Journal of Thermal Analysis, Vol. 38 (1992) 437-443

FROM THERMAL ANALYSIS TO SAFETY SCIENCE

A. Raemy

NESTLÉ RESEARCH CENTRE, VERS-CHEZ-LES-BLANC, CASE POSTALE 44, CH-1000
LAUSANNE 26, SWITZERLAND

The approach of thermal analysis and explosion in relation to safety science is based on investigation methods in the mining and chemical industries. Once adapted to the particularities of foods, these methods correspond well to the needs of the food industry. Thus, thermal analysis and explosion simulation techniques as part of safety science (or loss prevention) participate to a large extent in the prevention of incidents and accidents by helping to take preventive measures.

Keywords: combustion of foods, industrial safety

Introduction

Specialized scientific procedures and methods which could serve as an intellectual basis for preventing accidents from what is called safety science [1] or the science of safety. Safety engineering is an equivalent term used when considering the safety action related to technology. If the term safety science is generally used to identify the discipline by which injury to persons is prevented, the term loss prevention [2, 3] is often used to define the same discipline when directed to the preservation of material properties. The means used for both objectives are the same and the consequences of accidents are sometimes unforeseeable, so there are generally no reasons to introduce a strict difference between these disciplines in the industrial context. Both terms therefore are considered here as synonyms.

As a thorough knowledge of the thermal behaviour of materials can provide greater safety in industrial operations, thermal analysis and calorimetry can, in some aspects, be considered as a part of safety science. A methodology developed in this context in relation to food processing is presented: exothermic reactions, self-heating, self-ignition, combustion and dust explosions are considered.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Exothermic reactions

Thermal analysis instruments

The instruments for studying exothermic reactions can be simple containers fitted with sensors which follow the rising temperature of a heating bench, or autoclaves with additional pressure sensors [4]. However, techniques such as differential thermal analysis (DTA), differential scanning calorimetry [5] (DSC), reaction calorimetry [6] or adiabatic calorimetry [7] allow one to obtain more detailed thermodynamic information. Other techniques, such as thermogravimetry, hot-stage microscopy, evolved gas analysis, or coupling with other instruments such as mass spectrometers can give additional data.

To study foods, which are often non homogeneous materials, it is sometimes preferable to select instruments allowing the analysis of large samples. This approach is particularly important in the context of safety.

Phenomena observed and parameters studied

The temperature range mostly considered when studying foods in relation to processing safety is the range between ambient and 300°C. The main exothermic phenomena described are lipid oxidation [8], fermentation [9] and carbohydrate decomposition [10]. Oxidation of other constituents such as polyphenols or proteins are also possible. The main endothermic phenomena observed in the temperature range mentioned are carbohydrate melting and water evaporation or boiling: these are also of interest for safety as they can either cause the product to be denatured, or prevent the temperature from rising beyond certain limits.

The main parameters determined by applying these techniques are thermodynamic, such as specific heat, onset temperature of exothermic (or endothermic) reactions, pressure data, kinetic constants, etc.

In addition, with adiabatic calorimeters runaway reactions can be followed and characterized with parameters such as self-heat rates, pressure rates, etc.

Simulation of process conditions

Thermal analysis techniques sometimes have to be applied in unusual ways, to carry out the measurements under conditions close to those of the process studied. Thus, for example, the calorimetric study of a sample in a sealed cell enables simulation of what happens in a homogeneously heated autoclave [11]. DTA and DSC measurements can also be carried out under constant pressure of inert gas [12].

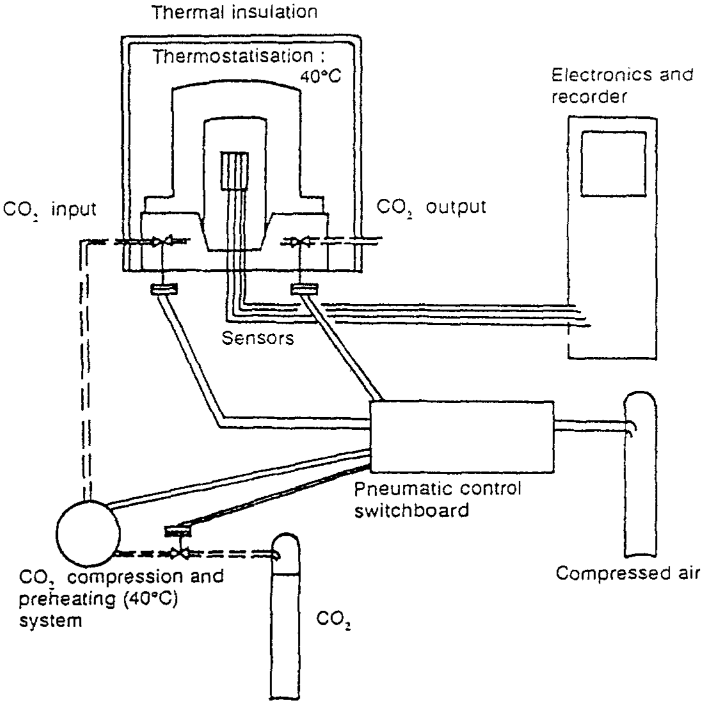

Fig. 1 Scheme of a DTA experiment under supercritical CO_2. High pressure DTA instrument Netzsch 404H

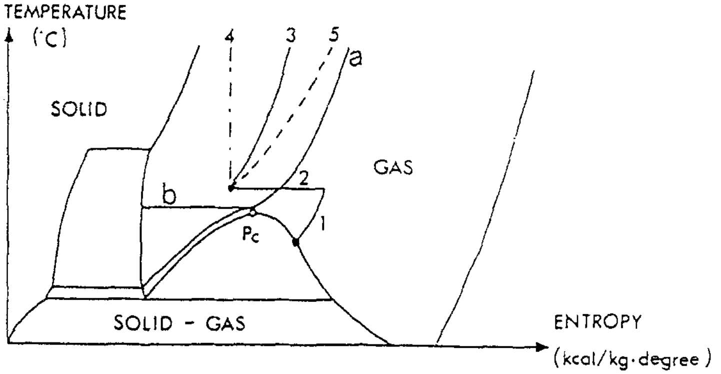

Fig. 2 Method used to perform a DTA measurement under supercritical CO_2 (P_c: critical point; a: critical isobar; b: critical isotherm; 1: heating at 40°C; 2: compression; 3: behaviour when heating the furnace; 4: isochor; 5: isobar).

Figure 1 shows schematically an experiment designed to study food samples in contact with supercritical CO_2, i.e. at temperatures above 31°C and pressures above 72.9 bar. With the help of high pressure DTA, it can be used to simulate solid-liquid extraction with supercritical gases as solvent [13–15]. Figure 2 indicates, in the CO_2 entropy diagram, the method to perform a DTA measurement under supercritical gas.

Rise in pressure and pressure reliefs

Exothermic pyrolysis reactions may present a hazard in certain industrial operations or during storage. The resulting rise in temperature may denature the product, but may also cause increases in temperature and pressure beyond safe levels. Further danger can be due to degassing associated with decomposition reactions: the evolved gases also lead to a rise in pressure (or self-ignite).

Reaction runaway in large industrial reactors can occur in short times; relief systems are sometimes necessary to avoid that pressure and temperature continue to rise until the reaction products are completely consumed (or decomposed). The data required for performing certain relief calculations can be determined in some cases with a specially designed calorimeter called Vent Sizing Package or VSP; this instrument is essentially an adiabatic calorimeter [16].

In order to carry out and interpret thermal analysis and thermomanometric measurements in the context of safety, it is also necessary to be familiar with the laws of ideal gases and with more specific behaviour patterns, for example of water or CO_2.

Self-ignition, combustion

Tools for analysis and studied parameters

The self-heating of the product resulting from exothermic reactions can lead to its self-ignition if sufficient oxygen is available.

Several techniques can be used for studying self-ignition of a sample; the simplest are plates or ovens heated to known temperatures. Some thermal analysis instruments also allow the analysis of products under ignition conditions, i.e. either by sweeping the sample with air or oxygen, or by keeping it under oxygen pressure [17]. The parameter determined by these techniques is the ignition temperature of a powder in deposit (or in layer).

Godbert-Greenwald's furnace allows ignition of a dust cloud kept at constant temperature [18]. This value is usually higher that the ignition temperature of a layer of dust.

Finally, the bomb calorimeter enables the study of the combustion of foods: an adequate igniting system and high oxygen pressure guarantee maximum combustion: the heat of combustion obtained are about 39 kJg^{-1} for fat, 23 kJg^{-1} for protein and 17 kJg^{-1} for carbohydrate.

Simulation of dust explosions

Tools and parameters

Several types of tools allowing simulation and analysis of dust explosions (closed containers of volume $V(m^3)$) are described in the literature [19–21]: among the best known are Hartmann's tube, the 20 l sphere and the 1 m^3 cylinder. In these instruments, the product is dispersed before being ignited. Several parameters are determined from the recording of pressure rise as a function of time, i.e. maximum explosion pressure (bar), maximum pressure increase rate (bar/s), minimum and maximum explosive concentrations (g/m^3). The K_{ST} value (bar m/s), a dust characteristic, is obtained from the maximum pressure increase rate by the formula:

$$(dp / dt)_{max} \cdot V^{1/3} = K_{ST}$$

This value enables one to classify particular products into categories expressing the violence of a possible explosion; it is also used for calculating vent areas. Finally, the minimum ignition energy (J) of a powdered product is determined with the help of electrical sources of ignition of known energy.

Data concerning dust explosion parameters of food products can be found in the literature [18–21]. For most processes, this information on explosion characteristics is an obligatory complement to the knowledge of the thermal behaviour of foods.

Conclusions

Thermal analysis can be considered as part of safety science as it can help to prevent accidents.

A list of bodies dealing with industrial safety if found in appendix.

Appendix

Bodies dealing with industrial safety problems

– Berufsgenossenschaftliches Institut für Arbeitsicherheit (BIA), Bonn, West Germany.

– Bergbau-Versuchssrecke (BVS), Dortmund, West Germany.

– Berufsgenossenschaft Nahrungsmittel und Gaststätten (BG), Mannheim, West Germany.

– Bundesanstalt für Materialprüfung (BAM), Berlin, West Germany.

– Christian Michelsen Institute, Fantoft, Bergen, Norway.

– Ciba-Geigy, Central Safety, Basel, Switzerland.

– Centre d'Etudes et Recherches des Charbonnages de France (Cerchar), Verneuil-en-Halatte, France.

– Columbia Scientific Industries Corp. International, Milton Keynes, England.

– Fire Research Station (FRS), Hertfordshire, England.

– La Société Natinale des Poudres et Explosifs (SNPE), Paris, France.

– National Fire Protection Association, Boston, USA.

– Stazione Sperimentale per i Combustibili, Milano, Italy.

– United States Bureau of Mines, Pittsburgh, USA.

Note: this list is not exhaustive. For farther details, see Refs [18] and [20].

* * *

The author gratefully acknowledges P. Lambelet for many helpful discussions and I. Horman for reviewing this text.

References

1 A. Kuhlmann, Introduction to Safety Science, Springer Verlag, New York 1986.
2 R. L. Browning, The Loss Rate Concept in Safety Engineering, Marcel Dekker Inc., New York 1980.
3 H. I. Joschek, Proceedings of the 5th International Symposium: Loss Prevention and Safety Promotion in the Process Industries, European Federation of Chemical Engineering, Société de Chimie Industrielle, Paris.
4 A. V. Zatka, Thermochim. Acta, 28 (1979) 7.
5 P. C. Bowes, Self-heating: evaluating and controlling the hazards, Elsevier Science Publishers, Amsterdam 1984.
6 W. Regenass, Thermochim. Acta, 20 (1977) 65.
7 D. I. Townsend and J. C. Tou, Thermochim. Acta, 37 (1980) 1.
8 A. Raemy, I. Froelicher and J. Loeliger, Thermochim. Acta, 114 (1987) 159.

9 I. Morison and U. von Stockar, Enzyme Microb. Technol., 9 (1987) 33.
10 A. Raemy and T. Schweizer, J. Thermal Anal., 28 (1983) 95.
11 A. Reamy and P. Lambelet, J. Technol., 17 (1982) 451.
12 A. Raemy, Thermochim. Acta, 43 (1981) 229.
13 A. Raemy, P. Lambelet and J. Loeliger, Thermochim. Acta, 95 (1985) 441.
14 G. M. Schneider, E. Stahl and G. Wilke, Extraction with supercritical gases, Verlag Chemie, Weinheim Germany 1980.
15 A. Raemy and M. Gardiol, ASIC, 12^e Colloque, Montreux 1987, p. 320.
16 J. C. Leung, H. K. Fauske and H. G. Fischer, Thermochim. Acta, 104 (1986) 13.
17 A. Raemy and J. Loeliger, Thermochim. Acta, 85 (1985) 343.
18 K. N. Palmer, Dust Explosions and fires, Chapman and Hall, London 1973.
19 W. Bartknecht, Explosions, Springer Verlag, New York 1981.
20 P. Field, Dust explosions, Elsevier Scientific Publishing Co., Amsterdam 1982.
21 K. L. Cashdollar and M. Hertzberg, Industrial dust explosions, ASTM publication, Philadelphia USA 1987.

Zusammenfassung — Die Ähnlichkeit von Thermoanalyse und Explosionssimulation in Bezug auf die Sicherheitswissenschaft basiert auf Untersuchungsmethoden, die im Bergbau und in der chemischen Industrie entwickelt wurden. Werden diese Methoden den Besonderheiten von Lebensmitteln angeglichen, befriedigen sie sehr gut die diesbezüglichen Bedürfnisse der Lebensmittelindustrie. Folglich sind Thermoanalyse und Explosionssimulationstechniken als Teil der Sicherheitswissenschaft (oder der Verhinderung von Verlusten) durch die Unterstützung der Ergreifung präventiver Maßnahmen zu einem großen Teil an der Verhinderung von Vorfällen und Unfällen beteiligt.