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Thermal-oxidative decomposition of edible oils and fats. DSC studies

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Abstract

The DSC scans of edible vegetable oils and of lard were measured by heating the samples up to 360 °C in an atmosphere of oxygen. The heating rates were in the range 5–20 °C min^{-1}. From the resulting DSC exotherms, their extrapolated onset and peak maximum temperatures were determined and used for the assessment of thermal-oxidative stabilities of the samples and for calculation of activation energies. Two samples of highly rancid rapeseed and sunflower oils and eighteen samples of rapeseed oil inhibited with 2-*t*-butyl-4-methoxyphenol, 2,6-di-*t*-butyl-4-methylphenol and propyl gallate were also studied. The onset oxidation temperatures of rancid oils were lowered by about 30–40 °C compared with fresh oils. An improvement in the thermal-oxidative stability of inhibited rapeseed oil, judged from the onset oxidation temperatures, depends on the antioxidant used. For 2-*t*-butyl-4-methoxyphenol and 2,6-di-*t*-butyl-4-methylphenol, this improvement was practically negligible, but for propyl gallate a substantial increase in the stability of rapeseed oil was found.

INTRODUCTION

It is widely known that fats and fat-based foods deteriorate during storage in an oxidising atmosphere; the process is referred to as autoxidation. When fats or oils are heated in such an atmosphere up to relatively high temperatures, their oxidation is not only accelerated but is followed by oxypolymerisation and thermal-oxidative destruction. This overall process is referred to as thermal-oxidative decomposition. As heat is the principal factor in food processing and fats or oils are commonly used as the heat-transfer media, their quality assessment for such applications is of paramount importance. Several methods for the high-temperature assessment of frying oils and fats have been developed. They are based on analytical determinations (acid, peroxide, anisidine and totox values) and physical determinations (viscosity, smoke point, fire point, etc.), or even on simple organoleptic testing (colour, smell, taste). Although such methods of assessment are popular, they all have some weak points in common: all of them are highly empirical or very subjective and none of them can be used for well established predictive calculations or even speculations.

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As thermal-oxidative decompositions of oils and fats are exothermal reactions, thermal analysis techniques can be used for their quantification. Thus the results obtained by DTA, TG [1–6] or DSC and PDSC [7–12] have been used for the assessment of the quality of oils and fats or of their stability in relation to heat and/or oxidative medium treatment.

The presented paper is an extension of our research programme on the use of thermal analysis techniques for investigations of fat-based foods at elevated temperatures. The purpose of this study was to provide experimental data for the assessment of the resistance of oils and fats to thermal-oxidative decomposition.

EXPERIMENTAL

Materials

Vegetable oils and samples of lard were the same as those reported in another paper where their parameters are given [13]. The abbreviations used in this paper for the samples are: rapeseed oil (RSO), soybean oil (SBO), sunflower oil (SFO), lard (LRD). The letters OOH in sample designations denote highly rancid oils and they are the same RSO-1 and SFO-1 oils [10,11] after 2 years of storing at room conditions. The antioxidants, 2-*t*-butyl-4-methoxyphenol (BHA), 2,6-di-*t*-butyl-4-methylphenol (BHT) and propyl gallate (PG), were the same as used in the earlier paper [14].

Apparatus and experiments

The instrument, its calibration, experimental and computation procedures were all the same as described previously [10,11]. The heating rates for the DSC scans were in the range 5–20 °C min^{-1} and the oxygen flow was maintained at the level of 10 dm^3 h^{-1}. For each oil or fat, 5–7 scans at different heating rates were performed and in each series the sample masses (3–4 mg) were kept as constant as possible. All the DSC experiments were recorded on 8 in floppy discs and then analysed using the Du Pont Oxidative Stability V2.0 and Interactive DSC V3.0 software programs for determinations of onset oxidation temperature (t_{on}) and peak maximum temperature (t_{max}), respectively.

RESULTS AND DISCUSSION

Typical scans obtained at the heating rate of 10 °C min^{-1} are shown in Fig. 1. The scans at other heating rates were similar but shifted: the higher the heating rate, the higher the t_{on} and t_{max} temperatures. Table 1 lists the t_{on} and t_{max} results obtained at a heating rate of 10 °C min^{-1}. These results can be used as the primary parameters of the resistance to thermal-oxidative

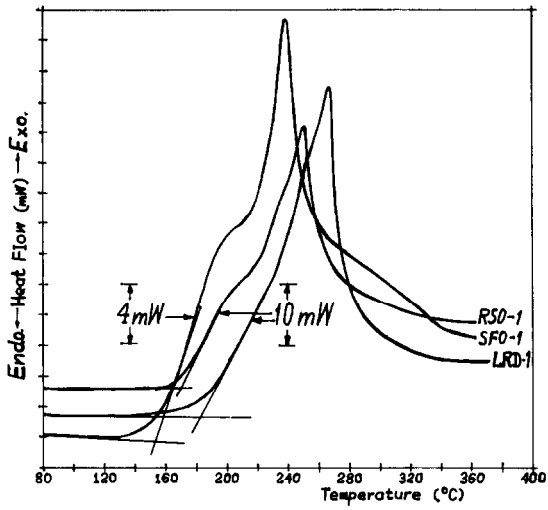

Fig. 1. DSC scans for rapeseed oil (RSO-1), sunflower oil (SFO-1) and lard (LRD-1). Heating rate 10 °C min^{-1}, oxygen flow 10 dm^3 h^{-1}.

decomposition. The sample with higher t_{on} and t_{max} is more stable than one for which these values are lower. The stability of the systems studied depends on the type of sample, decreasing in the sequence: LRD > RSO > SBO > SFO, although there are some irregularities among RSO and SBO oils. This sequence correlates well with the unsaturation of the fats. Some results listed in Table 1 for cow tallow, chicken fat, margarines and cow butter-fat confirm this conclusion. As the plots of the log of the heating rate versus the reciprocal of the peak maximum absolute temperatures showed acceptable linearities, approximate apparent activation energies were calculated from their slopes and then improved until the final activation energies (E) were obtained. From the activation energies, the pre-exponential factors (Z) of the Arrhenius equation were calculated. At high partial pressures of oxygen ($p_{oxyg} >> 13$ kPa) the thermal-oxidative breakdown of vegetable oils is an apparent first-order reaction [10]. Thus the specific rate constants and selected conversion times can be calculated and used as additional parameters for the assessment of the thermal-oxidative stability of edible oils and fats. As a full analysis (4–5 measurements and calculations leading to the E, Z and kinetic values) can be performed in about four hours or even faster, the DSC method can be applied as a routine quality control procedure for the stability of oils, fats and fat-based foods.

Rancid oils

The changes in the chemical composition of edible oils and fats in the course of their deterioration (rancidification) influence the thermoanalytical scans of the samples. Based on thermogravimetry, Wesołowski has shown

TABLE 1

DSC data (t_{on} and t_{max}) obtained at a heating rate of 10 °C min^{-1}, and activation energies (E) and pre-exponential factors (Z) of the Arrhenius equation

Sample	t_{on} (°C)	t_{max} (°C)	E (kJ mol^{-1})	log Z (min^{-1})
RSO-1 [a,b]	170.7	253.0	64.8	5.875
RSO-2 [b]	165.8	248.3	62.3	5.685
RSO-3	179.7	260.1	71.5	6.489
RSO-4	176.6	256.3	66.6	6.031
RSO-5	180.1	261.6	72.0	6.519
RSO-6 [b]	166.9	250.7	63.6	5.791
RSO-7 [b]	169.3	252.8	64.3	5.837
RSO-8	179.6	258.3	68.9	6.244
RSO-9	177.6	251.5	66.1	6.074
RSO-10	182.1	262.1	73.4	6.656
SBO-1 [b,c]	170.9	245.0	62.8	5.783
SBO-2	172.2	251.1	62.3	5.647
SBO-3	168.4	246.3	63.6	5.852
SBO-4 [b]	164.9	242.4	65.1	6.069
SBO-5	169.9	246.8	63.0	5.781
SBO-6 [b]	171.3	245.9	63.6	5.858
SFO-1 [b,c]	150.3	238.4	60.7	5.618
SFO-2	150.2	236.0	61.3	5.747
SFO-3 [b]	147.3	229.7	64.0	6.136
SFO-4 [b]	148.1	231.6	63.0	5.997
SFO-5	155.2	237.8	59.8	5.557
SFO-6	160.0	239.0	62.4	5.825
LRD-1 [b]	182.9	268.2	92.9	8.551
LRD-2 [b]	184.1	269.3	91.6	8.400
LRD-3	180.3	266.1	90.3	8.325
LRD-4	184.7	270.1	93.4	8.567
LRD-5 [b]	183.3	270.6	92.2	8.437
RSO-1/OOH [d]	128.0	263.0		
SFO-1/OOH [d]	101.0	242.0		
cow tallow [e]	176.3	293.0		
chicken fat [e]	161.9	–		
vegetable butter [f]	167.4	260.0		
margarine [f]	189.0	283.0		
cow butter fat [f]	195.7	258.8		

[a] Data from ref. 10.
[b] Commercial fats.
[c] Data from ref. 11.
[d] Highly rancid oils.
[e] Samples characterised in refs. 15 and 16.
[f] Data from ref. 17.

[3,4] that the onset temperatures of thermal decomposition curves of rancid medicinal cod-liver oils, technical fish oils and fish-meal residual oils are lower than those of high quality products. During the autoxidation of oils

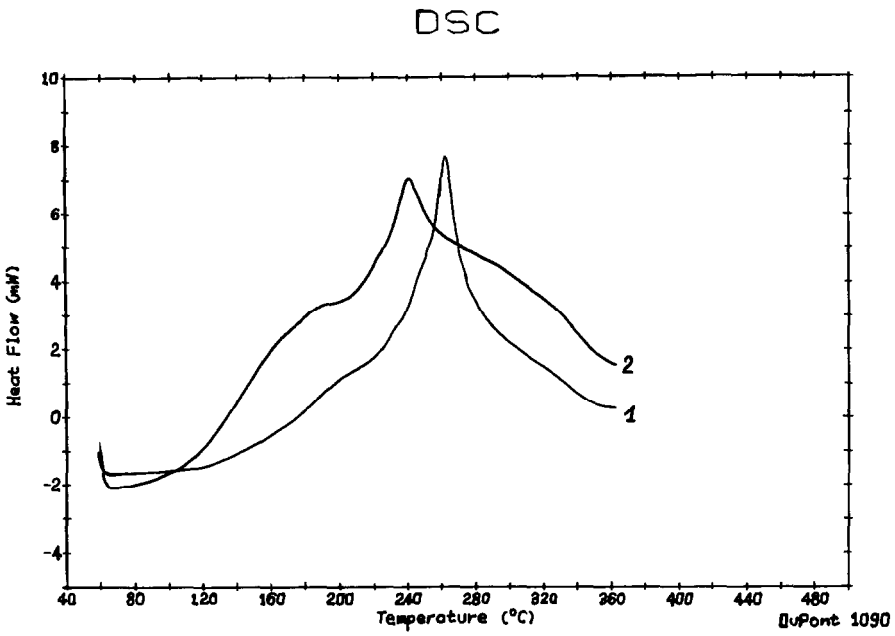

Fig. 2. DSC scans of rancid oils: 1, RSO-1/OOH; 2, SFO-1/OOH. Conditions as in Fig. 1.

their defence system formed by antioxidants both natural or added, which stabilises them, is destroyed or at least considerably depleted. Therefore the DSC traces (in oxygen) of rancid oils should display no or very short induction periods in the isothermal measurements or extrapolated onset temperatures in dynamic measurements which are lower than for fresh samples. Figure 2 shows the DSC scans for highly rancid oils (RSO-1/OOH and SFO-1/OOH). The t_{on} values for these oils are lowered by about 30–40 °C compared with fresh oils. The first deviations from the DSC base lines for the RSO-1/OOH and SFO-1/OOH samples are about 100 and 80 °C, respectively.

Inhibited rapeseed oil

The aim of this part of the study was to investigate the potential of DSC to evaluate the efficiency of antioxidants in the protection of oils and fats from thermal-oxidative decomposition. As model systems for these investigations, 18 samples of RSO inhibited by different amounts of BHA, BHT and PG were prepared. The RSO oil showed relatively high stability as determined by its t_{on} value. The average result from five determinations was 179.1 °C; the reproducibility of the t_{on} measurements (near 180 °C) was about 1.5%. As the antioxidants' efficiency was judged from the t_{on} values, the scans of inhibited oils were performed up to 220 °C. A typical scan for inhibited RSO is shown in Fig. 3; scans for RSO inhibited with PG are

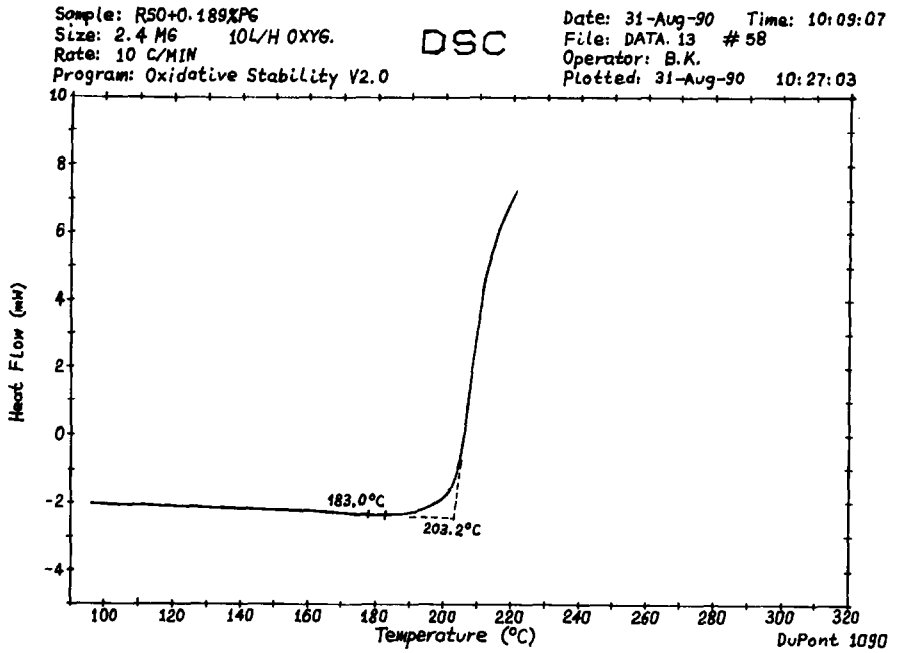

Fig. 3. DSC scan for the mixture RSO + 0.189% PG. Conditions as in Fig. 1.

illustrated in Fig. 4. All results obtained for the RSO samples containing different concentrations of BHA, BHT and PG are listed in Table 2. The addition of antioxidants to oils or fats should increase their t_{on} values. The

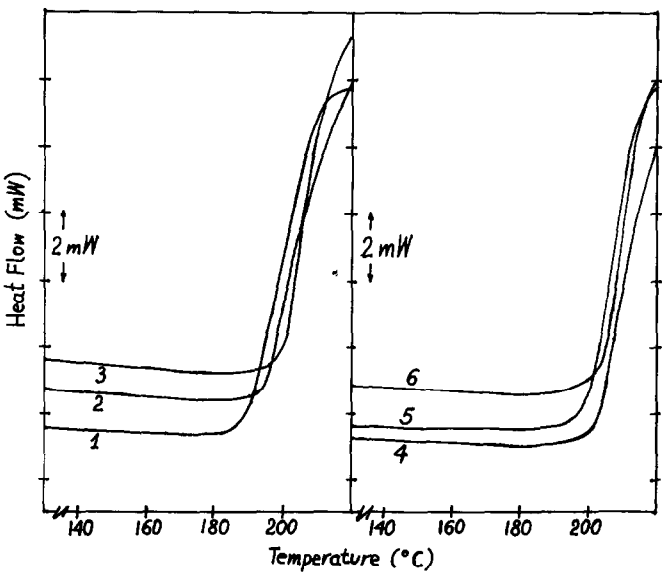

Fig. 4. DSC scans of RSO containing: 1, 0.012%; 2, 0.020%; 3, 0.044%; 4, 0.070%; 5, 0.095%; 6, 0.189% PG. Conditions as in Fig. 1.

TABLE 2

DSC onset oxidation temperatures (t_{on}) of RSO and RSO inhibited with antioxidants

Sample	t_{on} (°C)	Sample	t_{on} (°C)
RSO	180.2	RSO+0.011% BHA	183.5
	176.7	RSO+0.033% BHA	181.9
	177.8	RSO+0.089% BHA	181.2
	180.8		180.5
	180.1	RSO+0.121% BHA	183.6
RSO+0.017% BHT	183.2		182.8
RSO+0.033% BHT	181.5	RSO+0.233% BHA	180.6
RSO+0.056% BHT	185.2		179.7
	184.8	RSO+0.012% PG	189.5
RSO+0.080% BHT	182.1	RSO+0.020% PG	195.2
RSO+0.112% BHT	183.5	RSO+0.044% PG	200.0
RSO+0.161% BHT	183.4	RSO+0.070% PG	202.0
	183.8	RSO+0.095% PG	200.2
RSO+0.203% BHT	182.7	RSO+0.189% PG	203.2
	183.2		

results obtained for the selected RSO oil show that the influence of the BHA and BHT on its thermal-oxidative stability is negligible. BHA and BHT are volatile and relatively susceptible to oxidation [14] so that under the experimental conditions they can escape from the heated oil or are consumed by reaction with oxygen. The evaporation of BHA and BHT from the oil seems

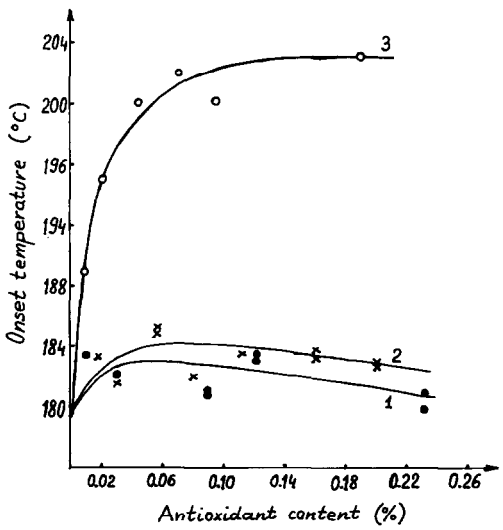

Fig. 5. The plots of DSC exotherm onset temperatures versus antioxidant content for RSO inhibited with: 1, BHA (●); 2, BHT (×); and 3, PG (○).

to be predominant. The PG incorporated in the RSO oil increases its t_{on} values by about 20 °C. As the thermal-oxidative stability of inhibited oils depends on both the base oil and the antioxidant used, a relationship between these two factors is often referred to as the activity of the antioxidant or as the response of the base oil on the antioxidant treatment. The increase of the t_{on} values due to inhibition can be interpreted as a measure of such activity or response, as illustrated in Fig. 5. A good antioxidant, if it passes health tests, should protect the oil or fat from autoxidation at low levels of treatment, usually below 0.05%. There are literature reports [18–20] that at relatively high concentrations of some phenolic-type antioxidants (e.g. BHA, tocopherols) their action on lipids can be inverted and they become pro-oxidants; therefore in this work more concentrated ($> 0.05\%$) model mixtures were also studied. No inversion in antioxidant action was found, although at concentrations $> 0.18\%$ of BHA and BHT, there was pronounced lowering of their efficiency.

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REFERENCES

1 I. Buzas, J. Simon and J. Holló, J. Therm. Anal., 12 (1977) 397.
2 I. Buzas, E. Kurucz and J. Holló, J. Am. Oil Chem. Soc., 56 (1979) 685.
3 M. Wesołowski, Sci. Pharm. (Wien), 54 (1986) 11.
4 M. Wesołowski, Seifen, Öle, Fette, Wachse, 112 (1986) 231.
5 M. Wesołowski, J. Therm. Anal., 32 (1987) 1781.
6 H. Lamparczyk and M. Wesołowski, Thermochim. Acta, 155 (1989) 327.
7 C.K. Cross, J. Am. Oil Chem. Soc., 47 (1970) 229.
8 R.L. Hassel, J. Am. Oil Chem. Soc., 53 (1976) 179.
9 A. Raemy, J. Froelicher and J. Loeliger, Thermochim. Acta, 114 (1987) 159.
10 B. Kowalski, Acta Aliment. Pol., 14 (1988) 195.
11 B. Kowalski and B. Kot, Acta Aliment. Pol., 15 (1989) 55.
12 B. Kowalski, Thermochim. Acta, 156 (1989) 347.
13 B. Kowalski, Thermochim. Acta, 173 (1990) 117.
14 B. Kowalski, Thermochim. Acta, 177 (1991) 9.
15 B. Kowalski, Int. J. Food Sci. Technol., 24 (1989) 415.
16 B. Kowalski, Właściwości Wody w Produktach Spożywczych; II Ogólnopolskie Seminarium, Puszczykowo, 8-10 Maja 1990, Wydawnictwo SGGW-AR, Warsaw, 1990, str. 81–87. (Water Properties in Food Products; 2nd Polish Seminar, Puszczykowo, 8–10 May 1990, Warsaw Agricultural University Press, Warsaw, 1990, pp. 81–87).
17 B. Kowalski and A. Orzeszko, Materiały XIX Sesji Naukowej, Postepy Technologii w Rozwoju Produkcji Zywności, Komitet Technologii i Chemii Zywności, Polska Akademia Nauk, Szczecin, 1988, str. 45. (Proc. 19th Scientific Session, Progress in Development of Food Production Technology, Committee of Food Technology and Chemistry, Polish Academy of Sciences., Szczecin, 1988, p. 45.).

18 C. Pietrzyk, Wpływ Steżenia Inhibitorów na Szybkość Autooksydacji Tłuszczów Jadalnych, Zeszyty Naukowe Politechniki Szczecinskiej – Prace Monograficzne, 37 (1962) 1–52. (The Influence of Inhibitors Concentration on the Rate of Autoxidation of Edible Fats, Scientific Publications of Szczecin Technical University – Monographs, 37 (1962) 1–52.).
19 J. Cillard, P. Cillard, M. Cormier and L. Girre, J. Am. Oil Chem. Soc., 57 (1980) 252.
20 J. Cillard, P. Cillard and M. Cormier, J. Am. Oil Chem. Soc., 57 (1980) 255.