ELSEVIER Thermochimica Acta 250 (1995) 197-205

thermochimica
acta

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Specific heats and kinetic parameters of thermo-oxidative decomposition of peanut oil

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Received 28 March 1994; accepted 15 June 1994

Abstract

The kinetics of thermo-oxidative decomposition of peanut oil have been investigated using a Du Pont differential scanning calorimeter. The measurements were carried out under dynamic conditions in an atmosphere of oxygen. The activation energy of oxidation of the oil is calculated using the Kissinger and ASTM methods. The specific heats of peanut oil have been measured at 70–140°C.

Keywords: Decomposition; DSC: Kinetics; Oil; Peanut oil; Specific heat

1. Introduction

The increasing production and consumption of edible oils has led to a great interest in the determination of their oxidative stability under various conditions. Auto-oxidation of oils and fats is one of the most important problems in storage and technology of food.

Because of lower contents of phospholipids and dye stuffs than in other oils, peanut oil can be easily refined and is one of the most valuable edible oils.

Peanut oil triacylglycerols contain eight fatty acids in concentrations equal to or greater than about 1%. Oleic and linoleic acid account for 75–80% of all fatty

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SSDI 0040-6031(94)01941-9

acids. The unsaturated fatty acids/saturated fatty acids ratio of 1.8 is lower in comparison with soybean oil (2.9) and corn oil (4.3) and higher than 0.5 for olive oil. As in most vegetable oils the biggest part of saturated fatty acids is located in position 1 or 3 or triacylglycerols.

Oxidative decomposition of oils and fats can occur in two ways. The radical mechanism of auto-oxidation has been the subject of many publications and books [1-4]. The above-mentioned process may be evoked by solar or thermal energy or some enzymes. Another way is oxidation of oil by oxygen in the singlet state after activation with $h\nu$ or metal ions, in which the oxygen reacts rapidly with unsaturated acyl groups creating hydroperoxides [4,5]. It is suspected that singlet state oxygen plays an important part in the initiation of radical oxidation of fatty acids.

The considerable progress made in thermal analysis is very helpful in the study of exo- and endothermal processes. The investigation of thermo-oxidation requires immediate and highly precise measurements of the amount of the emitted heat and related parameters. DSC is a very suitable method for collecting and presenting the data. In this paper the thermal oxidation of peanut oil has been investigated under dynamic conditions based on applying different linearly programmed heating rates. The temperatures of the onset points and peak maxima were then used to compute the kinetic parameters.

Apart from the kinetic data the scanning calorimeter can deliver important information about the specific heat of the measured medium, which is crucial for our investigation of peanut oil and is very helpful in elucidating its deep frying properties and other similar processes.

2. Experimental

2.1. Oil

Commercial peanut oil was used in the investigation. The iodic and saponification numbers of peanut oil were determined in accordance with Polish standard [6]. The fatty acid composition of the sample were determined by GLC [7]. The refractive index n_D^{20}, iodic number, saponification number and fatty acid composition of the peanut oil are listed in Table 1. In order to avoid uncontrolled auto-oxidation of oil it was kept in an atmosphere of nitrogen in darkness.

2.2. Apparatus and experiments

A Du Pont 910 differential scanning calorimeter with a Du Pont 9900 thermal analyzer and a normal pressure cell were used in dynamic method measurements. Calibration of the apparatus was carried out with a high-purity indium standard.

Oil samples (2-4 mg) were placed in aluminium sample pans and heated at rates of 4 K min^{-1}, 5 K min^{-1}, 7.5 K min^{-1}, 10 K min^{-1} or 12.5 K min^{-1} in a DSC cell. The reference aluminium pan (which was as nearly identical as possible to the

Table 1
Parameters and fatty acid composition of peanut oil

Parameter	Value	
	This work	Literature
Refractive index, n_D^{20}	1.4662	
Iodic number	96.0	84–104 [13]
Saponification number	193.0	188–195 [13]
Fatty acids C_m^n/% [a]		
C_{16}^{0}	10.0	6–12 [14]
C_{18}^{0}	4.0	2–4 [14]
C_{18}^{1}	53.0	42–72 [14]
C_{18}^{2}	18.0	13–28 [14]
C_{20}^{0}	1.65	1.25–1.88 [15]
C_{20}^{1}	1.18	5– 7 [14]
C_{22}^{0}	2.96	2.16–3.59 [15]
C_{22}^{1}	0.98	1 [16]
C_{24}^{0}	1.48	0.98–1.67 [15]

[a] *m* is the number of carbon atoms and *n* is the number of double bonds.

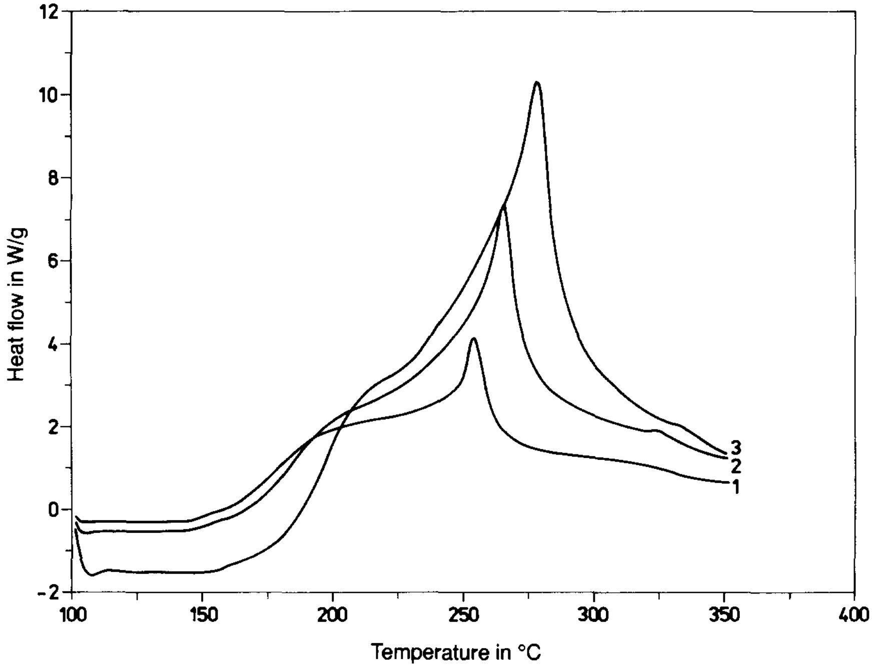

Fig. 1. Thermograms of peanut oil: curve 1 heating rate 5 K min^{-1}; curve 2, heating rate 7.5 K min^{-1}; curve 3, heating rate 12.5 K min^{-1}.

Table 2
Temperature values obtained from DSC curves

β/ (K min^{-1})	T_{ON1}/ K	T_{PEAK1}/ K	T_{ON1}/ K	T_{PEAK2}/ K
4.0	421.58	462.10	489.16	510.16
5.0	431.84	469.34	512.23	524.18
7.5	437.06	470.95	519.92	538.69
10.0	445.41	479.68	513.15	543.40
12.5	450.00	482.95	518.63	551.82

sample pans) was left empty. Experiments were performed in an atmosphere of oxygen at a gas flow rate of 15 lh^{-1}

A typical curve for peanut oil is shown in Fig. 1. The values of the points T_{ON1}, T_{ON2}, T_{PEAK1} and T_{PEAK2} are listed in Table 2. These values refer to the temperature of the maximal point of the two peaks (T_{PEAK1}, T_{PEAK2}) and their onset points (T_{ON1}, T_{ON2}). They were used to calculate the kinetic parameters by the Kissinger and ASTM methods [8,9].

To determine C_p for peanut oil, two dynamic experiments (heating rate 10 K min^{-1}) were performed. In the first, the instrument was operated under the desired conditions with empty sample and reference pans. In the second the sample was placed in one pan while the reference pan was left empty and both pans were closed with lids. The measurements were performed in an atmosphere of nitrogen. The difference between the blank and sample offset thermograms was used to calculate the specific heat at constant pressure. The C_p values are the averages of at least three determinations.

3. Results and discussion

Our experiments demonstrated the general rule that increasing the heating rate gives a higher peak temperature T_{PEAK}. For a constant heating rate, the values of the points T_{ON1}, T_{ON2}, T_{PEAK1} and T_{PEAK2} are characteristic for given substances. The maximum temperature occurs at a constant value of conversion and this fact can be used to determination the activation energy in two ways.

Putting values of T_{PEAK} or T_{ON} from Table 2 into the equation $\lg \beta = aT_{\mathrm{PEAK}}^{-1} + b$, where β is the heating rate, we found a linear dependence and coefficients a and b were calculated by means of the least squares method. The activation energy of the process was calculated from the equation

$$E = -2.19R\frac{\mathrm{d}\log\beta}{\mathrm{d}T_{\mathrm{PEAK}}^{-1}} \tag{1}$$

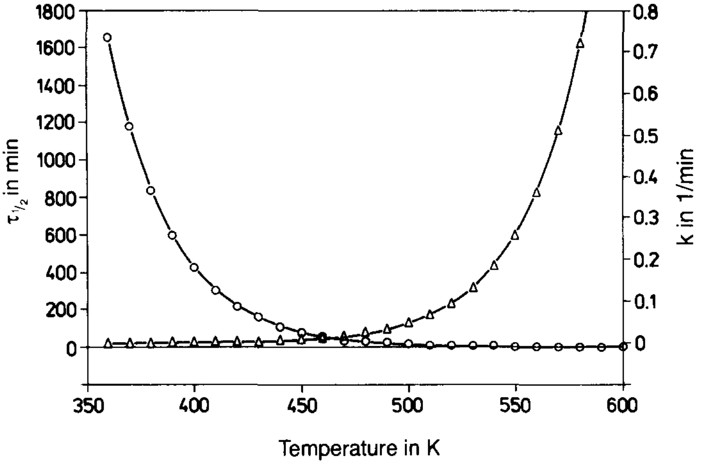

Fig. 2. The change in k/min^{-1} (△) and $\tau_{1/2}$/min (○) vs. temperature/K for peanut oil.

Table 3
Parameters calculated by the ASTM and Kissinger methods

Parameter	T_{ON1}/K	T_{PEAK1}/K	T_{ON2}/K	T_{PEAK2}/K
a	−3410.0	−5320.0	−3130.0	−3420.0
b	8.66	12.1	7.0	7.3
D	−6980.0	−11300.0	−6200.0	−6810.0
d	5.8	13.5	1.6	2.2
r [a,c]	0.98	0.97	0.75	0.98
r [a,d]	0.98	0.97	0.70	0.97
σ [b,c]	0.03	0.04	0.12	0.04
σ [b,d]	0.08	0.10	0.28	0.08
E/(J mol^{-1}) [c]	62.1	96.9	57.0	62.3
E/(J mol^{-1}) [d]	58.0	93.9	51.5	56.6

[a] r, Correlation coefficient. [b] Standard deviation. [c] Obtained by the ASTM method. [d] Obtained by the Kissinger method.

Introducing the $E = 62.2$ kJ mol^{-1} into the equation gives

$$Z = \frac{\beta E \exp[E/RT]}{RT^2} \tag{2}$$

and with $\beta = 7.5$ min^{-1} and $T_{\mathrm{PEAK}} = 538.69$ K we obtain $Z = 2.06 \times 10^5$ min^{-1}. Parameters Z, T and E were used to predict the series of specific rate constants from the Arrhenius equation $k = Z \exp[-E/RT]$ for the temperatures 360 K to 550 K and the half-time for the first order reaction calculated from

$$\tau_{1/2} = \frac{\ln 2}{k} \tag{3}$$

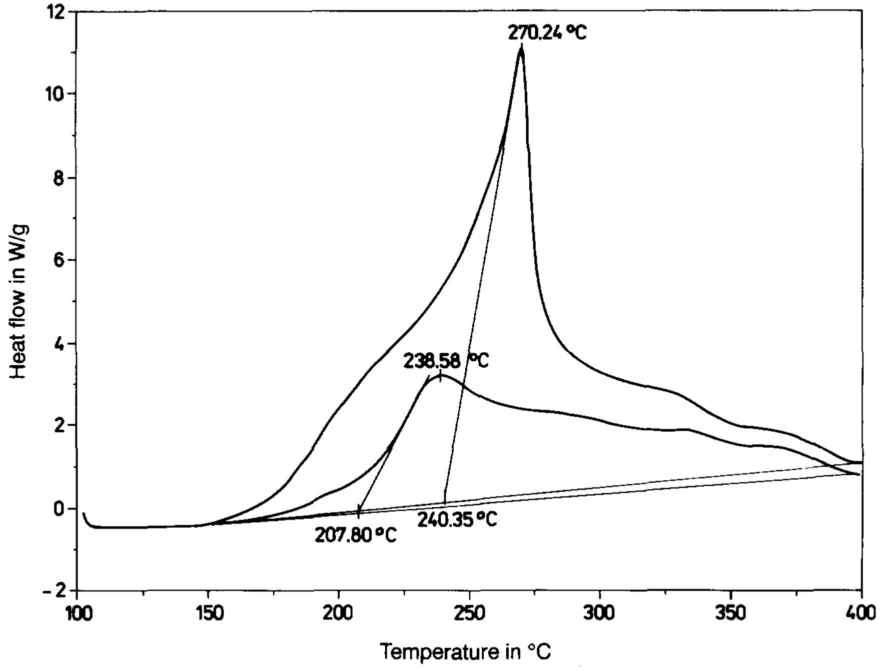

Fig. 3. Comparison of DSC curves for fresh (top line) and aged (bottom line) peanut oil.

Values k and $\tau_{1/2}$ versus temperature for the peak temperature–heating rate relationship are shown in Fig. 2.

The other method used for investigating the oil is the Kissinger method, in which there is a linear relationship between the values of T_{PEAK}^{-1} and $\ln(\beta/T_{\mathrm{PEAK}}^{2})$ which is also valid for T_{ON}

$$\ln\frac{\beta}{T^2} = -D\frac{1}{T} + d \tag{4}$$

where $D = -E/R$, d is a coefficient and T is either T_{PEAK} or T_{ON}. Results of our calculation using both ASTM and Kissinger methods are given in Table 3.

That the observed reaction was first order was verified by the thermoanalytical procedure described in Ref. [10]. The sample of peanut oil was aged at 440 K for 1 h (which is the half-time for this temperature calculated from Eq. (3) under an atmosphere of oxygen flowing at a rate 15 l h^{-1}. Next the aged oil sample was quickly cooled and in the second step the previous conditions of heating were changed to dynamic, with a heating rate of 10 K min^{-1}. The integrated peak area of aged oil was 47% of the area obtained for the fresh oil under the same dynamic conditions, as is shown in Fig. 3, and this is in good agreement with the expected value of 50% for a first order reaction.

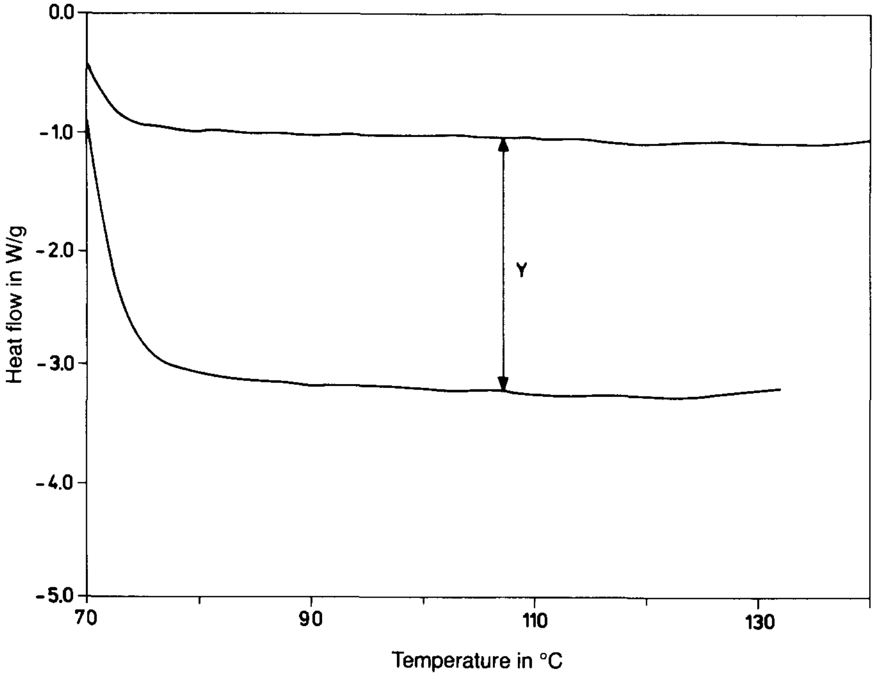

Fig. 4. Blank (top line) and sample (bottom line) DSC scans for peanut oil. Heating rate 10°C min^{-1}.

The specific heats of the peanut oil from 70 to 140°C were calculated from

$$C_p J\ K^{-1}\ g^{-1} = \frac{60CY}{H_r m} \tag{5}$$

where C_p is the specific heat, C is the coefficient of cell calibration, H_r is the heating rate in °C min^{-1}, Y is the measured difference in the positions of the blank/sample thermograph in mW at the desired temperature and m is the sample mass in mg; see Fig. 4. All the experimental values of C_p are listed in Table 4. They were correlated with the equation

$$C_p = -29.668 + 0.229T - 5.42 \times 10^{-4}T^2 + 4.24 \times 10^{-7}T^3 \tag{6}$$

adjusted by means of the least squares method.

It follows from the experiment that for peanut oil the specific heat did not vary substantially in the temperature range studied and changes of specific heat can be neglected during oxidation of oil in the DSC experiment. Our values of C_p are similar to the data reported for other edible oils [11,12], but because of the specific character of the investigated material it is not possible to compare it directly with the literature data.

The activation energy for the first peak (T_{PEAK1}) or for the first onset point (T_{ON1}) is higher than for the second one. If we consider that the investigated oil is

Table 4
Experimental specific heat values (C_p) and those calculated from Eq. (6) for peanut oil

Temperature/K	$C_p/(\mathrm{J\ K^{-1}\ g^{-1}})$	
	Exp.	Calc.
343	2.232	2.226
348	2.264	2.269
353	2.291	2.295
358	2.314	2.316
363	2.333	2.343
368	2.347	2.332
373	2.358	2.358
378	2.365	2.359
383	2.370	2.369
388	2.371	2.374
393	2.371	2.377
398	2.368	2.376
403	2.363	2.357
408	2.357	2.350
413	2.350	2.353

a mixture of saturated and unsaturated triacylglycerols and their derivatives, it seems probable that the activation energy calculated for the first peak corresponds to the auto-oxidation of saturated compounds which requires more energy to start the process, while the second peak is associated with the oxidation of unsaturated compounds.

Because of higher contents of unsaturated fats and difficulties in determining T_{PEAK1} and T_{ON2} the activation energy for T_{PEAK2} is more representative for the thermo-oxidative decomposition of peanut oil.

In order to verify this suggestion further investigation, especially analytical measurement of reaction progress for saturated and unsaturated ingredients of oil, seem to be necessary.

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