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DETERMINATION OF SPONTANEOUS IGNITION TEMPERATURES OF EDIBLE OILS AND FATS BY PRESSURE DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Samples of vegetable, edible oils and animal fats were intensively oxidized in the cell of a pressure differential scanning calorimeter (PDSC). At high oxygen pressures (800–2800 kPa) and at high heating rates (40–90 °C min^{-1}) the samples undergo spontaneous ignition. The temperatures at which ignition occurs were determined from PDSC scans. The influence of heating rate, pressures of oxygen and presence of copper on spontaneous-ignition temperatures for the studied oils and fats are discussed.

INTRODUCTION

When a flammable substance is heated to an elevated temperature in an oxidizing atmosphere, a reaction is initiated that may proceed with sufficient rapidity to ignite the substance. The time that elapses between the instant the substance temperature is raised and that in which a flame appears is called the time delay before ignition. This time decreases as the temperature of the flammable mixture increases. The temperature at which the flame appears is called the autoignition temperature (AIT) or spontaneous-ignition temperature (SIT) or, sometimes, self-ignition temperature.

Two types of SIT data are reported in the literature. The first type is usually obtained at high temperatures where the ignition delay is relatively short (less than 1 s) and it is applicable for controlled combustion (i.e. in engines). The second type is obtained for situations where the combustible material and the air can remain in contact with hot surfaces for an indefinite period, in experiments practically up to 4–5 min. Such data are usually the qualities of interest in safety work.

During deep frying or cooking, fats or oils are heated well above 180 °C, which requires that the equipment is heated to 250–300 °C. At these temperatures there are serious oil-fire or explosion hazards as the potential exists for the heat-transfer oils used to come into contact with hot surfaces (e.g. heaters) by spillage or leakage. However, vegetable oils are also used as components of diesel-fuel blends. The need to know the SITs for oils and fats in both food and non-food applications is evident, and most of the legal regulations use SITs as the criteria for classification schedules.

The SIT data are usually obtained by dropping the flammable fluid into a cavity in a heated metal block or by heating the sample on a hot surface. As these methods have rather poor reproducibility, being tedious and time consuming, the use of thermal-analysis techniques has been proposed [1–4].

The data reported in the literature on limits of flammability, autoignition temperatures and burning rates for edible oils and fats are rather poor. The most comprehensive, single source of flammability characteristics elaborated by Zabetakis [5] does not even mention these products. In the last decade the situation has improved, good examples are the papers published by the research group from the Nestle Research Department in Vevey, Switzerland [3,6,7]. Although these papers are concerned mainly with food powders some data for edible oils and fats are also reported.

In this work the SITs of edible oils and fats were studied by PDSC and this paper is an extension of the research programme on the use of thermal-analysis techniques for the investigation of fat-based foods at elevated temperatures [8–10].

EXPERIMENTAL

Oils and fats

A total of 19 samples of vegetable oils (nine rapeseed oil (RSO), five soybean oil (SBO), five sunflower oil (SFO)) and five samples of lard (LRD) were used. The oil samples were either commercial brands or obtained from a local factory; two samples of lard were prepared in the laboratory by melting pork fat and three were of commercial origin. All samples were fresh

TABLE 1

Parameters of samples

Sample	Peroxide value	Iodine value	Acid value
RSO [a]	2–3	115–125	0.2–0.4
RSO	0–1	115–125	0.1–0.2
SBO [a]	2–3	125–130	0.2–0.3
SBO	0–1	130–136	0.1–0.2
SFO [a]	2–4	122–130	0.2–0.4
SFO	1–2	125–135	0.1–0.2
LRD	2–3	60– 65	0.2–0.3

[a] Commercial oils.

and some of their parameters, determined in accordance with Polish Standards [11,12], are listed in Table 1. In order to protect the samples from uncontrolled autoxidation, they were kept at 7 ° C under nitrogen in darkness, packed in glass ampoules.

Apparatus and experimental procedure

A Du Pont 1090 B thermal analyser and a Du Pont 910 differential scanning calorimeter equipped with a DSC pressure cell (PDSC, model 900830-902) were used The instrument was calibrated using high-purity indium and tin as standards. PDSC experiments were carried out under the following conditions: dynamic mode, heating rates variable 25–90 ° C min^{-1}; sample masses 3–5 mg; sample pans open, aluminium (in some experiments rods of copper were placed in sample pans); oxygen pressure variable 800–2800 kPa (most of the experiments were performed under 2000 kPa of oxygen). For further experimental details see text and Refs. 8 and 10. The experiments were recorded on 8-in floppy discs from which heat-flow curves and sample temperatures as a function of time were plotted. The SITs were determined as extrapolated onset temperatures of the sharp peaks which show the rapid rise in temperatures of the heated samples.

RESULTS AND DISCUSSION

Typical PDSC exotherms and sample temperatures for the oils studied are shown in Figs. 1–8. As can be seen from these figures the rapid rises in temperature, more than 100 ° C, of the samples allows their SITs to be determined. Apart from the temperature rise of > 100 ° C, other criteria mentioned by Zeman and Binder [4] (i.e. explosion noise detectable with stethoscope, rapid decrease in heat flow after ignition, and empty sample pan after the test) were also met. When the sample masses were > 5 mg, the pans after the test contained coked residue due to incomplete burning. When the sample masses were < 2 mg ignition did not occur.

Analysis of the results shows that the heating rate plays an important role in the SIT determinations. If the masses of the samples of a given material and the pressure of oxygen are kept constant there is a minimal heating rate, β_{min}, at which ignition occurs. It was found that the values of β_{min} must be higher than 30 ° C min^{-1} for RSO and SBO, 40 ° C min^{-1} for SFO, and 25 ° C min^{-1} for LRD. More than 90% of the samples ignited when the applied heating rate was 5 ° C min^{-1} higher than the listed β_{min} values. There is a general tendency for the SITs to increase with increasing heating rate, but for the materials studied such a conclusion could not be quantified. As can be seen from Figs. 1–8, the PDSC diagrams sometimes show two peaks for the heat flow; the sharp peak of the temperature rise corresponds

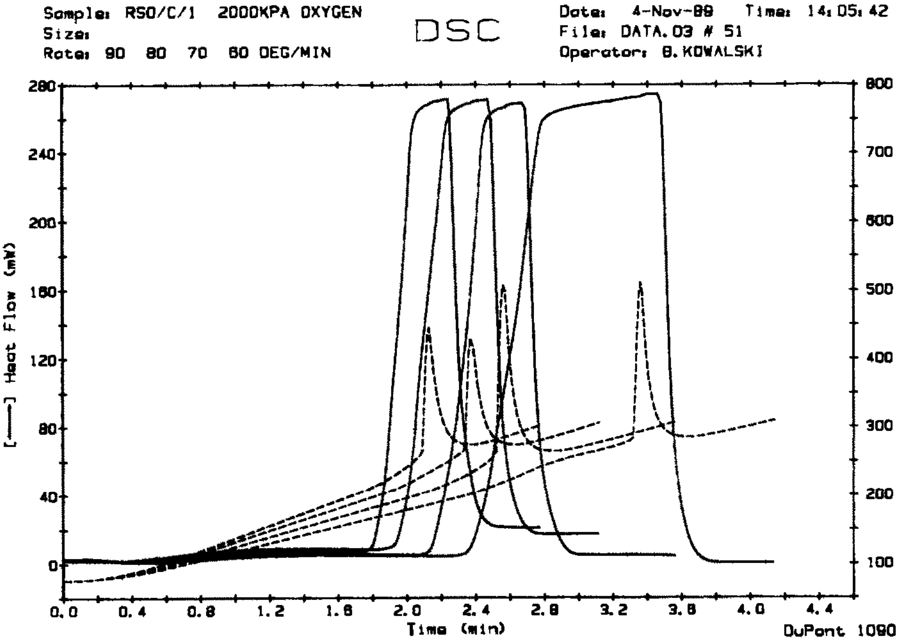

Fig. 1. PDSC exotherms and sample temperatures of rapeseed oil heated at rates of 90, 80, 70 and 60 °C min^{-1}; oxygen pressure 2000 kPa (scans from left to right).

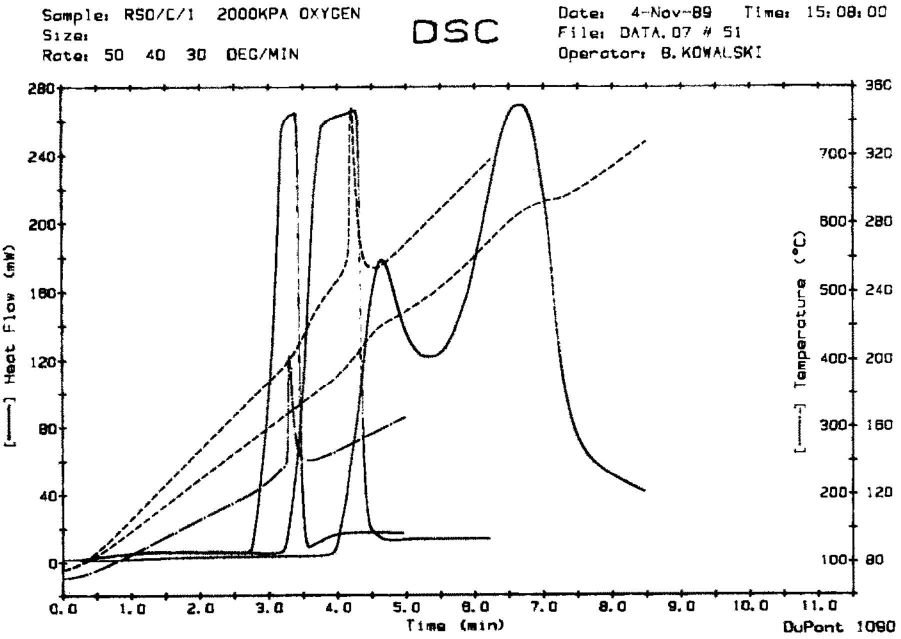

Fig. 2. PDSC exotherms and sample temperatures of rapeseed oil heated at rates of 50, 40 and 30 °C min^{-1}; oxygen pressure 2000 kPa (scans from left to right).

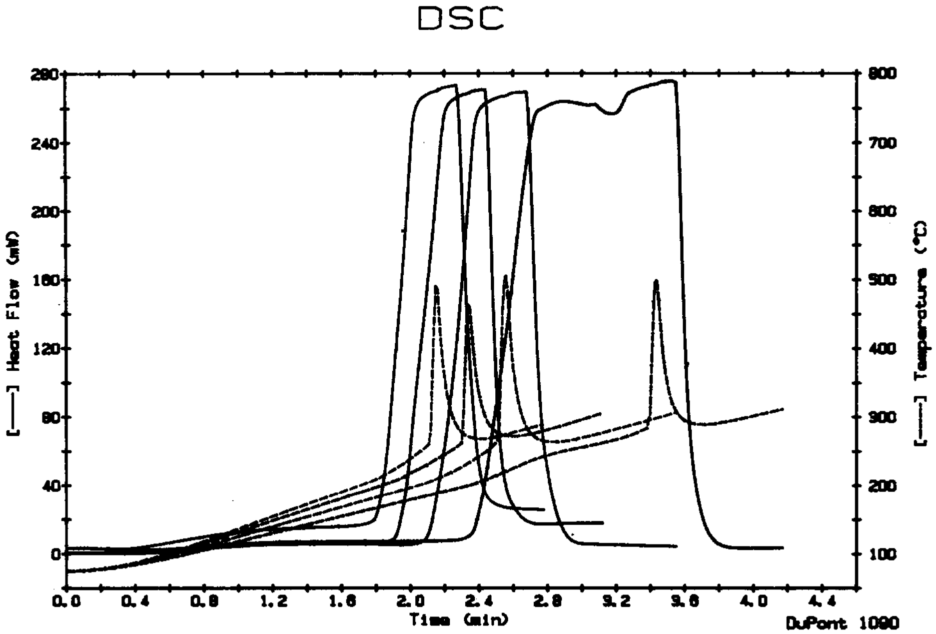

Fig. 3. Plot as in Fig. 1 for soybean oil.

to the second peak of the heat flow. This phenomenon is frequently observed with relatively low heating rates or oxygen pressures. Although the criteria for ignition were also finally reached, the measured SITs correspond

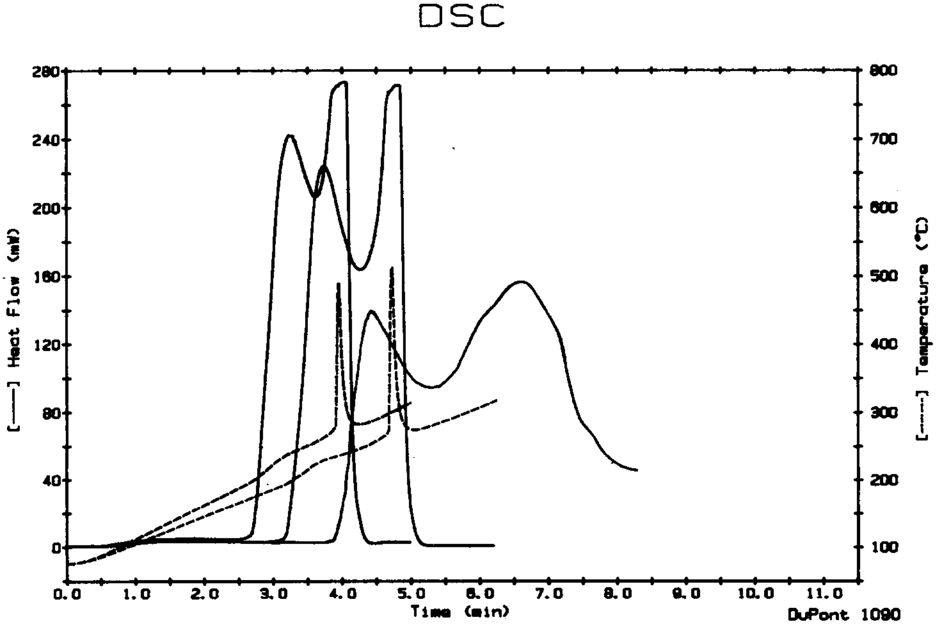

Fig. 4. Plot as in Fig. 2 for soybean oil.

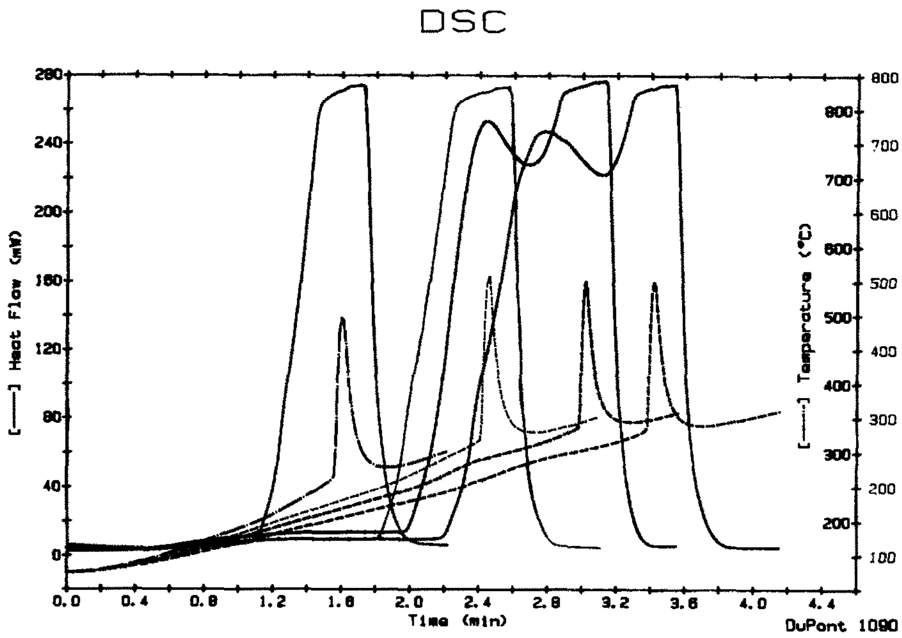

Fig. 5. Plot as in Fig. 1 for sunflower oil.

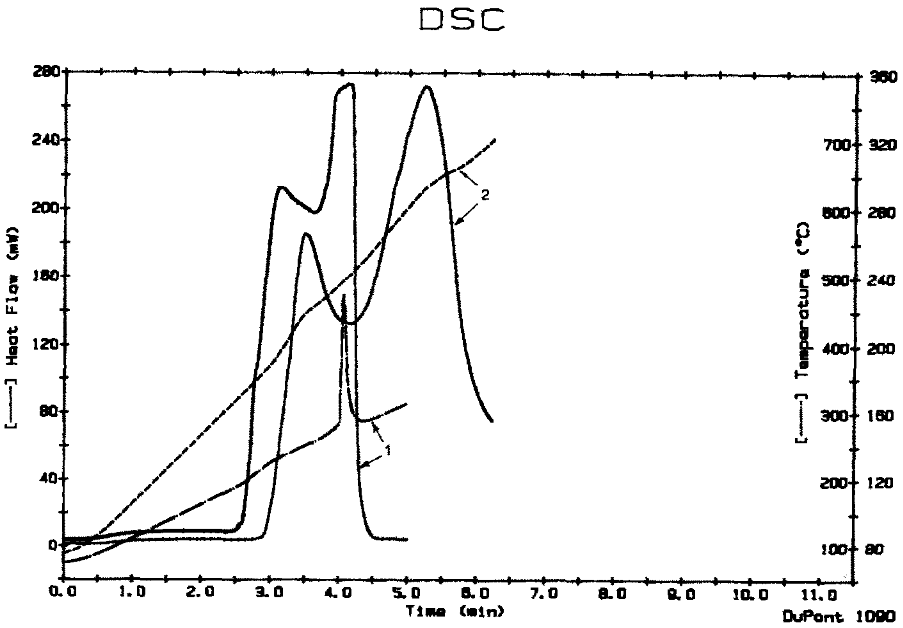

Fig. 6. PDSC exotherms and sample temperatures of sunflower oil heated at rates of (1) 50 and (2) 40 ° C min^{-1}; oxygen pressure 2000 kPa.

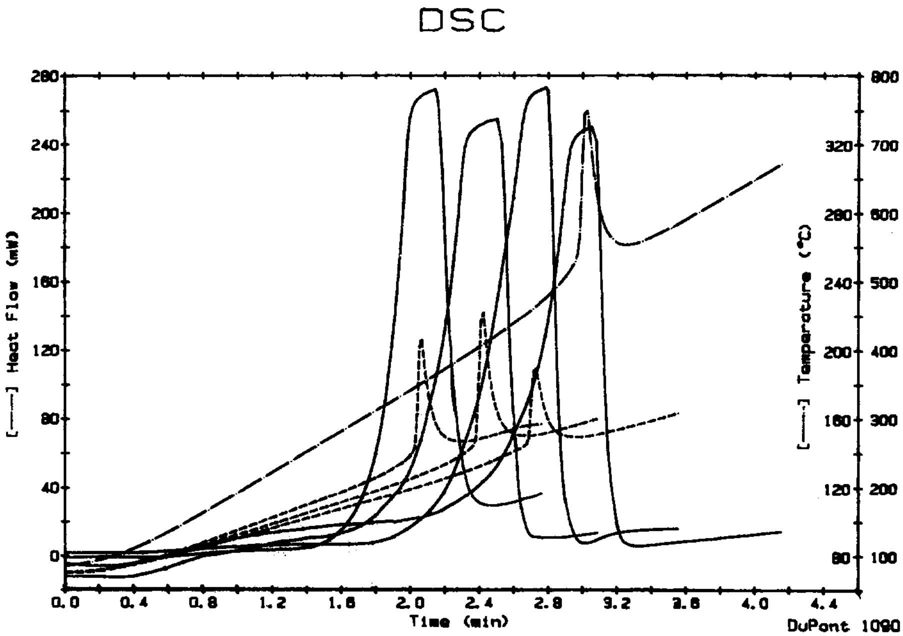

Fig. 7. Plot as in Fig. 1 for lard.

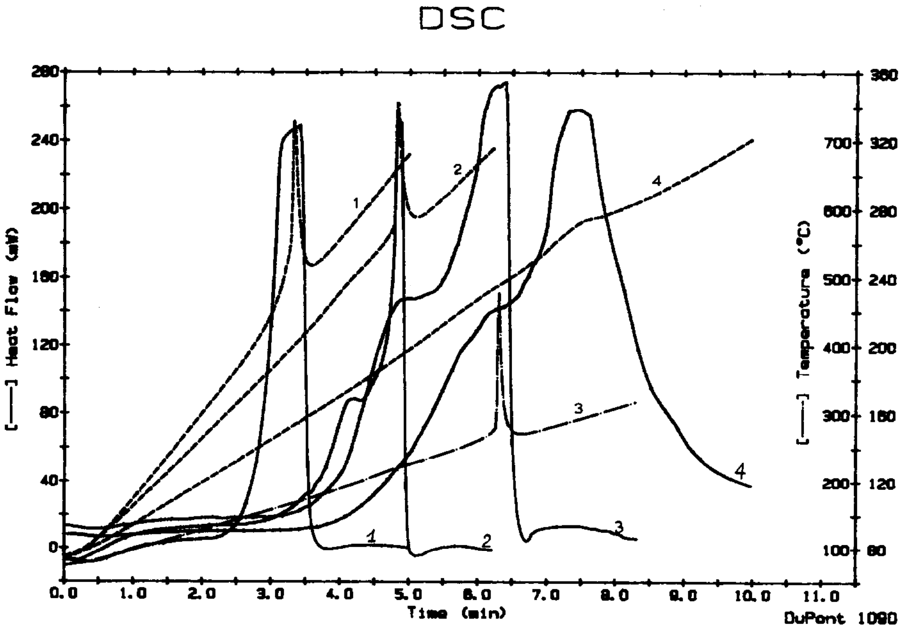

Fig. 8. PDSC exotherms and sample temperatures of lard heated at rates of (1) 50, (2) 40, (3) 30 and (4) 25 °C min^{-1}; oxygen pressure 2000 kPa.

TABLE 2

Spontaneous ignition temperatures of samples obtained by PDSC at heating rates of 40–90 °C min^{-1} and at 2000 kPa of oxygen pressure

Sample	Range of SITs (°C)
RSO	230–285
SBO	260–290
SFO	260–290
LRD	220–280

to heavily oxidized and polymerized or even decomposed samples. Because of this, and taking into account that the SITs depend on many different parameters such as sample size, instrument type, etc., the results from various sources usually cover some temperature range. Table 2 lists the ranges of SITs for the investigated materials, obtained at heating rates of 40–90 °C min^{-1} and 2000 kPa pressure of oxygen. The agreement of our results with the corresponding ones reported by Raemy and his colleagues [3,6,7] is rather good. The measured SITs show a rough trend of increasing with increasing unsaturation of the fats.

Effect of copper

It is commonly known that some metals, among them copper, accelerate the autoxidation reactions by catalytic influence [13], and evidence of this for lipids has also been obtained by thermal analysis [14]. The influence of copper on the oxidation and the SITs of SBO and SFO are illustrated in Figs. 9 and 10. The examples shown are typical. The acceleration of the oxidation of oils in the presence of copper is evident, as can be determined from the first deviation from the base line and the extrapolated onset of the PDSC exotherms. It was expected that the presence of copper in the sample would help in differentiating the SITs for oils and fats. The results show that copper generally lowers the SITs by about 5–15 °C, depending on both the sample and the heating rate as shown in Figs. 9 and 10. A few oil samples appeared to be virtually insensitive to the presence of copper, which might suggest that they contained some natural metal deactivators. It can be concluded that the presence of copper in the oils when studied by PDSC gave restricted possibilities to differentiate their SITs.

Oxygen pressure

An increase in pressure generally decreases the SIT of a combustible material in a given oxidant. Increasing oxygen pressure reduces the relative reduction in the SITs and the SIT dependence on the oxidative medium pressure can be represented by exponential equations. It has been found by

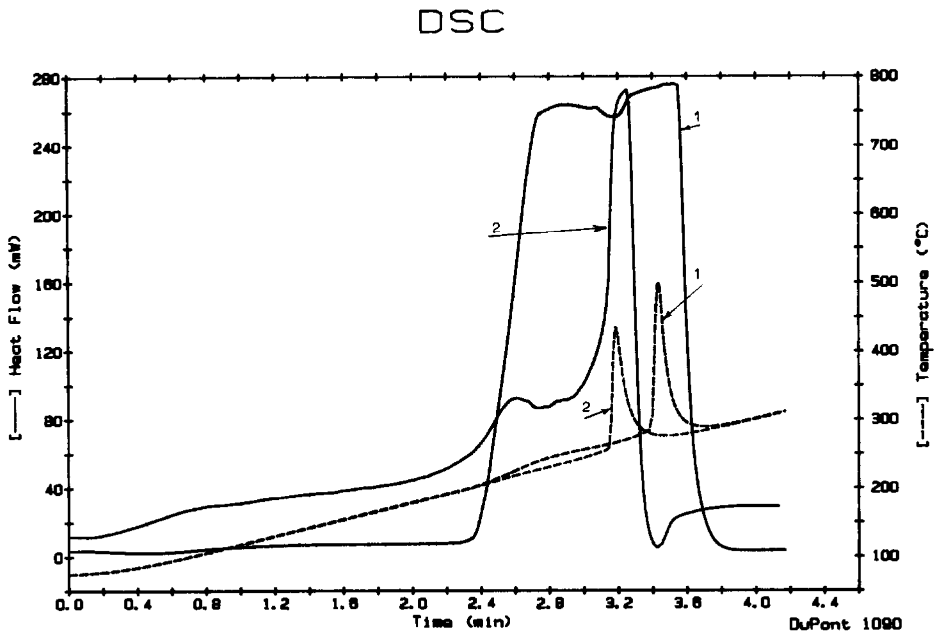

Fig. 9. PDSC exotherms and sample temperatures of soybean oil (1) and soybean oil in presence of copper (2). Heating rate 60 °C min^{-1}; oxygen pressure 2000 kPa.

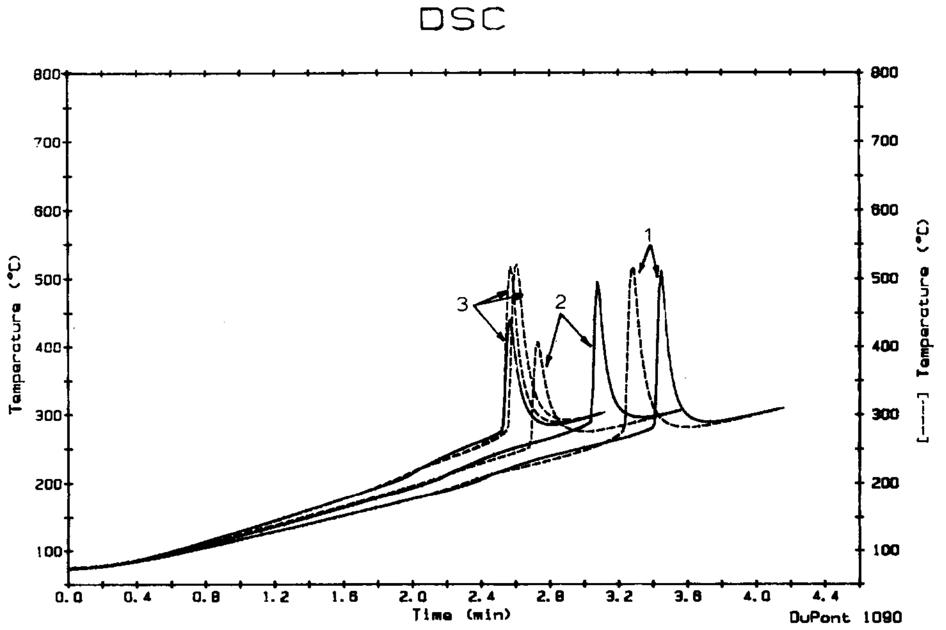

Fig. 10. Sample temperatures of sunflower oil (———) and sunflower oil in the presence of copper (— — —) determined in PDSC experiments. Heating rates (°C min^{-1}): (1) 60, (2) 70 and (3) 80. Oxygen pressure 2000 kPa.

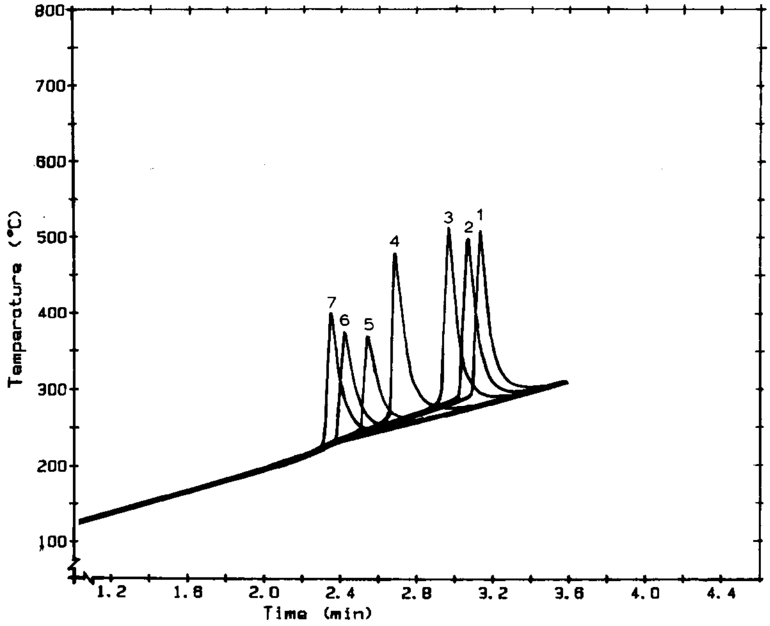

Fig. 11. Sample temperatures of rapeseed oil heated at a rate of 70 °C min^{-1} under oxygen pressures of (1) 800, (2) 1200, (3) 1600, (4) 1800, (5) 2000, (6) 2400 and (7) 2800 kPa.

Zabetakis et al. [15] that the SITs of several hydrocarbons obey Semenov's equation over a limited pressure range. The SITs of oils and fats obtained by PDSC are also dependent on the oxygen pressure, but the problem appears to be complicated. An increase in the oxygen pressure influences, probably by altering kinetic features of the thermal-oxidative decomposition of the

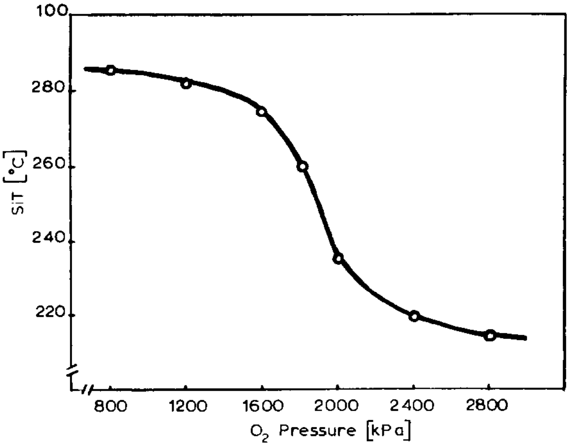

Fig. 12. Plot of SITs (determined by PDSC) versus oxygen pressure for rapeseed oil; heating rate 70 °C min^{-1}.

sample, the shape of the PDSC exotherm, especially when there is a double PDSC peak. If the oxygen pressure is increased substantially the second peak disappears, which in turn influences the SIT of the sample. In Figs. 11 and 12 such influences are shown for a sample of RSO heated at a rate of 70 °C min^{-1} with variable (800–2800 kPa) oxygen pressure. As there are few SIT–oxygen pressure data available for vegetable oils, a more detailed study in this field is needed.

CONCLUSION

PDSC was used successfully to determine the SITs of edible oils and fats. Using this method the spontaneous combustion of the materials studied was clearly detected and their SITs were precisely determined under well-defined measurement conditions.

Although such extreme measurement conditions do not correspond to real industrial situations of fats processing, the measured SITs can be applied to situations where, due to possible problems in the plants, fire and explosion hazards can develop.

The SITs obtained by PDSC allow a ranking of the oils and fats and can provide data for correlation with results measured by other methods.

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