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## THERMOANALYTICAL INVESTIGATIONS OF EDIBLE OILS AND FATS. III. KINETICS OF THERMAL-OXIDATIVE DECOMPOSITION OF CORN OIL

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

Corn oil was oxidized in an atmosphere of oxygen in the cell of a Differential Scanning Calorimeter (DSC). From the outcoming heat flow curves obtained at different heating rates ( $\beta$ ) the peak maximum temperatures were selected ( $T_{\text{peak}}$ ). From linear dependence  $\lg \beta = f(T_{\text{peak}}^{-1})$  the apparent activation energy and kinetic parameters for thermal-oxidative decomposition of oil were calculated.

### INTRODUCTION.

The free radical mechanism of autoxidation of lipids has been commonly accepted and some of its basic principles were discussed in earlier papers from this series [3, 4]. As chain propagation reactions in the autoxidation scheme are exothermal and the reaction of peroxy radicals with fat components plays a decisive role in the overall reaction rate, the kinetic studies of the process can be based on calorimetical or thermoanalytical measurements.

For technical purposes it is convenient to describe the thermal-oxidative process by the apparent reaction:



parameters can be easily calculated from the DSC scans as reported in detail previously [3, 5].

Recent developments in the DSC have shown that this method can be used for the investigation of autoxidation of natural products for which, because of their complex composition, the use of analytical methods is difficult, time consuming and often very unprecise. The DSC and its high pressure modification have been applied for autoxidation studies of wood resins [7] and vegetable oils [1, 2, 3, 4, 6]. A similar paper with the use of high pressure DTA for oxidation studies of methyl esters of fatty acids and triacylglycerols has been also published [9]. All those substances undergo oxidation acc. to the radical mechanism.

In previous articles from this series the results for rapeseed oil [3], soybean and sunflower oils [4] were reported. In the present paper commercial corn oil has been used and the aim of the study was to investigate the kinetic features of thermal-oxidative decomposition of this oil based on DSC measurements.

## EXPERIMENTAL

### MATERIALS

Commercial corn oil imported from USA was used. As stated on the package the producer adds the mixture of TBHQ + citric acid soluted in propylene glycol to retard autoxidation. For this oil acid and peroxide values were determined in accordance with Polish Standards [8] and the results were 0.4 and 2.2 respectively. The fatty acids composition was determined by GLC and the percent rage contents were as follow:  $C_{16}^0 = 8.51$ ,  $C_{18}^0 = 1.40$ ,  $C_{18}^1 = 25.31$ ,  $C_{18}^2 = 63.32$ ,  $C_{18}^3 = 0.42$ ,  $C_{20}^0 = 1.03$ .

### APPARATUS AND EXPERIMENTS

The apparatus, its calibration, and procedures used for measurements and calculations were all the same as those reported previously [3, 4]. The experiments were carried out in an oxygen atmosphere under oxygen gas flowing at the rate of  $100 \text{ cm}^3 \text{ min}^{-1}$ . The heating rates were: 7.5 K/min., 10 K/min., 12.5 K/min., 15 K/min., and 20 K/min. For the sake of comparison some experiments were performed in an atmosphere of flowing nitrogen.

## RESULTS

Scans for corn oil in an oxygen atmosphere are of a complex nature. The typical scan obtained at the heating rate of 10 K/min. is shown, in Fig. 1. Scans at other heating rates are similar. As can be seen from Fig. 1, where apart from the heat flow curve its derivative is also shown, the scan consists of three peaks. The second is the main one and the shift of its position against temperature depends on heating rate as shown in Fig. 2. Accordingly, the position of this peak was taken into account in determination of  $d \lg \beta / dT_{\text{peak}}^{-1}$ . This value was calculated by the least squares fit procedure as the slope of the line described by the equation

$$\lg \beta = 2625.36 T_{\text{peak}}^{-1} + 6.213 \quad 1$$

The linear correlation is significant ( $r = 0.9956$ ) and experimental results fit equation (1) with the standard deviation  $\sigma = 0.0166$ . From the calculated slope of line showed in Fig. 2 the approximate Arrhenius activation energy was calculated and then improved in iterative procedure until final activation energy  $E = 47400 \text{ J/mole}$  was obtained. This value was used to calculate the preexponential factor  $Z = 1.87 \cdot 10^4 \text{ min}^{-1}$  from Arrhenius equation. Using  $E$  and  $Z$

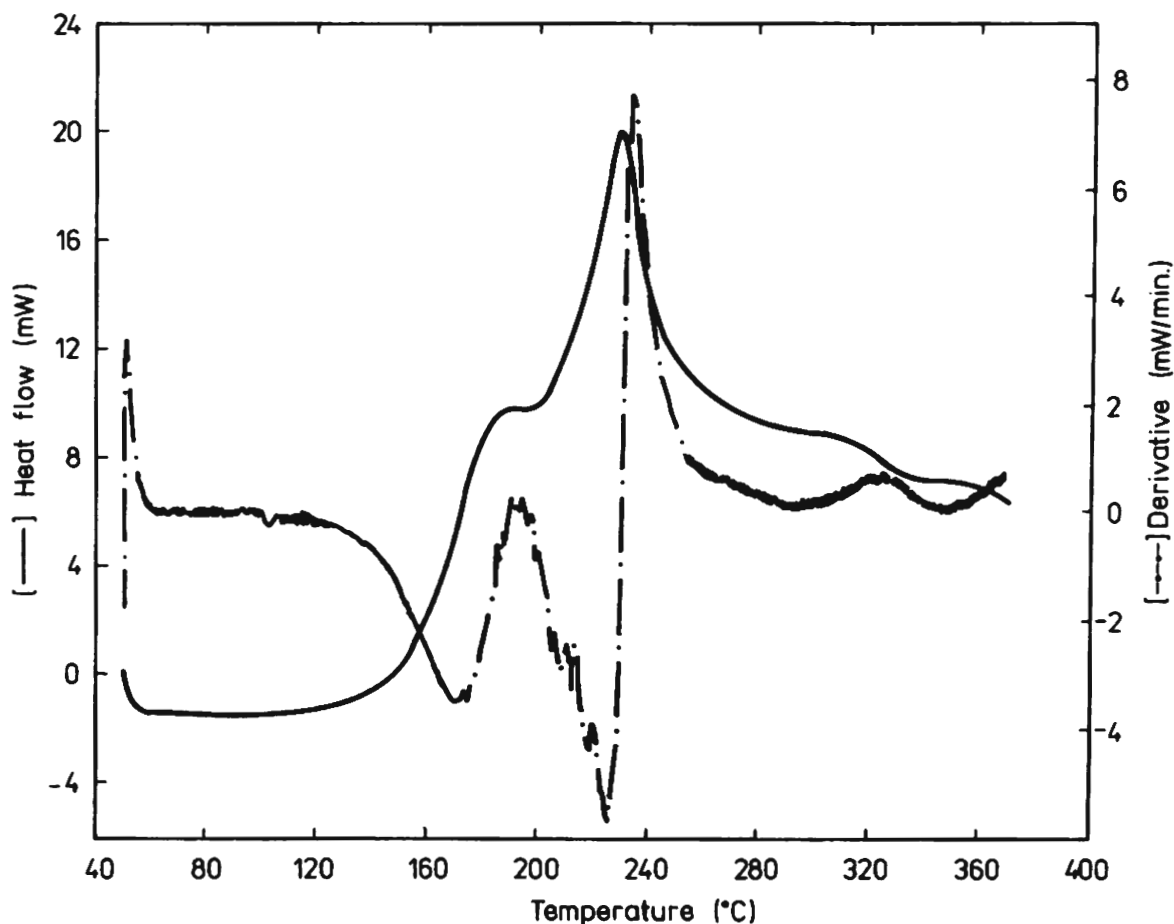


Fig. 1. DSC scan for corn oil obtained at heating rate  $\beta = 10 \text{ K/min.}$ /mass of sample = 2.5 mg, oxygen flow =  $100 \text{ cm}^3 \text{ min}^{-1}$

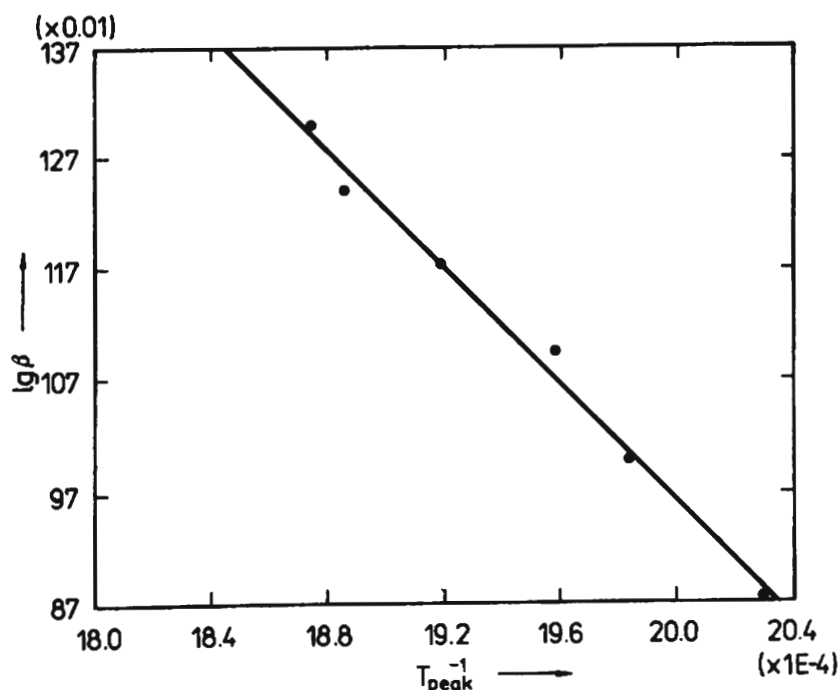


Fig. 2. Shift of the maximum of peak on the DSC scans of corn oil as a function of heating rate

values and assuming that the reaction is of the first order the series of rate constants  $k$  and then half-life times  $\tau_{1/2}$  of the reaction at the temperature range of 360 K to 570 K at 10 K steps were calculated. The results are shown in Fig. 3.

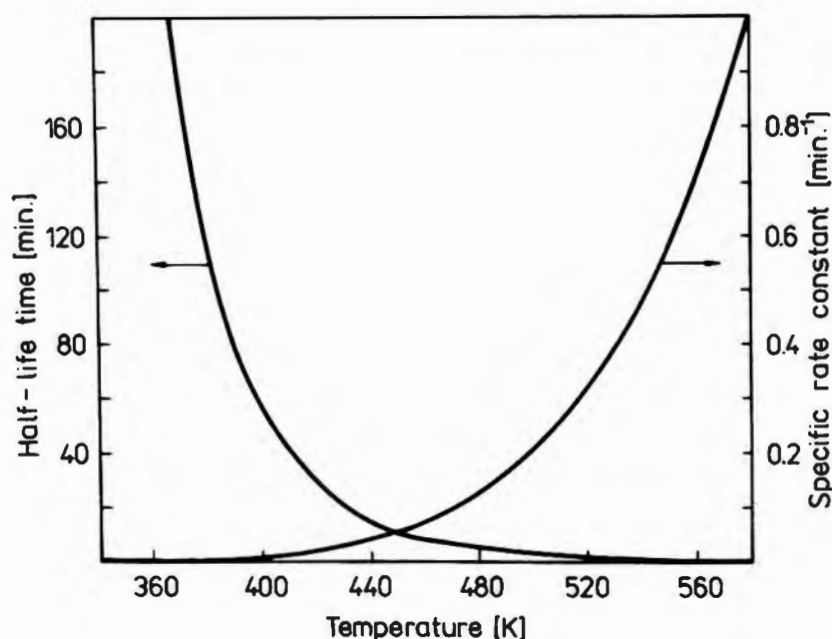


Fig. 3. Temperature dependencies of specific rate constant and half-life time for thermal-oxidative decomposition of corn oil

## DISCUSSION

The apparent activation energy for thermal-oxidative decomposition of the studied sample of corn oil is about 27-22 percent lower than for thermal-oxidative decomposition of rapeseed, soybean and sunflower oils which were investigated earlier [3, 4, 5]. The kinetic parameters of thermal-oxidative decomposition of studied corn oil showed that it is less stable than other above listed examples of vegetable oils despite the fact that corn oil was inhibited. This lower stability can suggest that the inhibiting system used is not effective for the stabilization of this corn oil in higher temperatures. As the amounts of antioxidants added and their interactions with various components of oil are unknown, no general conclusion can be drawn.

The comparison of fatty acids compositions of the investigated samples of sunflower [4] and corn oils shows them to be similar. Corn oil contains 89.05% unsaturated acids and sunflower oil 88.68%. Both studied oils have almost the same content of  $C_{18}^3$  but corn oil contains 4% more of  $C_{18}^1$  and 3% less of  $C_{18}^2$  than sunflower oil so corn oil can be expected to be more stable than sunflower oil. The kinetic results have shown that we cannot predict the thermal-oxidative stability of oil simply from their acids compositions, especially when they are similar. In such cases any components, present in oils even on a trace level, which have active pro- or antioxidative properties at higher temperatures play a decisive role.

It should be noted that the experimental results concern with the samples studied. It is known from industrial practice that commercial oils are not "pure oils", but rather blends of oils which are composed so as to achieve the desired useful parameters. From this reason the experimental results obtained cannot be generalized of given type of commercial labeled oil. Gathering of experimental results from oils of different composition, physico-chemical state and origin can

improve the situation, but at the present stage looking for new, fast and reliable methods of kinetic studies seems to be the most important. The kinetic results are more informative than analytical ones if oil stability is considered. As the thermoanalytical methods are capable to provide us quickly with data for kinetic analysis and modern TA apparatuses are compatible or even equipped with computers, they are valuable tools for research and control laboratories. Additionally, the thermoanalytical methods make it possible to study fats or fat containing food in their natural or processed state which enhances the importance of these methods. The kinetic parameters for thermal-oxidative decomposition the sample of corn oil studied is a good example cannot be recommended for high temperature applications.

## CONCLUSIONS

The developed method based on the DSC measurements was used successfully to determine the kinetics of thermal-oxidative decomposition of commercial labelled corn oil. Although the results have shown that studied oil is less resistant to thermal-oxidative degradation than other oils investigated previously the conclusions concerning the thermal-oxidative stability of oils cannot be generalized. This is due to the fact that commercial oils are mixtures of various oils and their compositions can vary either for main or trace components. Because of this any predictive speculations about the thermal-oxidative stabilities of oils based on their fatty acids compositions can be misleading. The experimental results obtained for samples of commercial sunflower and corn oils have confirmed this conclusion. On the other hand, the results obtained in this series of papers have shown that the method based on the DSC experiments can be applied for various oils as it provides:

- a well established quantitative background for extrapolations,
- reliable parameters for an assessment of oils stability at higher temperatures,
- information on the theoretical and engineering aspects of oils autoxidation.

## LITERATURE

1. Cross. C. K.: J. Amer. Oil Chem. Soc., 1970, **47**, 229.
2. Hassel R. L.: J. Amer. Oil Chem. Soc., 1976, **53**, 179.
3. Kowalski B.: Acta Aliment. Polonica 1988, **14**, 195.
4. Kowalski B.: Kot B.: Acta Aliment. Polonica 1989, (in print).
5. Kowalski B.: XIX Sesja Naukowa K. T. Ch. Ż., PAN, Postępy technologii w rozwoju produkcji żywności. 1988, 44. Szczecin.
6. Kowalski B., Orzeszko A.: XIX Sesja Naukowa K. T. i Ch. Ż., PAN, Postępy technologii w rozwoju produkcji żywności. 1988, 45. Szczecin.
7. Minn J.: Thermochemica Acta 1984, **80**, 1.
8. Polish Standards: PN-60/A-86914, PN-60/A-86921.
9. Yamazaki M., Nagao A., Komamiya K.: J. Amer. Oil Chem. Soc., 1980, **57**, 59.

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TERMOANALITYCZNE BADANIA OLEJÓW I TŁUSZCZÓW JADALNYCH.  
III. KINETYKA TERMOUTLENIAJĄCEGO ROZKŁADU OLEJU KUKURYDZIANEGO.

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Streszczenie

Olej kukurydziany z obrotu handlowego utleniano tlenem w komorze pomiarowej różnicowego kalorymetru skanningowego (DSC) rejestrując zmiany przepływu ciepła kompensującego efekt energetyczny reakcji. Stosując różne szybkości ogrzewania reagującego układu z zarejestrowanych termogramów DSC obliczono energię aktywacji pozornej reakcji:

olej + O<sub>2</sub>(nadmiar)  $\xrightarrow{T}$  produkty utleniania i rozkładu, oraz jej parametry kinetyczne.

Uzyskane wyniki wykazały, że badany olej kukurydziany jest mniej odporny na rozkład termoutleniający niż stosowane wcześniej próbki handlowych olejów: rzepakowego, sojowego i słonecznikowego. Znaczne różnice w stabilności termoutleniającej badanych olejów: słonecznikowego i kukurydzianego przy podobnych składach kwasów tłuszczowych próbek sugerują, że nie ma podstaw do przeprowadzania prognoz odnośnie stabilności olejów w oparciu o ogólne wyniki analiz ich składu. Biorąc pod uwagę, że oleje handlowe są zwykle mieszankami różnych olejów uzyskiwanych wyników nie należy uogólniać na dany typ handlowo oznakowanego oleju. Jednakże otrzymywane w stosowanej procedurze pomiarów termooanalitycznych charakterystyki kinetyczne rozkładu termoutleniającego różnicują właściwości danych prób olejów, a zaproponowana metoda jest stosunkowo szybka i obiektywna tak, że stanowi ona cenne narzędzie badawcze.