

## THERMOANALYTICAL INVESTIGATIONS OF EDIBLE OILS AND FATS

### I. KINETICS OF THERMAL-OXIDATIVE DECOMPOSITION OF RAPESEED OIL

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Key words: edible oils, rape seed oil, kinetics of oxidation, thermal analysis, differential scanning calorimetry.

Experiments with rapeseed oil using the differential scanning calorimeter have been carried out. From DSC traces obtained at different heating rates the peak maximum temperatures were selected and used for calculation of kinetic parameters and Arrhenius activation energy of thermal-oxidative decomposition of oil.

#### INTRODUCTION

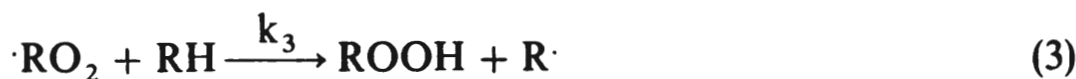
The autoxidation of edible oils and fats is one of the most important problems in storage and processing technology of fat containing food. The free radical mechanism of autoxidation has been well documented in many papers starting with the Farmer's school work [5, 6] and there are several books and review articles covering this problem [7, 12, 17, 18, 24]. At normal or subambient temperature the autoxidation reaction rate is relatively low but at elevated temperature and a sufficiently high partial pressure of oxygen the rate of autoxidation increases strongly [9]. When fats or oils are heated well above 400 K or 500 K, as in deep frying or cooking, one may expect their fast thermal oxidation and possible oxypolymerization or thermal destruction [10, 11, 20]. It is the purpose of this series of papers to investigate the kinetic features of thermal-oxidative decomposition of edible oils and fats and the presented paper is the first in this series.

#### THEORY

Despite the varied composition of various oils and fats the development of their oxidation as a chain reaction can be described by the common set of equations for RH fat molecules:



where  $R\cdot$  shown on the right side of the equation (1) is assumed to result from either a chain transfer step of  $RO\cdot$  with  $RH$  or by selfdismutation of  $RO\cdot$  to  $R\cdot$



At high partial pressure of oxygen  $p_{O_2} \gg 13$  kPa, and only such cases were considered in this paper, steps (4) and (5) can be neglected and as the product of  $k_2 k_3^{-1}$  is of the order of  $10^4$ - $10^6$  which means that the concentration of the radicals ( $R\cdot$ ) is very low compared with that of ( $RO_2\cdot$ ), only the reaction (6) is relevant for the termination step. If oxidation is performed at high oxygen concentration, in pure oxygen in extremal case, using the so-called Bodenstein's steady state principle (1), which is obtained through generalizations and simplified assumptions, according to which in the autoxidation process

$$\frac{d(R\cdot)}{d\tau} = \frac{d(\cdot RO_2)}{d\tau} = 0 \quad (7)$$

where  $\tau$  denotes time, we can get the rate of uninhibited reaction ( $r_u$ ) at oxygen saturation

$$r_u = (r_i/k_6)^{1/2} k_3 [RH] \quad (8)$$

where  $r_i$  denotes the rate of reaction (1). The equation (8) is of paramount importance. It shows that at conditions mentioned above the reaction rate is independent of the oxygen concentration and what is more the oxidation of bulky fat can be treated as a first order reaction with respect to concentration of fat especially at the initial step when the forming of secondary products of thermal-oxidation or destruction is of minor importance.

The oxidation kinetics according to equation (11—16) has been investigated for years and the experimental designs were based mainly on analytical methods (determination of peroxide concentrations) or on volumetrical methods in which the rate of oxygen consumption is measured. Relatively less attention was paid to the indirect methods such as measurement of the intensity of chemiluminescence or measurement of the enthalpy changes by calorimetry or thermal analysis. The lack of commercial apparatuses for chemiluminescence measurements is the main reason of the fact that this method has not yet gained popularity. On the other hand, however, the very fast development in thermal analysis methods and apparatuses make it possible to use them for an investigation of oils and fats

[3, 14, 21]. The above listed reactions (2) and (3) are obviously exothermal. It is the sensitivity and capability of the thermal instrument to measure with high precision the amount and/or rate of heat evolved or related parameters that determine the possibility of using the thermo-analytical method for an investigation of the thermal oxidation kinetics. The method used in this paper is based on DCS experiments in which the peak maximum temperature  $T_{\text{peak}}$  on the resulting heat flow curves are determined for exothermal reactions. Several experiments are usually performed at different linearly programmed heating rates and the temperature shift of the peak maximum is used to compute the kinetic parameters. The calculations are based on three assumptions:

1. For each heating rate  $\beta$  the DCS peak maximum represents a system of constant conversion.

2. The temperature dependence of specific rate constant  $k$  is described by Arrhenius equation

$$k = Z e^{-E/RT} \quad (9)$$

where  $Z$  is the pre-exponential factor,  $E$  is Arrhenius activation energy,  $R$  is the gas constant and  $T$  absolute temperature.

3. The reaction is of the first order and can be described by the general rate equation

$$\frac{dc}{d\tau} = k(1-c)^n \quad (10)$$

where:  $n = 1$ ,  $c$  is fractional conversion and  $\tau$  is time. The details of the method are described in relevant publications [2, 4, 8, 15, 19].

## EXPERIMENTAL

### MATERIALS

Commercial rapeseed oil was used. Oil's samples were purchased on the local market. For these samples peroxide, iodine and acidic numbers were determined in accordance with Polish Standards [16]. There were no substantial differences between the different samples so that the selected one may be considered as typical. Its parameters and fatty acids composition determined by GLC are shown in Table 1. In order to prevent an uncontrolled autoxidation of oil it was kept under nitrogen in darkness.

### APPARATUS AND EXPERIMENTS

Du Pont 1090 B thermal analyzer with Du Pont 990 differential scanning calorimeter equipped with a normal pressure cell was used. The instrument was calibrated using high purity indium and tin metal standards. Oil samples weighing 3-4 milligrams were placed in aluminium sample pans and after being

Table 1. Parameters and fatty acids composition of rapeseed oil studies

Determination	Result
Peroxide number	5.0
Iodice number	123.0
Acid value	0.53
Fatty acids $^+ C_m^n$ : (%)	
$C_{14}^0$	0.09
$C_{16}^0$	4.12
$C_{16}^1$	0.30
$C_{18}^0$	1.35
$C_{18}^1$	51.32
$C_{18}^2$	22.95
$C_{18}^3$	1.55
$C_{20}^0$	8.03
$C_{20}^1$	3.28
$C_{22}^1$	6.98

\* m = number of carbon atoms

n = number of double bonds

inserted into the heating chamber of DSC cell they were heated at the rates of 4 K/min, 5 K/min, 7.5 K/min, 10 K/min and 20 K/min in a subsequent experiment. The aluminium reference pan, as identical as possible with sample pans was left empty. Studies were performed in an atmosphere of oxygen under oxygen gas flowing at the rate of  $85 \text{ cm}^3 \cdot \text{min}^{-1}$  or  $100 \text{ cm}^3 \cdot \text{min}^{-1}$ . For each programmed heating rate at least triplicate determinations were carried out. The course of experiment was continuously displayed on the instrument's monitor screen and recorded on 8-inch magnetic floppy-discs. When the run was completed the recorded data were analyzed by means of the apparatus internal computer and programmes loaded into Du Pont 1091 memory set which is an integral part of the instrument. The courses of experiments were also recorded by the plotter of the instrument. After the conclusion of each measuring cycle sample pans were carefully examined and reweighed.

## RESULTS AND CALCULATIONS

The typical scan obtained at the heating rate of 10 K/min is shown in Fig. 1, scans at other heating rates were similar but shifted versus the general rule; the higher the heating rate the higher the peak temperature. The DSC exothermal plots are asymmetrical but the position of peak maximum temperature  $T_{\text{peak}}$  can be obtained without any difficulty and corrected for temperature scale, heating rate and thermal lag what gives the final  $T_{\text{peak}}$  value. The Table 2 summarizes experimental results. The plot of  $\lg\beta$  versus  $T_{\text{peak}}^{-1}$  shows the linear dependence (Fig. 2) which has been described by the equation

$$\lg\beta = -3834.25 T_{\text{peak}}^{-1} + 8.28. \quad (11)$$

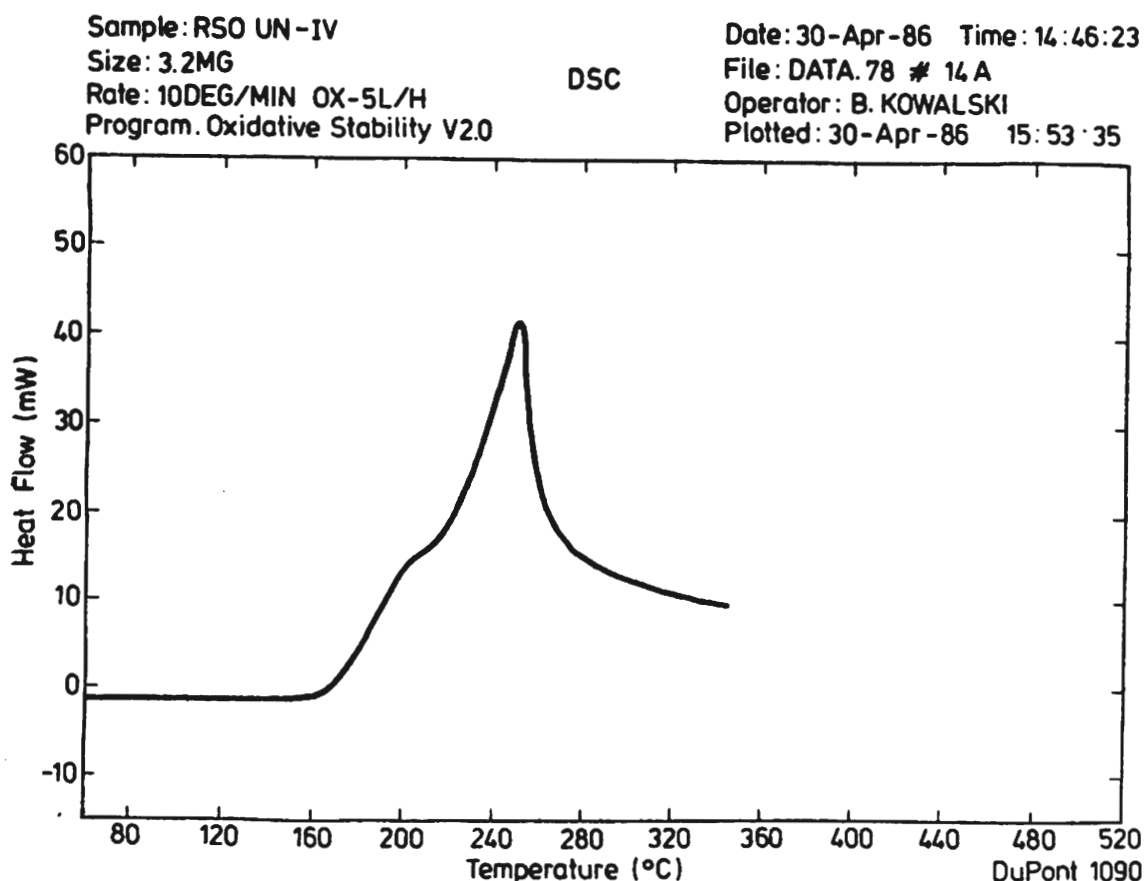


Fig. 1. DSC curve of thermal-oxidation of rapeseed oil; heating rate  $10 \text{ K} \cdot \text{min}^{-1}$ , oxygen flow  $85 \text{ cm}^3 \cdot \text{min}^{-1}$

Table 2. The results obtained for rapeseed oil in DSC experiments

Heating rate K/min	Corrected peak temperature ( $T-273.15$ )K	$1000.1/T_{\text{peak}}$ $\text{K}^{-1}$
20.0	276.6	1.819
10.0	253.0	1.901
7.5	244.6	1.931
5.0	232.4	1.978
4.0	226.6	2.001

Equation (11) describes the experimental results with the standard deviation  $\sigma = 0.0068$ . Taking into account the first assumption introduced in the general method of computation of parameters the equation can be written as follows:

$$E' = -2.19 R \frac{d \lg \beta}{dT_{\text{peak}}^{-1}} \quad (12)$$

where  $E'$  is approximate Arrhenius activation energy of the process. The solution of equation (12) was obtained from a calculation of the slope of the line in Fig. 2 followed by computer iterative calculations with  $\beta = 7.5 \text{ K/min}$  and  $T_{\text{peak}} = 517.75 \text{ K}$  to improve  $E'$  value until the final activation energy was obtained. The value of  $64800 \text{ J/mole}$  was obtained for activation energy as compared with  $E' = 69800 \text{ J/mole}$  calculated from a simple substitution of  $-3834.25$  to the

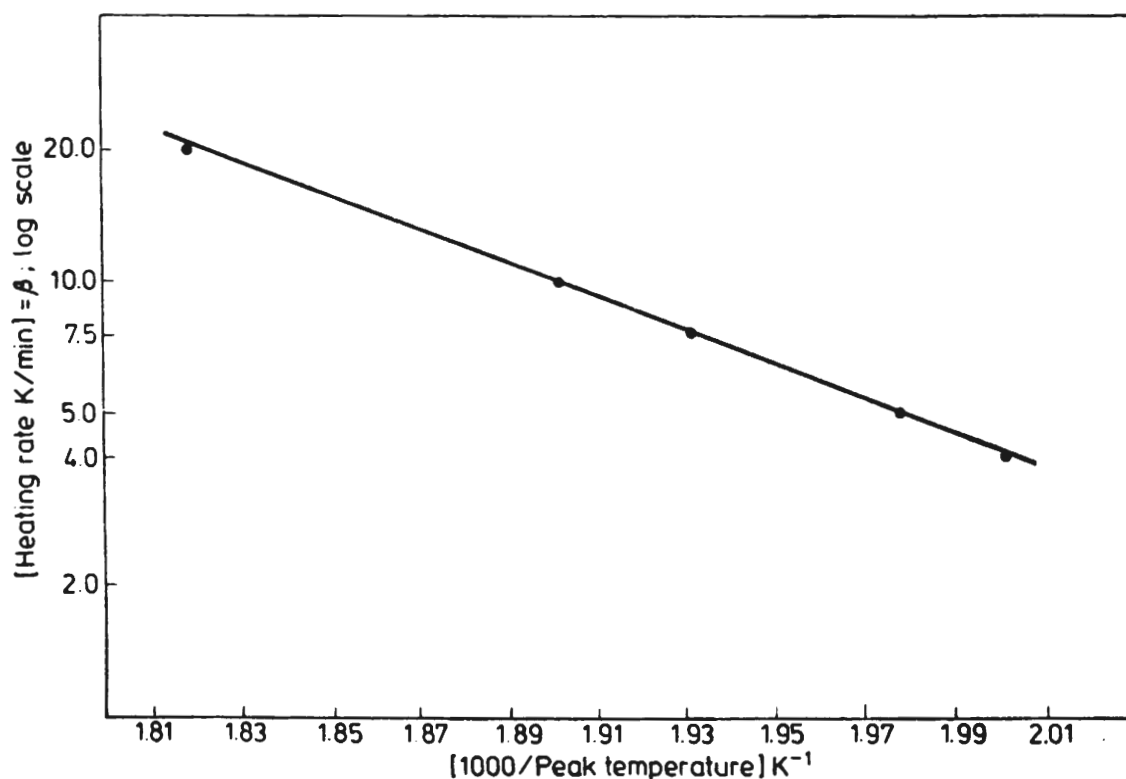


Fig. 2. Temperature shift of peak maximum of DSC curves for rapeseed oil versus  $\log \beta$ ;  $\beta = \text{heating rate K} \cdot \text{min}^{-1}$

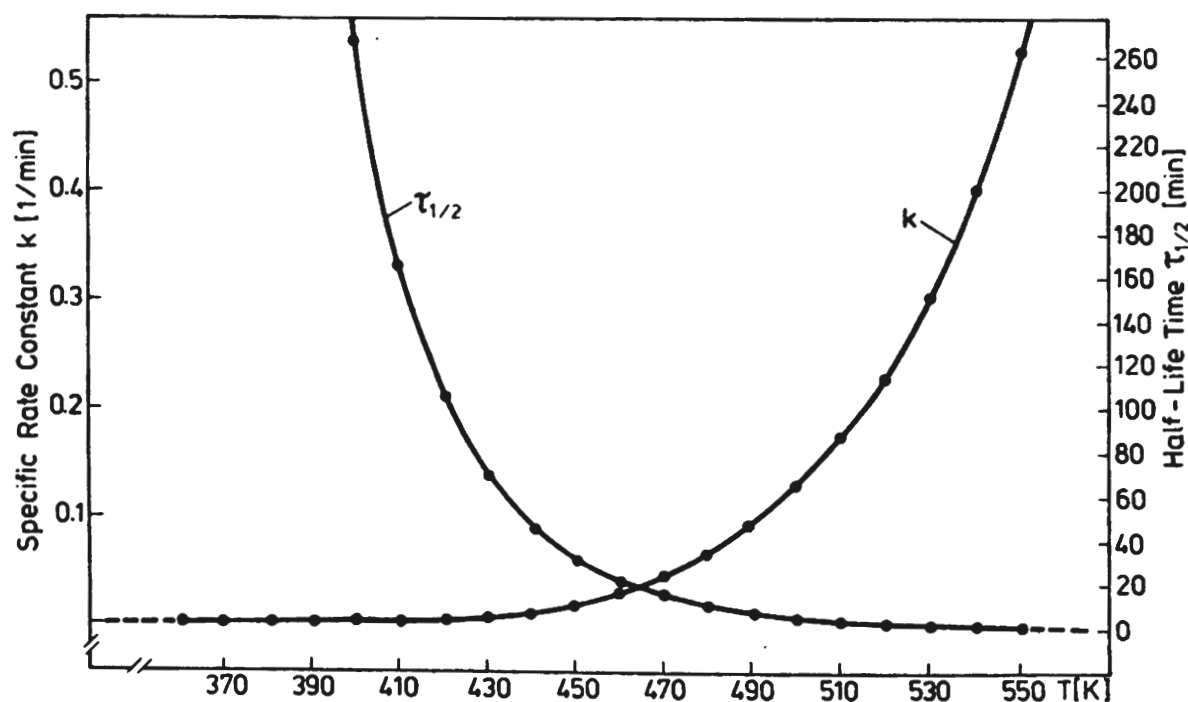


Fig. 3. Specific rate constant ( $k$ ) and half-life time  $\tau_{1/2}$  plots versus temperature for thermal-oxidation of rapeseed oil

equation (12). Having the activation energy, the pre-exponential factor  $Z = 7.5 \times 10^5 \text{ min}^{-1}$  was calculated according to:

$$Z = \frac{\beta E e^{E/RT}}{RT^2} \quad (13)$$

where  $\beta = 7.5 \text{ K/min}$  and  $T = 517.15 \text{ K}$ .

With the use of equation (9) the series of rate constants  $k$  for the temperature range of 360 K—550 K at 10 K steps was calculated and the results are shown in Fig. 3. For each  $k$  result the half-life time  $\tau_{1/2}$  of reaction was calculated from:

$$\tau_{1/2} = 0.693 k^{-1} \quad (14)$$

and the results are shown in Fig. 3.

### CONSISTENCY OF RESULTS

The kinetic parameters obtained make it possible to verify the reliability of method and results. As the experiments were carried out in large excess of oxygen, the molar ratio of oil to oxygen is about  $1:10^4$ , the consumption of oxygen can be neglected. On the other hand as shown by equation (8) the reaction can be assumed to be of the first order as long as the rate of initiation ( $r_i$ ) is constant. If it is constant the consistency test of results can be performed. For this purpose from the plot of half-life time against temperature the value of  $\tau_{1/2} = 60$  minutes was selected. This time corresponds to a temperature of reaction of about 433 K. A complex experiment was programmed in which three steps were combined and performed in DSC apparatus. The first step consisted of heating the oil in an atmosphere of flowing nitrogen from ambient temperature to 433 K. In the second step the atmosphere was changed from nitrogen to oxygen without stopping the experiment and the oil was kept isothermally at 433 K for 60 minutes, under oxygen gas flowing at the rate of  $100 \text{ cm}^3 \cdot \text{min}^{-1}$  (ageing procedure). Next the oil sample was quickly cooled with the use of Du Pont coolcan filled with an acetone + solid carbon dioxide mixture. In the third step the sample of aged oil was rescanned in an atmosphere of oxygen from ambient to 660 K with the same rate of heating 10 K/min and oxygen flow as in the second step. The resulting heat flow curve was compared with the one obtained for fresh oil in the same conditions of experiment as in the third step. If thermal oxidative decomposition is a first order reaction and the weights of samples are the same, the ratio of integrated areas under each of the curves should equal 0.5. The results obtained in experiments carried out in accordance with the above described procedure are shown in Fig. 4 and Fig. 5. In reality the enthalpies of reactions per gram of sample were measured. These enthalpies are directly proportional to the integrated areas under the curves and calorimetric cell constant determined in calibration procedure with high purity indium as a standard. The ratio of these enthalpies gave the value of:

$$q = \frac{\Delta H_A}{\Delta H_F} = \frac{1696}{3796} \left[ \frac{\text{J/g}}{\text{J/g}} \right] = 0.447 \quad (15)$$

where: A and F denote aged and fresh oils respectively and  $q$  is the coefficient of consistency whose theoretical value equals 0.5.

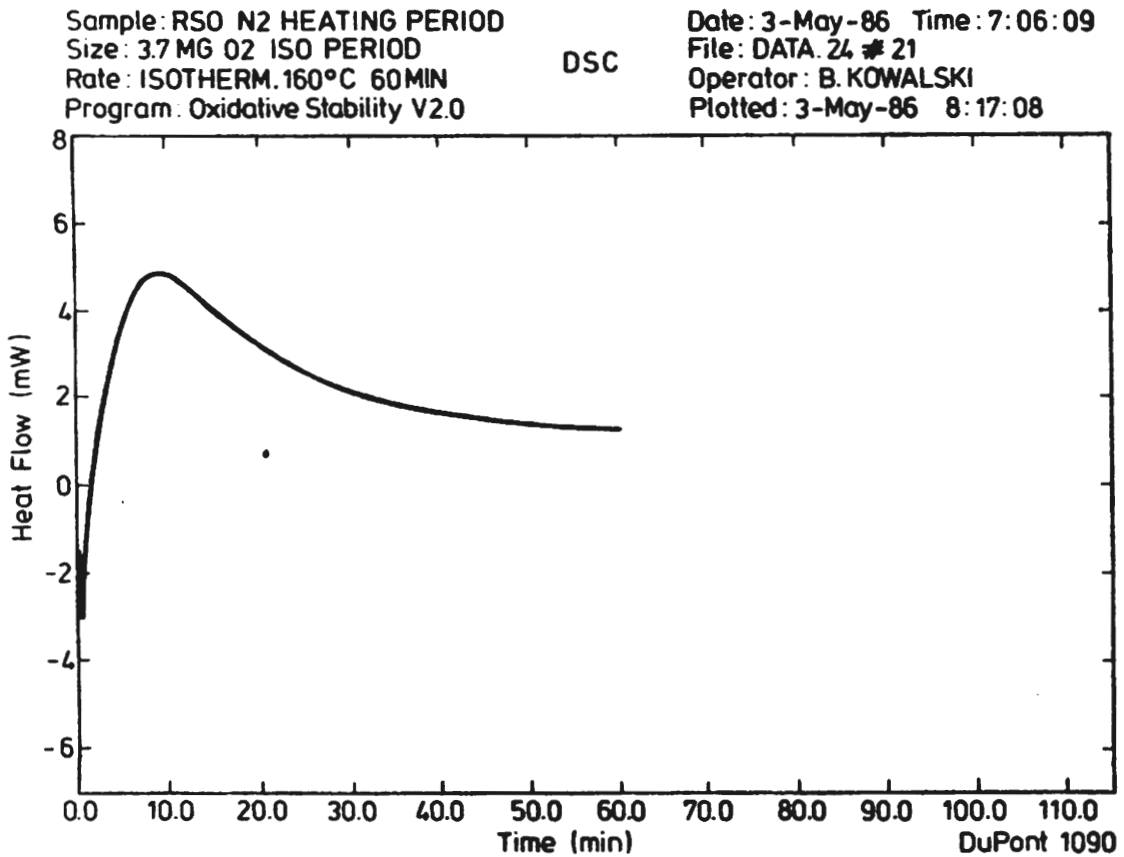


Fig. 4. DSC curve for 60 minutes ageing of rapeseed oil at 433 K in atmosphere of oxygen

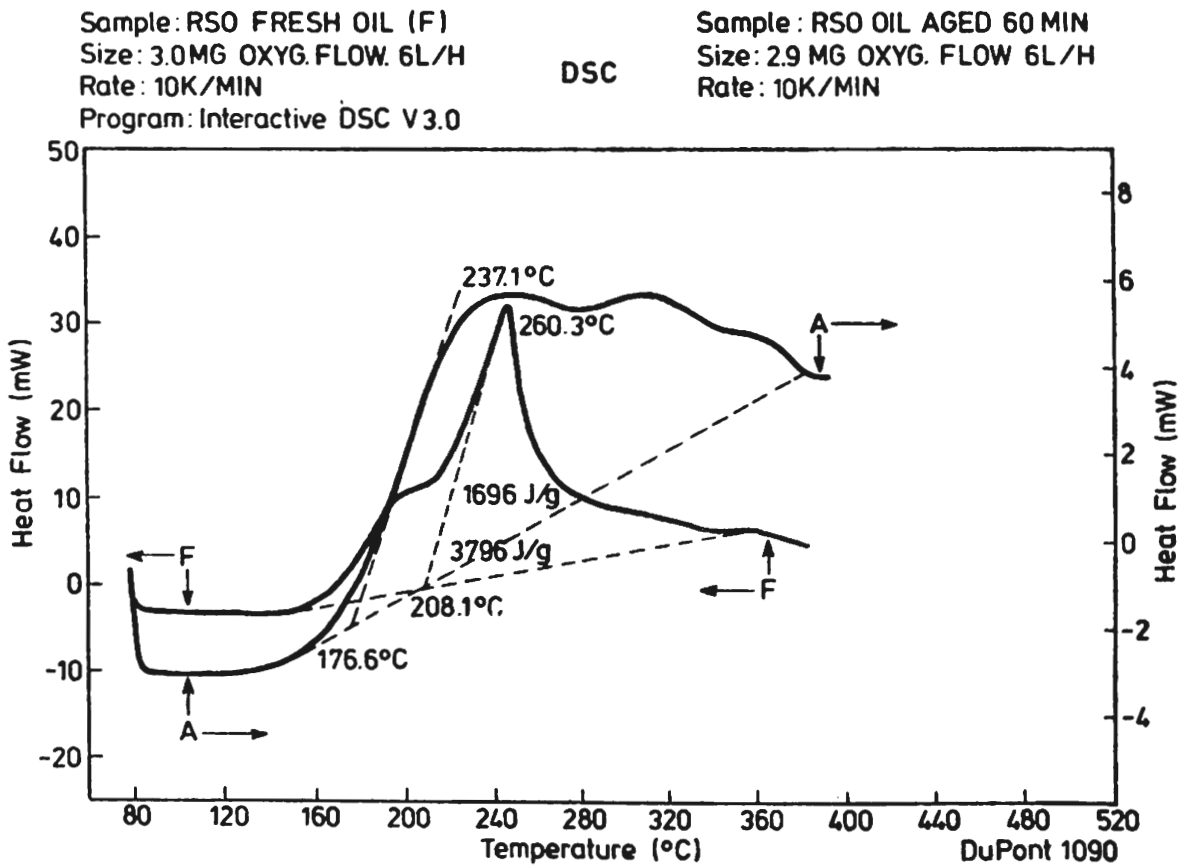


Fig. 5. The comparison of DSC curves of fresh (F) and aged (A) rapeseed oil

The heating of oil in nitrogen is not thermally neutral which is shown in Fig. 6 where the endotherm heat flow curve is recorded. This endotherm resulted mainly from evaporation of volatile components from sample so that a correction



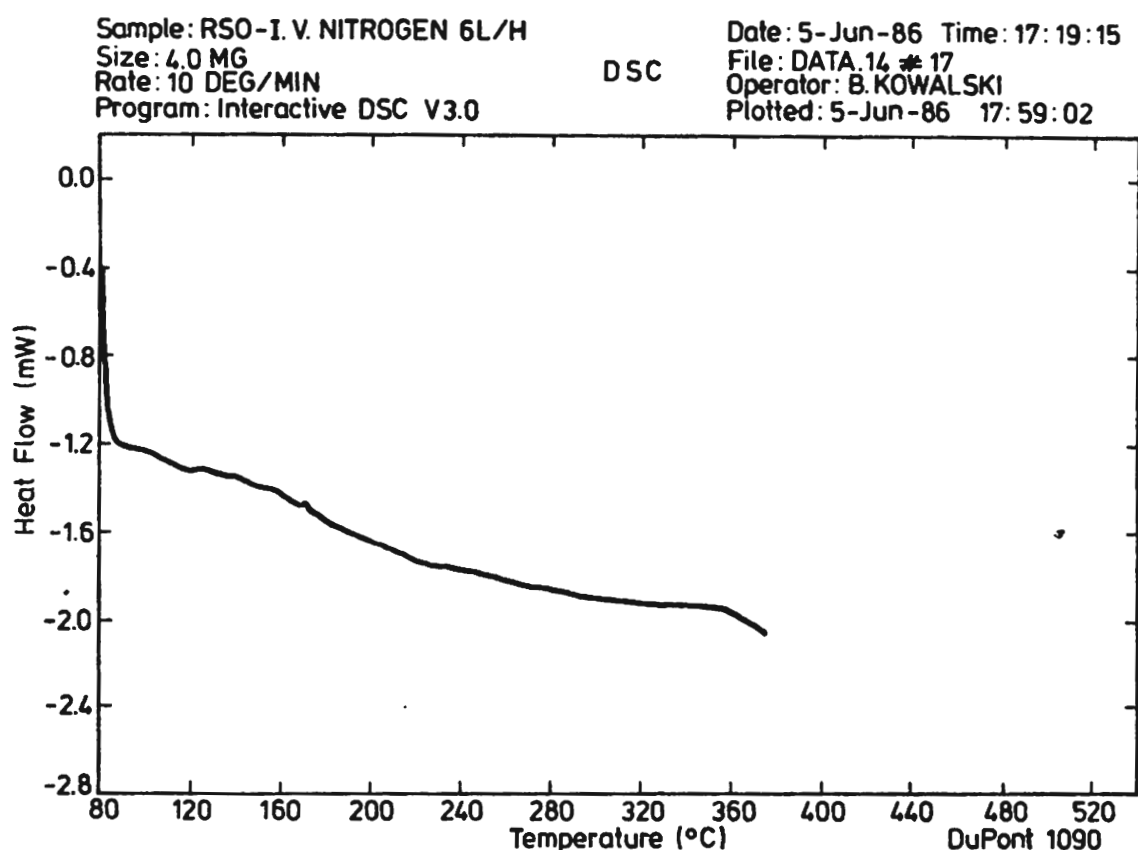


Fig. 6. DSC curve of rapeseed oil in atmosphere of nitrogen; heating rate  $10 \text{ K} \cdot \text{min}^{-1}$ , nitrogen flow  $100 \text{ cm}^3 \text{ min}^{-1}$

for sample weight loss during  $\text{N}_2$  heating period can be made. Recently Wesółowski has shown [22, 23] that losses of sample masses for technical fish oils and medicinal cod-liver oils heated up to 450 K in a thermogravimeter were about 1 percent or less. Assuming that the differences in chemical composition of his oils and rape seed oil can be neglected for thermal analysis, if Wesółowski's findings were used the coefficient  $q$  determined here would be even closer to 0.5.

## DISCUSSION

As expected there were no differences in results when the rate of oxygen flow was changed in the range  $85 \text{ cm}^3 \cdot \text{min}^{-1}$  to  $100 \text{ cm}^3 \cdot \text{min}^{-1}$ . The kinetic parameters determined can be used for a determination of series of predictive calculations. These predictions are based on the integration of the rate equation and substitution of kinetic constants. In this way the conversion time versus temperature and isothermal conversion versus time can be calculated. Other predictions based on extrapolations to storage or process parameters can be done easily.

As can be seen from results and calculations the thermal-oxidative decomposition of rape seed oil described by apparent first order reaction gave reasonably good results, but for a more detailed analysis the DSC method should be coupled with DTA, TG and others methods. Analysis of conditions of experiments shows that they are idealised ones. The small quantity of oil is dispersed in the form of a thin film on the bottom of sample pan and the ratio

surface mass of oil is large, oxygen is in large excess and temperature is well controlled. Accordingly the requirements for absence of temperature gradients are fulfilled and diffusion disturbances are eliminated.

The value of activation energy 64.8 kJ/mole (15.5 kcal/mole) determined in this paper is in a very good agreement with the results reported in literature. Marcuse [13] reports approximately 15 kcal/mole for activation energy for ordinary autoxidation. Richardson and Korycka-Dahl [18] list the values of 15.2-17.2 kcal/mole for autoxidation of linoleic acid and its esters. On the other hand, however, the activation energies of autoxidation for commercial fats reported by Zwierzykowski [24] are in the range of 20-25 kcal/mole and for methyl linoleate [25] of 28.5 kcal/mole. Both results were obtained by measuring of pressure drop of oxygen in modified Warburg apparatus. Unfortunately for other kinetic parameters no previous results have been found with which to compare the results reported in this paper. Detailed discussion has to be put off until more experimental evidence is available.

## CONCLUSIONS

The kinetic parameters for thermal-oxidative decomposition of rapeseed oil were determined on the basis of DSC experiments. These parameters can be useful for predicting oil stability and for technical designing purposes. It has been experimentally proved that in laboratory DSC conditions the reaction is of the first order, but for oxidation of bulky oil the disturbances resulting from temperature gradients and diffusion of oxygen and oxidised molecules of oil has to be taken into account. The DSC method requires very small samples and with the high degree of automation of modern apparatuses this method is very convenient for such studies. As vegetable oils are very complicated systems, gathering of experimental evidence is indispensable.

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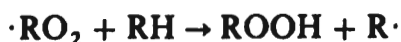
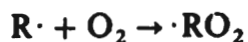
B. Kowalski

## TERMOANALITYCZNE BADANIA OLEJÓW I TŁUSZCZÓW JADALNYCH. I. KINETYKA TERMOUTLENIAJĄCEGO ROZKŁADU OLEJU RZEPAKOWEGO

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### Streszczenie

W rodnikowym mechanizmie utleniania tłuszczów (RH) reakcje przenoszenia łańcucha:



są egzotermiczne. Rejestracja wydzielanego ciepła pozwala na śledzenie postępu reakcji, a uzyskiwane dane energetyczne mogą być wykorzystane do wyznaczenia kinetyki procesu. Jeżeli utlenianie zachodzi przy wystarczająco wysokim stężeniu tlenu, to ograniczenie reakcji zakończenia łańcucha do rekombinacji rodników  $RO_2\cdot$  i uwzględnienie dużego molowego nadmiaru tlenu pozwala na przyjęcie opisującego proces równania kinetycznego pierwszego rzędu (równanie 8).

W przeprowadzonych badaniach utleniano olej rzepakowy tlenem przy molowym stosunku oleju do tlenu 1:10<sup>4</sup>. Reakcję prowadzono w komorze grzejnej Różnicowego Kalorymetru Skanningowego (DSC) połączonego z Analizatorem Termicznym 1090 B firmy DuPont. Wybrano dynamiczną opcję pracy aparatu stosując zmienne w zakresie 4 K/min do 20 K/min szybkości ogrzewania próbek ( $\beta$ ). Stwierdzono, że wraz ze wzrostem wartości  $\beta$  temperaturowe maksimum piku ( $T_{pik}$ ) na wynikowej krzywej różnicowego przepływu ciepła przesuwają się w kierunku wyższej temperatury i że istnieje liniowa korelacja

$$\lg \beta = -3834,25 T_{pik}^{-1} + 8,28.$$

Zakładając, że dla każdej ze stosowanych wartości  $\beta$  stopień konwersji próbki oleju w temperaturze odpowiadającej maksimum piku na wynikowych zapisach DSC jest stały wyznaczono energię aktywacji procesu  $E = 64,8$  kJ/mol. Z wyznaczonej energii aktywacji, równania Arrheniusa dla temperaturowej zależności stałej szybkości reakcji i ogólnego równania kinetycznego reakcji pierwszego rzędu obliczono pozostałe parametry kinetyczne. Wyznaczony w przeprowadzonym teście zwartości wyników współczynnik konsystencji  $q = 0,447$  jest w dobrej zgodności z wartością

teoretyczną 0,5. Uwzględniając, że metoda DSC rejestruje wypadkowy efekt energetyczny oraz fakt, że eksperymenty prowadzono do celowo wysokiej temperatury uzyskane wyniki odnoszą się do termoutleniającego rozkładu oleju. Wskazano na możliwość przewidywania danych na podstawie obliczeń kinetycznych ekstrapolacji. Oceniono, że stosowana metoda termoanalityczna jest szczególnie użyteczna dla tego typu badań.