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THERMOANALYTICAL INVESTIGATIONS OF EDIBLE OILS AND FATS. PART II. KINETICS OF THERMO-OXIDATIVE DECOMPOSITION OF SOYBEAN AND SUNFLOWER OILS

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Soybean (SBO) and sunflower (SFO) oils were oxidized in an atmosphere of oxygen in the cell of the Differential Scanning Calorimeter (DSC). The peak maximum temperatures on monitored differential heat flow curves were measured and used for the calculation of Arrhenius activation energy and kinetic parametres of the process.

INTRODUCTION

In the autooxidation of lipids the chain propagation reactions

are exothermal and moreover the reaction [2] is so slow that it plays a decisive role in the kinetics of the process. Schaich [6] has put it in generalized terms saying that for the overall oxidation of lipids the rate of oxidation is directly proportional to the amount of lipid present, to the amount of lipid present, to the amount of peroxide produced and at low oxygen partial pressure, to the oxygen concentration. When oxygen concentration is increased a point is reached above which the rate of oxidation is not limited by oxygen. At atmospheric pressure the rate of oxidation is independent on oxygen concentration. In advanced autooxidation taking place in such conditions the termination reactions are well recognized as dependent on peroxy radical concentration, and the overall rate of oxidation can be assumed as a rate of first order reaction. When fats or oils are heated in an oxygen rich atmosphere up to relatively high temperatures their oxidation is not only accelerated but it is followed by thermal destruction, oxypolymerization and physical changes of the sample. This overall process is referred to as thermal-oxidative decomposition.

It is well know that thermoanalytical methods are well suited for kinetic studies when enthalpy changes in the system studies can be measured or parametrized. The heat evolved during autoxidation of lipids gives a unique possibility to apply thermal analysis for determining the kinetics of the process. The DSC seems to be the most profitable in such studies.

The purpose of this series of papers is to study the kinetic features of thermo-oxidative decomposition of edible oils and fats. Part I [2] was deooted to investigations of rape-seed oil; the present paper deals with soybean and sunflower oils. Both oils are nearly as popular on our market as rape-seed oil.

EXPERIMENTAL

MATERIALS

Commercial soybean and sunflower oils were used. The samples were selected from a series of over 20 bottles purchased on the local market at different times from April till October 1986 and the samples studies may be considered as typical. Parameters of the samples determined in accordance with Polish Standards [4] were: for SBO, perioxide number = 4.2, acid number = 0.40, iodine number = 138, and for SFO peroxide number = 5.1, acid number = 0.56, iodine number = 141. The fatty acids compositions were determined by standard GLC procedure [7] using a column packed with 10 per cent PEGA on Chromosorb W and Pye-Unicam apparatus. The results are listed in Tab. 1.

Table 1. Fatty acids composition of oils studied

Fatty acids*) C_m^n	Fatty acids percentage content	
	soybean oil	sunflower oil
Saturated	total: 17.27	total: 10.93
C_{16}^0	8.36	6.45
C_{18}^0	3.36	4.48
C_{20}^0	5.55	trace
Unsaturated	total: 82.62	total: 88.68
C_{18}^1	23.52	21.67
C_{18}^2	57.78	66.33
C_{18}^3	1.32	0.68

*) m   number of carbon atoms
   n   number of double bonds

APPARATUS AND EXPERIMENTS

DuPont 1090B Thermal Analyzer System and DuPont 990 Differential Scanning Calorimeter equipped with a normal pressure cell were used. Experiments were carried out in an atmosphere of flowing oxygen ($100 \text{ cm}^3\text{min}^{-1}$) and the heating rates were 5, 7.5, 10, 15 and 20 K/min. For the sake of comparision

some experimentes were performed in an atmosphere of flowing nitrogen. The measuring and computation procedures and all remaining detalis were the same as reported previously [2].

Calibration since the expected first deviation from base line or onset oxidation and peak maximum temperatures on DSC thermograms of the oils studied are close to 420 K and 500 K respectively high purity indium and tin were as standards for calibration. Results of calibration are shown in Figs 1 and 2. The stabilities of base lines and conformity of the melting temperatures of standards with their theoretical values were excellent.
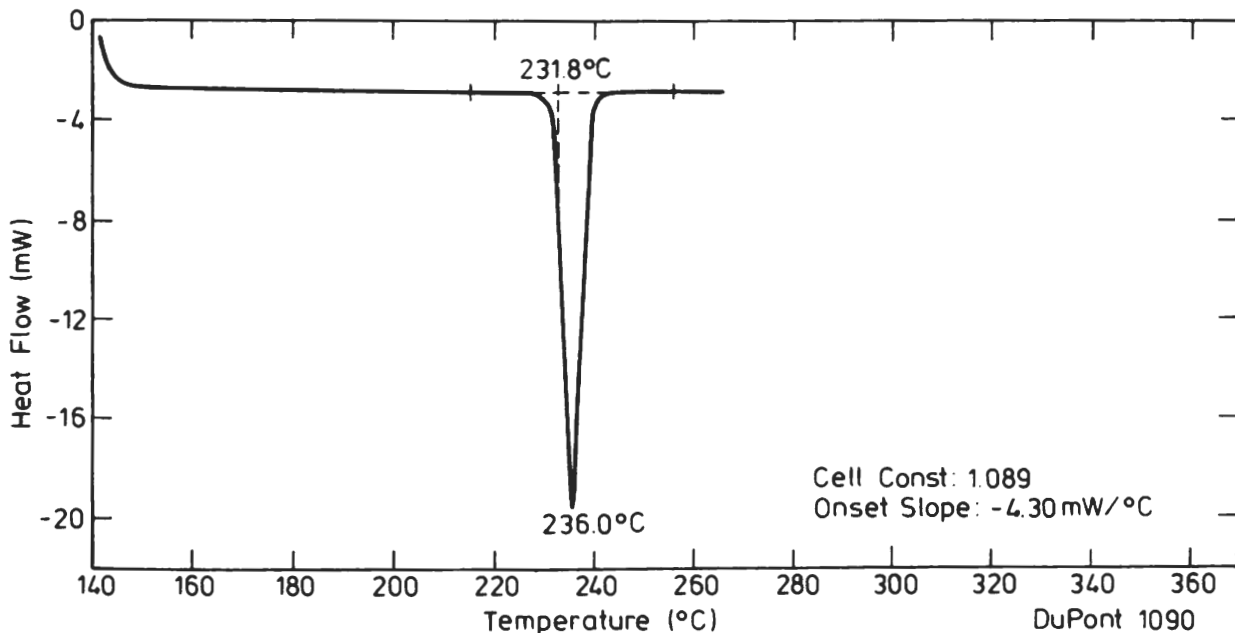
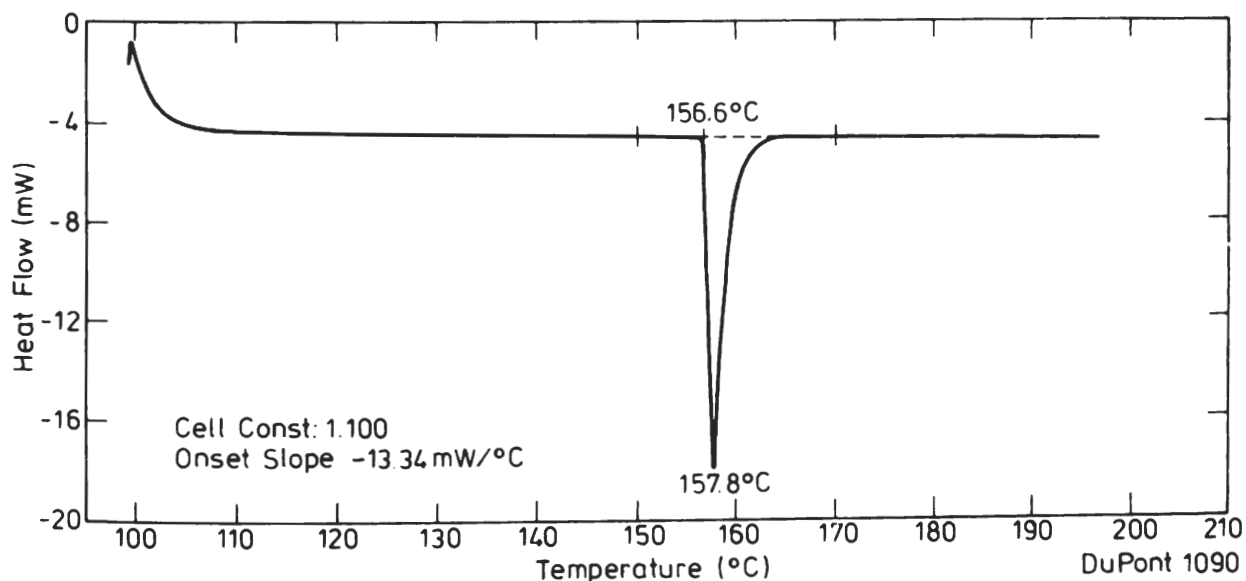Fig. 1. DSC trace of indium standard, heating rate 10 K/min

Fig. 2. DSC trace of tin standard, heating rate 10 K/min

RESULTS

Examples of scans obtained in the experiments are shown in Figs. 3 and 4. Table 2 summarizes the experimental results. Plots of log versus T^{-1}_{max} show
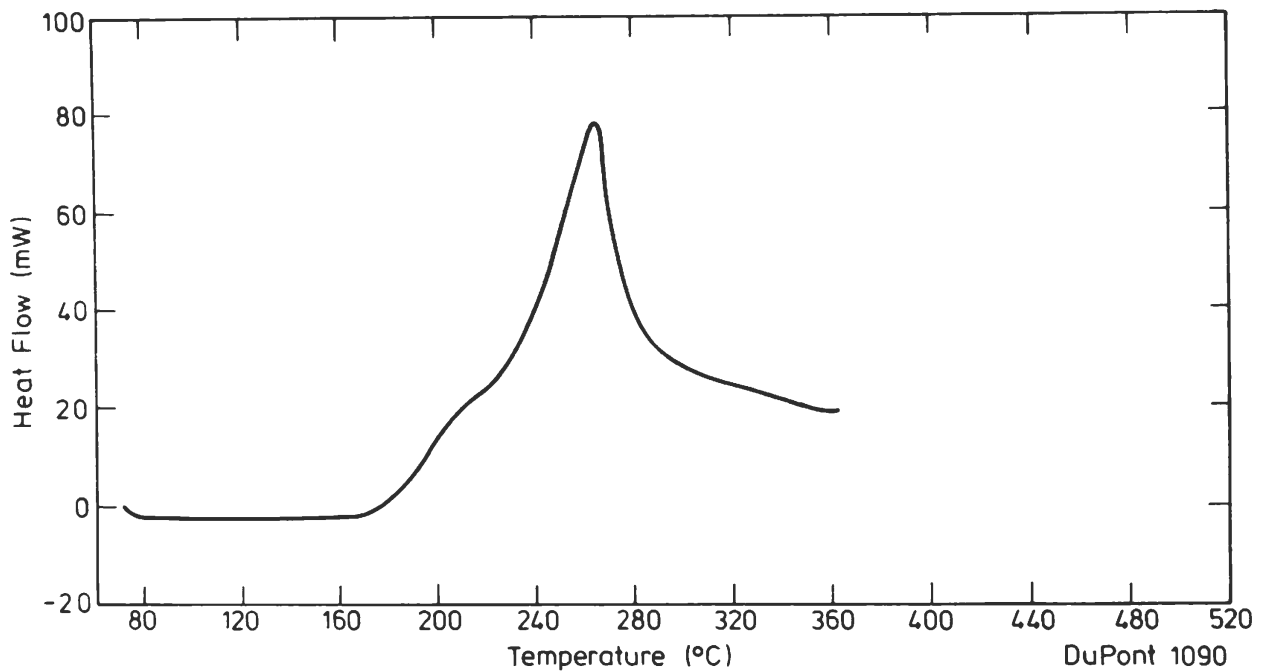
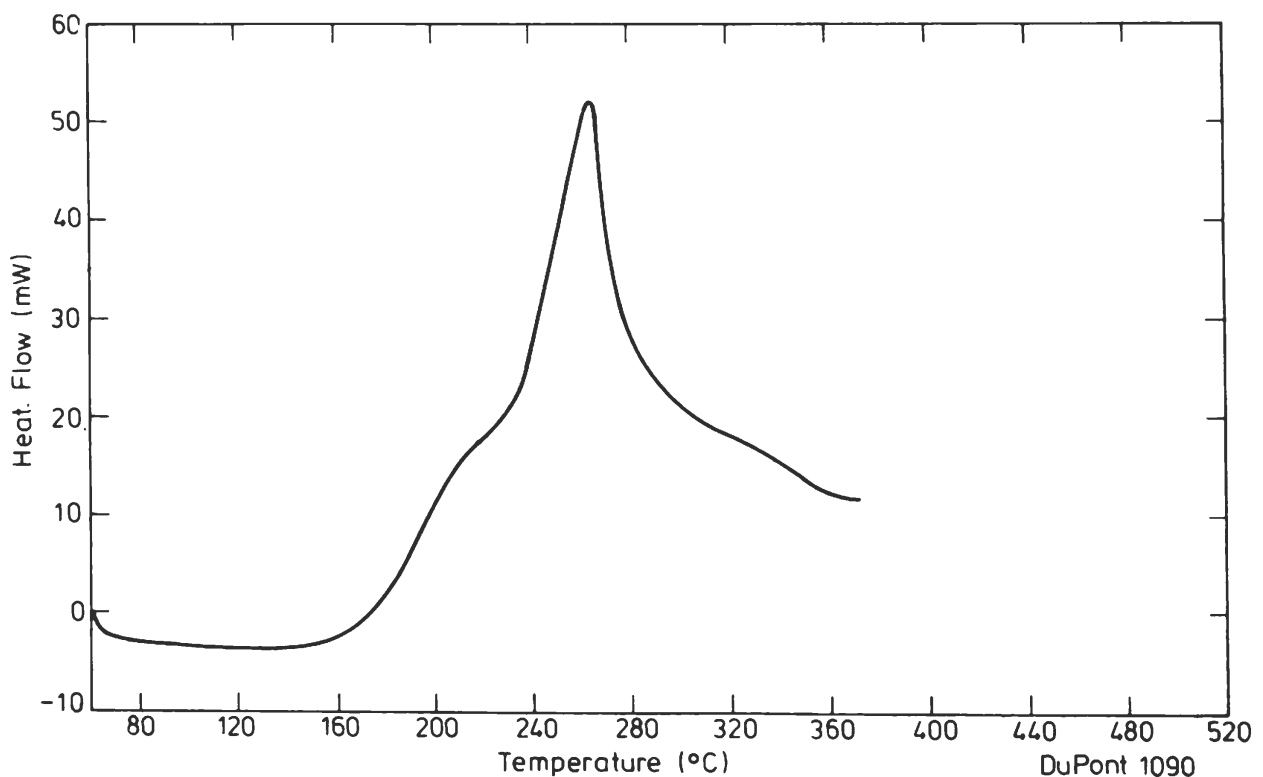Fig. 3. DSC trace of soybean oil, heating rate 20 K/min

Fig. 4. DSC trace for sunflower oil, heating rate 20 K/min

linear dependences expressed as:

$$\log \beta = -a\, T_{max}^{-1} + b \tag{3}$$

where β denotes the heating rate in K/min. Coefficients a and b from equation (3) were calculated by the least squares fit procedure and the values obtained are listed in Tab. 3 together with standard deviations σ. The approximate Arrhenius activation energies E were calculated from calculated slopes of lines showed in Fig. 6 and the they were improved according to an interative procedure with

Table 2. Results obtained for soybean oil and for sunflower oil in DSC experiments

Heating rate β K/min	Soybean oil	Sunflower oil
	peak maximum temperature T_{max} [K]	peak maximum temperature T_{max} [K]
5.0	496.9	494.3
7.5	509.1	504.5
10.0	518.1	511.5
15.0	531.8	528.9
20.0	539.8	537.2

Table 3. Coefficients of equation (3) and standard deviations

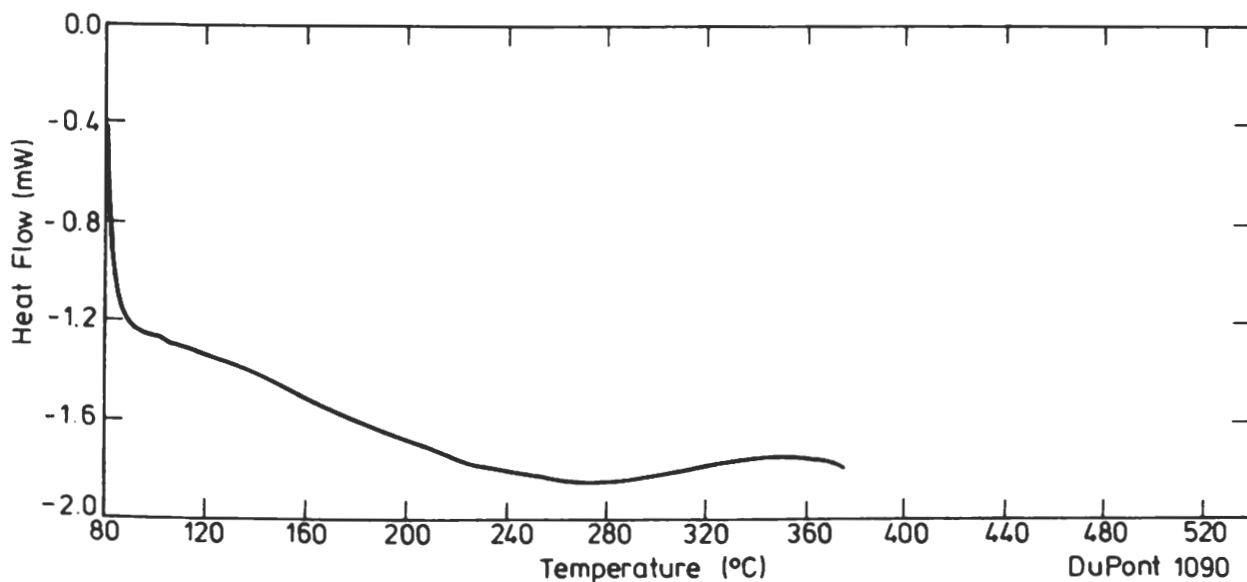| Sample	Coefficients of equation (3)		Standard deviations σ
	a	b	
Soybean oil	3716.2 ± 67.6	8.1736 ± 0.2917	0.8671 E-02
Sunflower oil	3604.5 ± 200.9	8.0124 ± 0.8733	0.2645 E-01

Fig. 5. DSC trace of soybean oil in nitrogen atmosphere, heating rate 10 K/min

values of β and T from the middle of their ranges. The final activation energies reached after 2 steps of improvement were: for soybean oil $E_{SBO} = 62800$ J/mole and for sunflower oil $E_{SFO} = 60700$ J/mole. With those energies and middrange heating rates and temperatures pre-exponential factors $Z_{SBO} = 6.07 \cdot 10^5$ min^{-1} and $Z_{SFO} = 4.15 \cdot 10^5$ min^{-1} were calculated. The series of rate constants k for temperature range of 350-600 K at 10 K steps were calculated from Arrhenius equation. For each k result the half-life $\tau_{\frac{1}{2}}$ of reactions, assuming their being of the first order were calculated. The results for both oils are shown in Fig. 7.
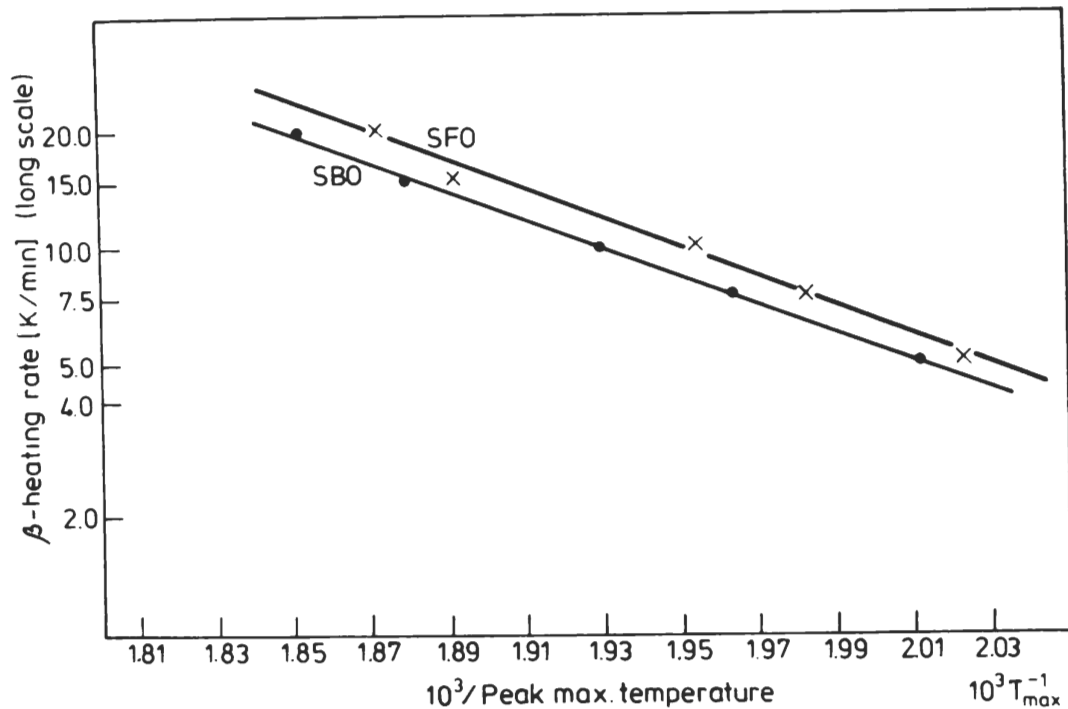
Fig. 6. Temperature shifts of peak maximum of DSC curves of soybean and sunflower oils versus log β, β — heating rate K/min
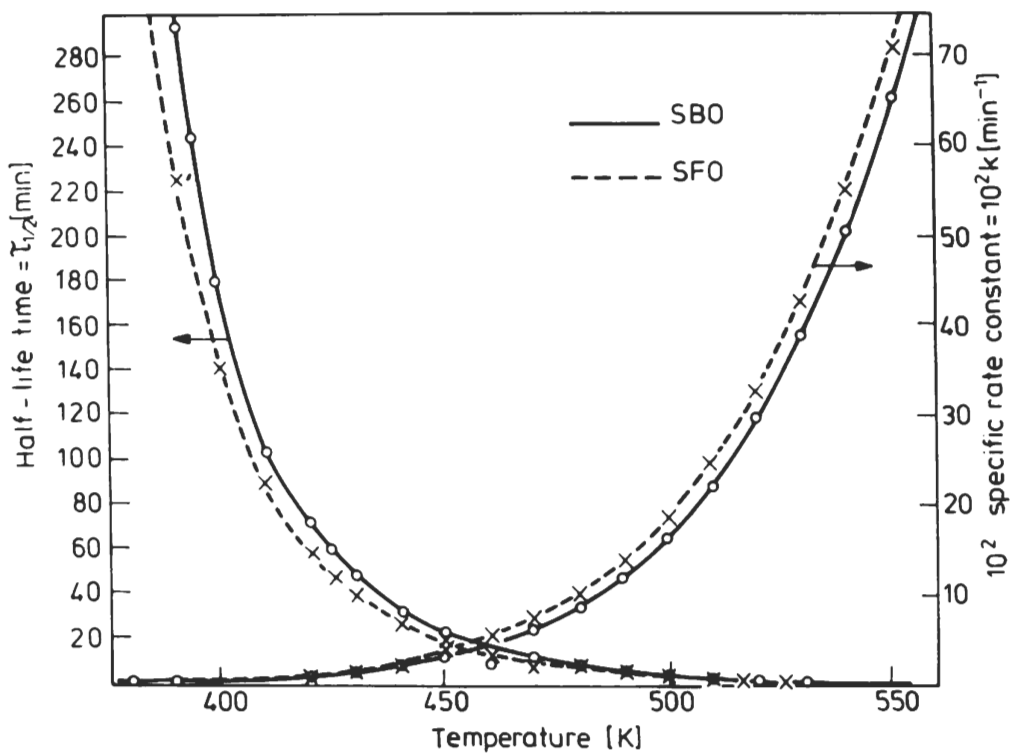

Fig. 7. Specific rate constants (k) and half-life times ($\tau_{\frac{1}{2}}$) plots versus temperature for thermal-oxidation of soybean and sunflower oils

DISCUSSION

The values of activation energy determined in this paper are in good agreement with these reported by Marcuse [3] and Richardson and Korycka-Dahl [5]. It should be noted that the activation energies obtained by DSC belong to the lower edge of reported ranges. The main reason of this is that the experiments were performed at relatively high temperatures and disturbance

arising from diffusion and temperature gradients were eliminated. The kinetic parameters obtained show that both oils behave in a similar way if their thermal-oxidative resistance is taken into account, but soybean oil is more resistant than sunflower oil. It is consistent with their chemical composition because SFO contains more unsaturated fatty acids especially with two double bonds than SBO. The atypical fatty acids composition of soybean oil (low content of C_{18}^3 and high content of C_{20}^0) may be due to an admixture of other oil during processing which might have influenced its thermal-oxidative resistance. Unsaturated acids are very susceptible to oxidation, presumably because they are easily initiated by single state oxygen. Although in the thermal-oxidation of lipids, forming of free radicals at the initiating stage is due to the thermal exitation of fat molecules, reaction with singlet state oxygen can play an important role. Singlet state oxygen readily reacts directly with double bonds of unsaturated acids which are also in singlet state and the process of generating of peroxides is spin-allowed [1]. On the other hand this chemical composition related picture of thermal oxidation of oils can be diminished by the presence of natural antioxidants. These natural compounds such as tocopherols may influence the induction period and play a decisive role in low temperature isothermal studies and practice. In this paper it was assumed that natural antioxidants were thermally destroyed and the results are related to a developed thermal-oxidative decomposition of oils. It is obvious that presence of oxygen is necessary in this process. In a nonoxidizing atmosphere, in nitrogen for example, at the temperature ranges studied the decomposition process is low and it is endothermal in its nature as shown in Fig. 5. Apparent first order reaction accepted and parametrized here for thermal-oxidative decomposition of SBO and SFO oils gives good results. The calculated parameters make possible a kinetic prediction for engineering design purposes and an assessment of oils stabilities at elevated temperatures.

CONCLUSIONS

The kinetical parameters calculated from DSC experiments showed that thermal-oxidative resistance of soybean oil is highethan of sunflower oil. The GLC determinations for the samples studied have shown that commercial oils can have an antypical composition of fatty acid. Apart from antioxidants and prooxidants, this composition is one of the most important parametres which can influence the thermal-oxidative decomposition of fat containing food. In some cases, e.g. in the experiment discussed, possible additions of other oils during preparation of commercial blends can change the normally accepted order for thermal-oxidative stability of oils heated in an oxidizing atmosphere. DSC method used in this experiment does not require any previous samples preparation. It requires only milligram amounts of oils and it is well suited for studying the thermal-oxidative decomposition of such complicated mixtures as vegetable oils.

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TERMOANALITYCZNE BADANIA OLEJÓW I TŁUSZCZÓW JADALNYCH.
CZ. II. KINETYKA TERMOUTLENIAJĄCEGO ROZKŁADU OLEJU SOJOWEGO
I SŁONECZNIKOWEGO

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Streszczenie

Oleje sojowy (SBO) i słonecznikowy (SFO) utleniano w komorze kalorymetru skanningowego (DSC) tlenem przepływającym przez komorę z szybkością 100 cm³/min. Postęp reakcji śledzono rejestrując różnicowy przepływ ciepła kompensujący efekt energetyczny reakcji. Stosując różne szybkości ogrzewania reagującego układu (β) oznaczono z termogramów temperaturę maksimum piku (T_{max}). Liniowe w półlogarytmicznym układzie współrzędnych zależności lg $\beta = f(T_{max})$ pozwoliły na wyznaczenie wartości dlg $\xi(dT_{max}^{-1})$. Z otrzymanych danych obliczono energię aktywacji procesu otrzymując dla oleju sojowego $E_{SBO} = 62800$ J/mol i słonecznikowego $E_{SFO} = 60700$ J/mol. Wartości te zostały użyte do wyznaczenia temperaturowych zależności zmian stałych szybkości reakcji (k) i połówkowych czasów reakcji ($\tau_{\frac{1}{2}}$) przyjmując, że są to reakcje p ierwszego rzędu. Sparametryzowane ilościowo ujęcie kinetyki procesu termoutleniania badanych olejów jest spójne z oznaczanymi metodą chromatografii gazowej zawartościami kwasów tłuszczowych w olejach. Otrzymane wyniki dyskutowano ze względu na chemizm wolnorodnikowego mechanizmu procesu autoutleniania lipidów. Wskazano na możliwość zastosowania wyznaczonych parametrów do oceny odporności olejów na rozkład termoutleniający oraz wykorzystania danych w obliczeniach projektowo-inżynieryjnych. Oceniono, że metoda DSC jest szczególnie użyteczna w badaniach termoanalitycznych i kinetycznych tak złożonych układów jak oleje roślinne.