

## Thermoanalytical investigation of edible oils

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### Abstract

The kinetics of thermo-oxidative decomposition of linseed, olive, castor and cod-liver oils have been investigated using a Du Pont differential scanning calorimeter by the Kissinger (Anal. Chem., 29 (1957) 1702) and ASTM (ANSI/ASTM E 698-79, 1979, standard method for Arrhenius kinetic constants for thermally unstable materials) methods.

### INTRODUCTION

The basic assumption in treating DSC data is that the heat of reaction evolved at any time is proportional to the amount of reactants consumed [1–3]. The Arrhenius rate equation [4] is

$$\frac{1}{H_T} \frac{dH}{dt} = Z e^{-E/RT} \left( \frac{H_T - H}{H_T} \right)^n \quad (1)$$

where  $H_T$  is the total heat evolved in the process (equal to the area under the DSC curve),  $H$  the heat of reaction evolved at the given time and temperature (equal to the partial area under the DSC curve),  $Z$  the pre-exponential factor,  $n$  the order of reaction,  $R$  the gas constant,  $T$  the temperature (K) and  $E$  the activation energy ( $\text{kJ mol}^{-1}$ ). Differentiating eqn. (1) with respect to time  $t$  and setting the value equal to zero leads to

$$\frac{E}{n} = \left( \frac{RT^2}{H_T \beta} \right) \frac{dH}{dt} \quad (2)$$

where  $H_T = H_T - H$  and  $\beta = dT/dt$ .

Comparing data obtained from different scans (different  $\beta$  values) at the constant degree of conversion  $H/H_T$ , we can plot  $dH/H dt$  vs.  $1/T$  and obtain a straight line whose slope equals  $-E/R$

$$\left[ \frac{\Delta \ln(dH/H_T dt)}{\Delta 1/T} \right]_{H/H_T} = \frac{-E}{R} \quad (3)$$

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For different  $\beta$  values, the maximum temperature occurs at a constant value of conversion  $H/H_T$ . Using eqns. (2) and (3) and assuming that  $E$ ,  $n$  and  $H_T/H_T$  are independent of the change in maximum temperature, we obtain

$$\frac{\Delta \ln(\beta/T_{mp}^2)}{\Delta(1/T)} = \frac{-E}{R} \quad (4)$$

The other method used for investigating the oils is the ASTM method [5]. We can assume that



By recording the heat flow liberated during the process, we can determine the temperature of the onset point,  $T_{on}$  (extrapolated to the beginning of the process) and the maximum heat flow temperature,  $T_{mp}$ . For a constant value of  $\beta$ ,  $T_{mp}$  and  $T_{on}$  are characteristic for given substances. It was proved that the fraction reacted at  $T_{mp}$  is constant, irrespective of the heating rate [6,7].

The recorded values of  $T_{on}$  and  $T_{mp}$  for different values of  $\beta$  can be described by

$$\log \beta = aT_{mp}^{-1} + b \quad (5)$$

The approximate value for  $E'$  can be calculated as follows:

$$E' = 2.19R \frac{d \log \beta}{dT_{mp}^{-1}} \quad (6)$$

The Arrhenius pre-exponential factor can be calculated from

$$Z = \frac{\beta E e^{E/RT}}{RT_{mp}^2} \quad (7)$$

where  $\beta$  and  $T_{mp}$  are taken from the middle of the range.

## EXPERIMENTAL

A Du Pont 9900 thermal analyser and a Du Pont 910 differential scanning calorimeter equipped with a pressure cell were used. The apparatus was calibrated using high purity indium. The investigated substances were commercial linseed, olive, castor and cod-liver oils. Their iodine, acidic and peroxide numbers were determined in accordance with the Polish standard [8]. In order to avoid uncontrolled auto-oxidation of oils they were kept in an atmosphere of nitrogen in darkness.

In order to investigate these oils by means of the above described dynamic methods, the following procedure was followed. Some oil samples of strictly determined masses (5–10 mg) were heated at rates of 4–25 K

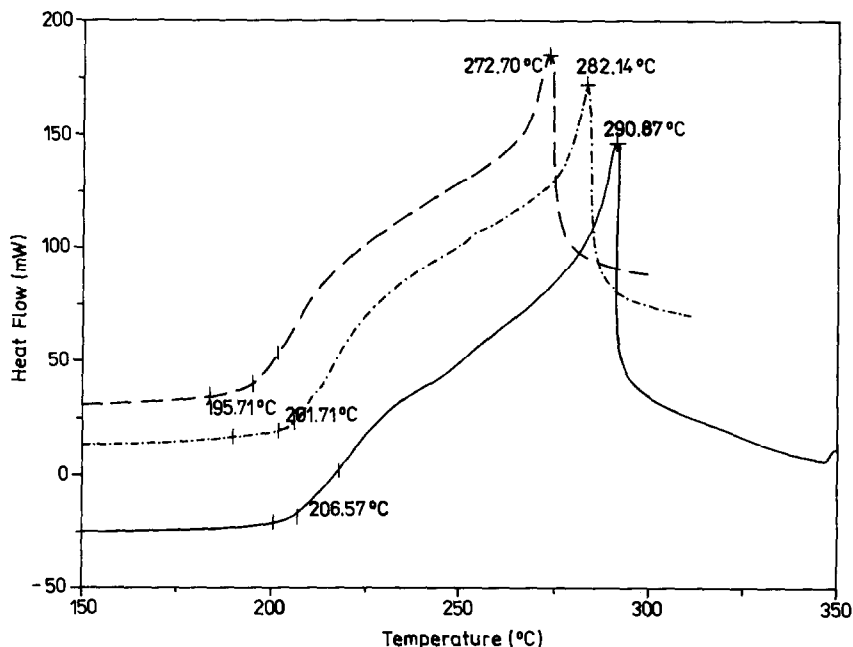


Fig. 1. Thermograms of castor oil (6.5 mg): solid line 10, K min<sup>-1</sup>; dash-dot line, 7.5 K min<sup>-1</sup>; broken line, 5 K min<sup>-1</sup>.

min<sup>-1</sup> in a PDSC cell (oxygen pressure 3 atm. flow 6 l/h<sup>-1</sup>). Figures 1–4 show thermograms obtained in the experiments. The values of the points  $T_{mp1}$ ,  $T_{mp2}$ ,  $T_{on1}$  and  $T_{on2}$  are listed in Table 1. These values refer to the temperature of the maximal point of the peak, or of the two peaks if a second one was present ( $T_{mp1}$ ,  $T_{mp2}$ ) and their onset points ( $T_{on1}$  and  $T_{on2}$ ) which are related to the extrapolated beginning of the given process. Using these points, the straight line equation was determined from eqn. (5) above, where  $a$  and  $b$  are coefficients calculated by means of the least-squares

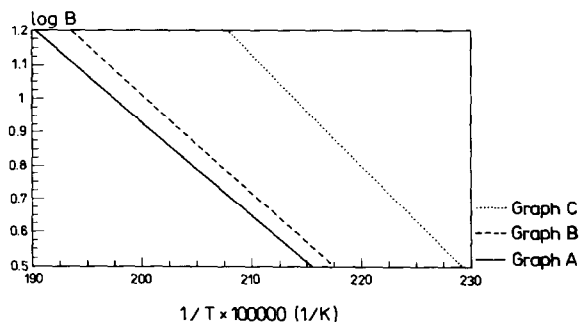


Fig. 2. Log  $\beta$  vs. reciprocal temperature (K<sup>-1</sup>) for linseed oil using the ASTM method. Curve A,  $T_{mp2}$ ; curve B,  $T_{on2}$ ; curve C,  $T_{mp1}$ .

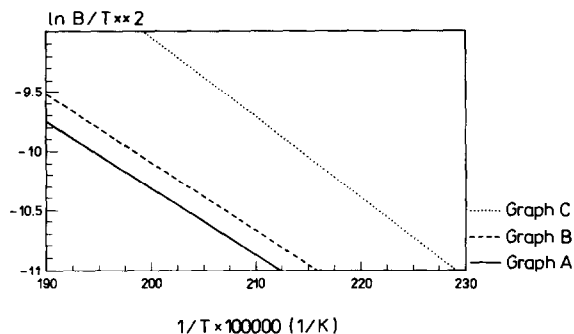


Fig. 3.  $\log D$  vs. reciprocal temperature ( $K^{-1}$ ) for linseed oil using the Kissinger method. Curve A,  $T_{mp2}$ ; curve B,  $T_{on2}$ ; curve C,  $T_{mp1}$ .

method,  $\beta$  is the heating rate ( $K \text{ min}^{-1}$ ) and  $T$  the temperature of one of the four points.  $T_{mp1}$ ,  $T_{mp2}$ ,  $T_{on1}$  or  $T_{on2}$ . The coefficients  $a$  and  $b$  for all the points are listed in Tables 2 and 3 (Figs. 2–4 for linseed oil). The activation energy  $E'$  was calculated for  $T_{mp2}$  using eqn. (6).

The value of  $E'$  was corrected according to the procedure described in ref. 9. Corrected activation energy values ( $E$ ) were used for pre-exponential factor calculation (eqn. (7)). Values of  $E$ ,  $a$ ,  $b$  and  $Z$  are listed in Table 2. Parameters calculated from the peak temperature–heating rate relationship were used to predict the specific reaction rate constant from the Arrhenius equation [10,11]

$$k = Z e^{-E/RT} \quad (8)$$

and the half-life time for the first-order reaction

$$\tau_{0.5} = \frac{0.693}{k} \quad (9)$$

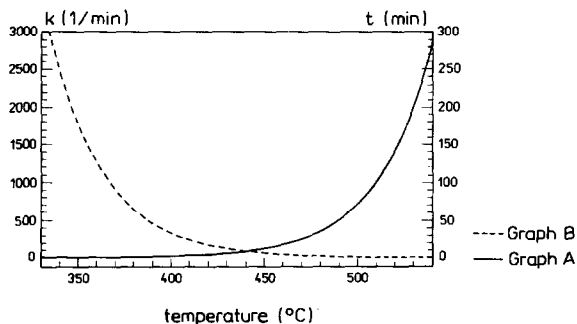


Fig. 4. The change in  $k$  ( $\text{min}^{-1}$ ) and  $\tau_{1/2}$  (min) vs. temperature ( $^{\circ}\text{C}$ ) for linseed oil. Curve A,  $k$ ; curve B,  $\tau_{1/2}$ .

TABLE 1

Temperature values obtained from DSC curves

Heating rate (K min <sup>-1</sup> )	$T_{on1}$ (K)	$T_{mp1}$ (K)	$T_{on2}$ (K)	$T_{mp2}$ (K)
<b>Linseed oil</b>				
10.0	432.9	467.3	500.0	507.6
7.5	425.5	458.7	483.1	490.2
5.0	421.9	448.4	478.5	483.1
4.0	418.0	440.5	475.5	478.6
<b>Cod-liver oil</b>				
10.0	420.2	452.5	518.1	531.9
7.5	418.2	446.4	515.5	526.3
5.0	409.8	438.6	497.5	510.2
<b>Castor oil</b>				
10.0	483.1	–	531.9	565.5
7.5	473.9	–	546.4	555.5
5.0	469.5	–	537.6	546.4
4.0	465.4	–	531.2	540.0
<b>Olive oil</b>				
20.0	–	–	558.6	578.0
17.5	–	–	561.8	581.4
15.0	–	–	543.5	565.0
7.5	–	–	531.9	540.5

The first order of the investigated reaction was verified by means of the thermoanalytical procedure [5,9]. The oil sample was aged at the selected temperature for the predicted half-life time. The aged sample was then

TABLE 2

Parameters calculated by means of the ASTM and Kissinger methods

Parameters	Linseed oil	Castor oil	Olive oil	Cod-liver oil
$a$	-2797.5	-4466.7	-3145.6	-3538.4
$b$	6.5	8.6	6.7	7.6
$D$	-5384.0	-10499.2	-6074.0	-7173.0
$d$	0.5	8.2	0.7	3.2
$\sigma$	0.05	0.06	0.20	0.05
$\sigma^a$	0.13	0.04	0.10	0.07
$Z$ (min <sup>-1</sup> )	$6.3 \times 10^5$	$3.9 \times 10^6$	$2.0 \times 10^4$	$1.0 \times 10^4$
$E^a$ (kJ mol <sup>-1</sup> )	56.3	77.0	74.9	59.7
$E^b$ (kJ mol <sup>-1</sup> )	44.7	87.2	84.8	64.4

<sup>a</sup> Obtained by the ASTM method.

<sup>b</sup> Obtained by the Kissinger method.

TABLE 3

Coefficients of straight lines for the two methods investigated

Coef- ficient	Point on ther- mogram	Linseed oil	Castor oil	Olive oil	Cod-liver oil
<i>a</i>	$T_{on1}$	-4750.0	-4750.0	-	-4483.9
	$T_{mp1}$	-3336.1	-	-	-4883.8
	$T_{on2}$	-2947.8	-5000.0	-3776.1	-3265.5
	$T_{mp2}$	-2797.5	-4466.7	-3145.6	-3538.4
<i>D</i>	$T_{on1}$	-10030.3	-10007.1	-	-9584.8
	$T_{mp1}$	-6795.1	-	-	-9013.5
	$T_{on2}$	-5746.3	-10500.0	-7517.4	-6552.6
	$T_{mp2}$	-5384.0	-10499.2	-6074.0	-7173.3
<i>b</i>	$T_{on1}$	12.0	10.8	-	11.6
	$T_{mp1}$	8.2	-	-	18.5
	$T_{on2}$	7.0	10.0	8.0	7.2
	$T_{mp2}$	6.5	8.6	6.7	7.6
<i>d</i>	$T_{on1}$	13.4	10.8	-	12.9
	$T_{mp1}$	4.6	-	-	10.0
	$T_{on2}$	1.4	30.0	3.7	2.3
	$T_{mp2}$	0.5	8.2	0.7	3.2
Max. error in ASTM method	$T_{on1}$	0.04	0.04	-	0.04
	$T_{mp1}$	0.02	-	-	0.01
	$T_{on2}$	0.06	0.01	0.09	0.05
	$T_{mp2}$	0.05	0.06	0.05	0.03
Max. error in Kissinger method	$T_{on1}$	0.10	0.10	-	0.10
	$T_{mp1}$	0.01	-	-	0.001
	$T_{on2}$	0.15	0.20	0.20	0.10
	$T_{mp2}$	0.13	0.04	0.10	0.07

heated at  $10 \text{ K min}^{-1}$ . The peak area of the aged sample appeared to be approximately half that for the unaged sample (Fig. 5). This relation proved that the auto-oxidation process is a first-order reaction. In the Kissinger method, the coefficient  $D$  is equal to  $-E/R$ . The data in Table 1 were used to calculate the activation energy  $E$  (Table 2).

## RESULTS AND DISCUSSION

The parameters obtained prove that the activation energy for the first peak ( $T_{mp1}$ ) or, if that did not occur, for the first onset point,  $T_{on1}$  is higher than for the second one. It is very probable that the first recorded thermal effect corresponds to the auto-oxidation of saturated compounds which require more energy for undergoing such a process than do unsaturated compounds. Of course, the recorded thermal effects can be considered only

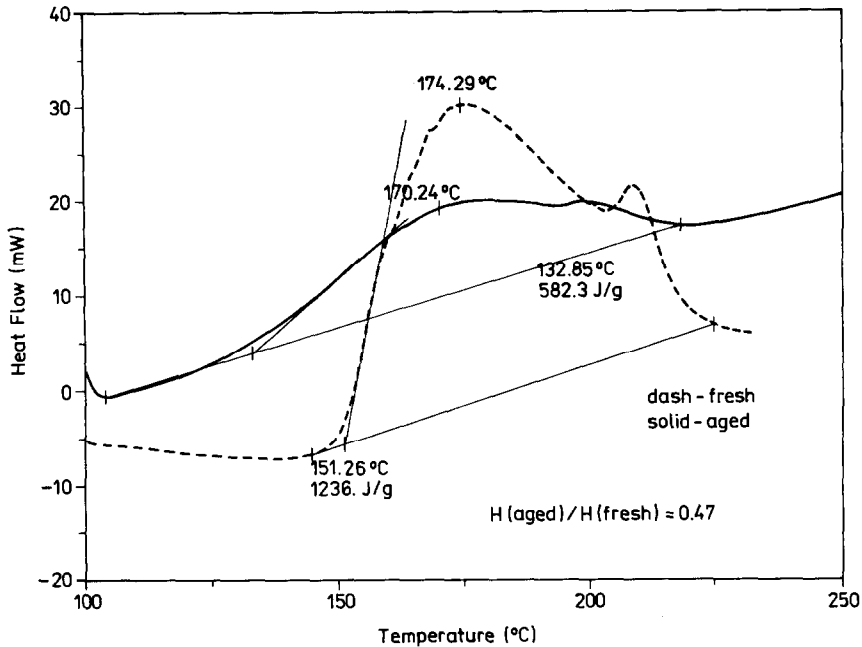


Fig. 5. The comparison of DSC curves for fresh (dashed) and aged (solid) linseed oil.

as the results of some different reactions; thus it is impossible to determine unequivocally the origin of a peak.

A literature survey concerning the investigated oils [5] revealed results agreeing with our measurements, i.e. lower activation energies for the second peak, this proves that the auto-oxidation of unsaturated compounds is associated with the second peak. Therefore the activation energy for  $T_{mp2}$  and  $T_{on2}$  is much more representative of the thermo-oxidative decomposition of fats, especially if we consider that the investigated oils are largely composed of unsaturated compounds. Taking into account the shape of the second peak (very sharp maximum) and the temperature–time plot of the sample, the following conclusion can be drawn: the second peak corresponds to the thermal effect associated not only with the auto-oxidation of the oils, but also with a thorough destruction of the lipids. This latter process can also be facilitated by an abrupt temperature increase of the sample. This rise in temperature is associated with the exothermicity of the process and with problems to do with the rapid removal of heat from the investigated sample.

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