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UNIVERSAL SYSTEM FOR INVESTIGATION OF THERMIC HAZARDS

L. Hub
SANDOZ Ltd., CH 4002 (Switzerland)

ABSTRACT

Modern chemical manufacturing processes operating under demanding conditions, such as high concentrations and temperatures, require improved testing for thermic hazards. Especially needed are instruments with a broad spectrum of measuring abilities. The new computer-based Thermal Safety Calorimeter TSC 500 provides all common measurement modes of testing such as screening, dynamic tests, isoperibolic and adiabatic measurements and also offers special features, e.g. isothermal and overadiabatic calorimetry. Measurements with various sample sizes in open tubes, under pressure or under special gas atmospheres are possible. Features for stirring, addition of components, gas rate measurements etc. are available.

INTRODUCTION

In recent years there was an increasing tendency to develop and introduce intensive chemical processes. These are often operating near to the potentially dangerous state and demand therefore highly reliable safety testing. Since the hazardous behaviour of chemicals can be triggered by a large number of various influences, it is obvious, that the necessary information cannot be derived from one simple measurement. A major source of hazards of repetitive chemical manufacturing processes is associated with their large variability of working conditions. Even seemingly small deviations, e.g. traces of impurities, variable duration of physical operations or access of oxygen from the air can significantly change the thermic behaviour of a given material. Consequently, conscientious testing, employing even superior instruments, but using only one experimental setup or only one testing method, can reveal one part of the potential danger, but fail to recognize another (ref. 1). Examples are, autocatalytic reactions tested over too short a time, oxidative reactions examined under confinement or volatile mixtures investigated in an open container.

After the period of intensive development there are today out-

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standing instruments available for safety testing. However, it may be fatal to rely on only one specialized method, regardless of the high qualities it posseses. It appears, that a sufficient reliability of hazard investigation can be achieved only by enlighting the complex process from various angles, using possibly different complementary measurements.

THERMAL SAFETY CALORIMETER TSC 500

In the search for suitable instruments for this purpose, TSC 500 (ref. 2) has been tested in our laboratories. In our experience it fulfils the major requirements, especially with respect to the above-mentioned need for the versatility of the experimental conditions.

Equipment

In two easily interchangeable ovens, which are based on the previous instruments SIKAREX (ref. 3) and SEDEX (ref. 4) a number of various sample containers can be mounted. Thus measurements in open tubes of various sizes, in autoclaves, under specified gas atmospheres, with provisions for stirring (also under pressure) and for addition of substances during the investigation can be carried out. Containers are made of glass or stainless steel. The sample temperature is measured by a sensor, placed directly in the material being tested.

Software

The TSC 500 is controlled by a computer, enabling the following measurements to be made:

- Rapid search for the overall thermal behaviour: scanning experiments
- Investigation of long term properties (autocatalytic reactions) and precise determination of the onset of the exothermic reaction: isoperibolic measurements.
- Simulation of the failure of the cooling system: measurements under adiabatic conditions.
- Special measurements, e.g. isothermal and overadiabatic calorimetry (ref. 5).

The computer enables the experiments to be carried out in the absence of laboratory personnel and provides features for on-line and off-line inspection and evaluation of the gathered data.

On-line early warning feasibility

A special novel feature of the TSC 500 is the possibility to simulate the performance of the On-line Warning System OLIWA (ref. 2). OLIWA is a commercial available early warning system, designed for installation on chemical laboratory and manufacturing equipments. This instrument provides a real-time analysis of the state of the process, identifies an approaching hazard of thermic explosion and gives a warning signal in advance (ref. 6). OLIWA has a complementary function to the off-line tests and can considerably increase the degree of safety. The new feature of the TSC 500 enables it to inspect the warning ability for the given process in advance.

CASE

A reaction mixture was tested in an open container, using scanning experiment with a linear increase of temperature. The result (Fig. 1) shows an endothermic reaction between 120 and 180°C and indicates exothermic reaction above 180°C.

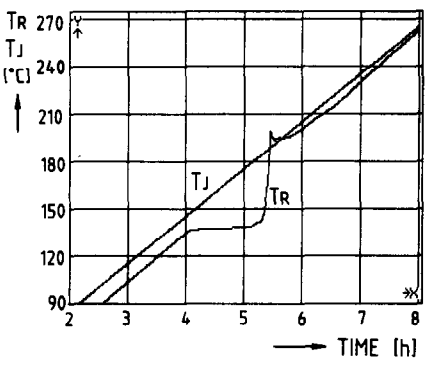

Fig. 1. Test in an open container

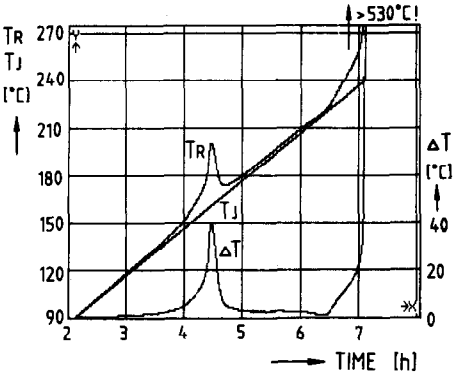

Fig. 2. Test in mesh-wire container

The following measurement demonstrates how dangerous it could be to rely only on this one measurement. Testing the same mixture under pressure in an autoclave revealed an exothermic reaction at 130°C (results not shown). The reaction mixture was then dried under vacuum and tested in a wire-mesh container. The first reaction at about 150°C is detected, in addition a second, very strong exotherm, is revealed above 210°C (Fig. 2).

Isoperibolic measurement indicates the beginning of the first exothermic reaction at the temperature of approximately 80°C (Fig. 3). The selfheating process under adiabatic conditions exhibits a dangerous course (Fig. 4). Measurements under various different conditions revealed new relevant information about the tested compound.

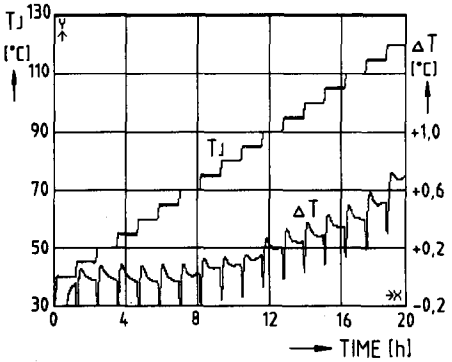

Fig. 3. Isoperibolic measurement

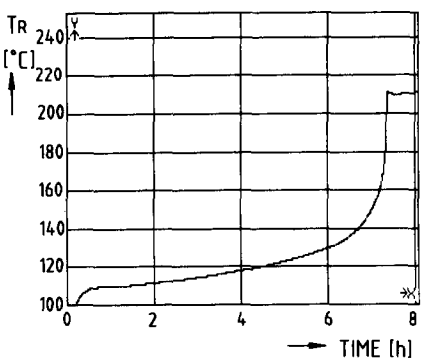

Fig. 4. Adiabatic measurement

REFERENCES

1 L. Hub: Can Thermic Hazard remain undetected ?
3rd International Symposium on Loss Prevention and Safety Promotion in the Process Industries, Basle, 1980.

2 Prospectus material of SYSTAG Ltd., Bahnhofstrasse 76, CH 8803, Rüschlikon, Switzerland
or
ASTRA Scientific Int. 410 Martin Avenue, Santa Clara, CA 95050

3 L. Hub: Two Calorimetric Methods for Investigating Dangerous Reactions
Hazard VI. Inst. Chem. Eng. Symposium Series No. 49

4 J. Hakl: SEDEX - Versatile Instrument for Investigating Thermal Stability
10th NATAS Conference, Boston, October 1980

5 J. Hakl: Overadiabatic Calorimetry (OAC)
6th Int. Conf. on Thermal Analysis, ICTA, Bayreuth, July 1980

6 L. Hub: On-Line Hazard Identification during Chemical Processes
2nd Int. Symp. on Loss Prevention and Safety Promotion, in the Process Industry, Sept. 77, Heidelberg