zersetzung. Die damit verbundenen Reaktionen wurden mittels einer Reihe komplementärer thermoanalytischer und kalorimertrischer Methoden erfasst und quantifiziert. Die vorgestellten Resultate sind für die Abschätzung von Prozessrisiken bedeutungsvoll.