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DYNAMIC AND ISOTHERMAL DSC INVESTIGATION OF THE KINETICS OF THERMOOXIDATIVE DECOMPOSITION OF SOME EDIBLE OILS

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Abstract

The kinetics of thermooxidation of edible oils: soybean oil, rapeseed oil, corn and peanut oil was investigated in two ways. The DSC and its pressure version (PDSC) were used for measurements under the isothermal and non-isothermal conditions in atmosphere of oxygen. Comparing these two methods for each oil the differences between the values of activation energies were observed. However, mechanism of oxidation in both method was different.

Keywords: DSC, isothermal method, non-isothermal method, thermooxidation of edible oils

Introduction

Experimental techniques as thermogravimetry (TG), differential scanning calorimetry (DSC) and its pressure version (PDSC) are being used increasingly for the identification and characterization of chemical substances and also for determining the kinetic parameters of simple and complex reactions.

Both isothermal and non-isothermal DSC techniques can be used for such exothermal reactions as thermal oxidative decomposition of oils and fats. These kinds of substance are mixtures of triacylglycerols of saturated, unsaturated, polyunsaturated acids, tocopherols and other organic compounds. Due to that complicated composition, the oils are treated as homogeneous material in TA experiments what is right for assessment of their quality and thermal stability. The aim of this research is to compare the dynamic and isothermal method of investigating of the kinetic behaviour of oils. Special accent was put on activation energy and kinetic parameters obtained independently from those different experiments.

In the thermal analysis experiments the rate of conversion ($d\alpha/dt$) is described by basic kinetic equation:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

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where α is the degree of conversion, $f(\alpha)$ the conversional factor and k is the rate constant assumed to have the Arrhenius form:

$$k = Ze^{-E/RT} \tag{2}$$

where Z is the pre-exponential factor, E the activation energy and R the gas constant. Arrhenius parameters can be obtained from isothermal and nonisothermal data. The development of non-isothermal (dynamic) techniques, simplicity and short time of experiment make them very popular in the study of reaction kinetic. In the ASTM method [1] the sample temperature is increased at linear heating rate (β). The recorded values of maximum heat flow temperatures (T_{MP}) for different values β can be described as:

$$\log\beta = aT_{MP}^{-1} + b \tag{3}$$

where a and b are coefficients.

The approximate values for activation energy and the Arrhenius preexponential factor are calculated as follows

$$E' = -2.19R\frac{\mathrm{d}\log\beta}{\mathrm{d}T_{MP}^{-1}} \tag{4}$$

$$Z = \frac{\beta Ee^{E/RT}}{RT_{MP}^{2}} \tag{5}$$

where β and T_{MP} are taken from the middle of the range.

In isothermal method the thermal effects recorded during heating the substance at constant temperature allow to appoint the time of maximum heat flow (τ_{MP}) from the several experiments, what gives linear dependence [2]:

$$\log\tau_{MP} = AT^{-1} + B \tag{6}$$

where A, B are adjustable coefficients, and activation energy is calculated:

$$E = 2.19R\frac{\mathrm{d}\log\tau_{MP}}{\mathrm{d}T^{-1}} \tag{7}$$

The analysis of reaction kinetics can be performed using either of two basic models: n-th order or general autocatalytic model. The n-the order assumed [3] that the reaction behaves according to Eq. (1) where

$$f(\alpha) = (1-\alpha)^n \tag{8}$$

In the more general autocatalytic model the function is presented as

$$f(\alpha) = \alpha^m(1-\alpha)^n \tag{9}$$

where m and n are parameters indicating reaction order [4].

Experimental

The soybean oil (SBO), rapeseed oil (RSO), corn (CRO) and peanut oil (PO) were used for investigation. The oils were protected against the light and oxidation by keeping in 4°C under nitrogen in darkness. The iodic number and fatty acids composition (determined by GLC analysis) are listed in Table 1. For this study a DuPont 910 Differential Scanning Calorimeter and a DuPont 9900 Computer/Thermal Analyzer were used.

For isothermal experiments the DSC module was equipped with a pressure cell where the reaction was carried out at a constant temperature under the oxygen pressure of 3 atm. Flow of oxygen (61/h) and the samples of oils (2–5 mg) were similar in both methods.

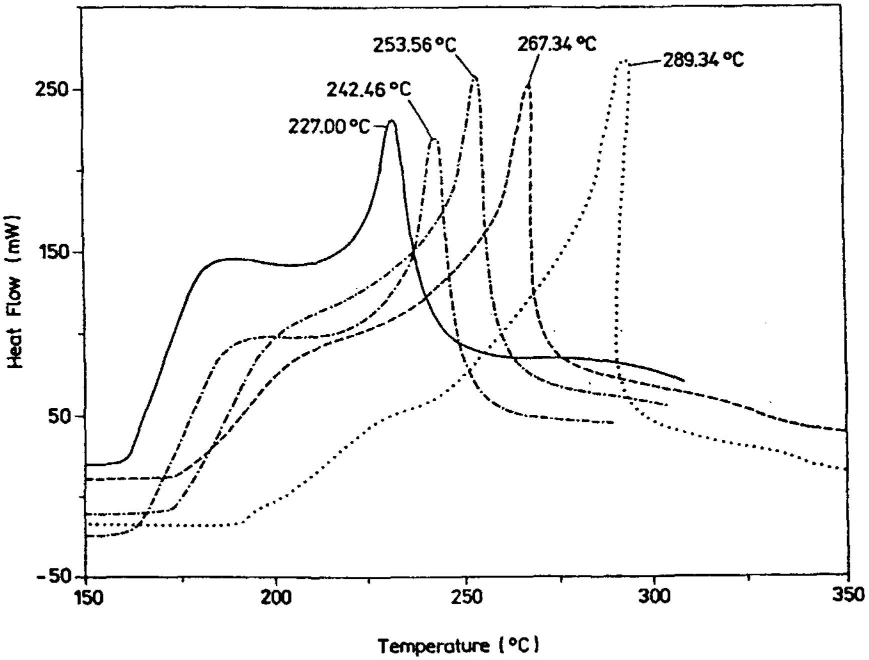

Fig. 1 DSC curves of rapeseed oil observed in dynamic method for different β:
1) 4 deg·min^{-1}; 2) 5 deg·min^{-1}; 3) 7.5 deg·min^{-1}; 4) 10 deg·min^{-1}; 5) 17.5 deg·min^{-1}

Table 1 The iodic numbers and fatty acid compositions of the oils investigated

Oil	Iodic number	Saturated fatty acids/ %	Fatty acids with duble bonds/ %			Other acids/ %
		C_{16}–C_{22}	Oleic	Linoleic	Linolenic	
Rapeseed	94–107	3	50	18	2	22
Corn	115–130	10	27	62	–	–
Soybean	114–135	12	38	39	6	–
Peanut	96	15	53	18	–	–

Non-isothermal method

The typical recorded plot of heat flow *vs.* temperature for different β is shown in Fig. 1. The series of T_{MP} with corresponding β showed linear dependences described by Eq. (3); coefficients a and b obtained by the least-squares method were used to calculation the values of activation energy E' (Eq. (4)). From the corrected values of E' (procedure described in Ref. [1]) were received the Arrhenius pre-exponential factors Z (from Eq. (5)) and rate constant k for individual oils. That data are placed in Table 2.

Assuming first order of observed reaction, for each oil was calculated (from equation $\tau_{1/2}=\ln 2/k$) half-life time for various temperatures and the sample of oil was aged at adequate temperature for an hour, what is the calculated anticipating half-life time in 425 K for RSO, 373 K for SBO, 396 K for CRO and 448 K for PO (constant T, oxygen flow the same as previous experiments), then it was rapidly cooled and the dynamic experiment with $\beta=10$ deg·min^{-1} was run. Comparison the peak areas for aged and unaged (fresh) oil or enthalpies for fresh (ΔH_f) and aged (ΔH_a) oil for example for peanuts oil (Fig. 2)

$$\frac{\Delta H_a}{\Delta H_f}=0.47$$

gives confirmation that observed oxidation of oil is first order reaction.

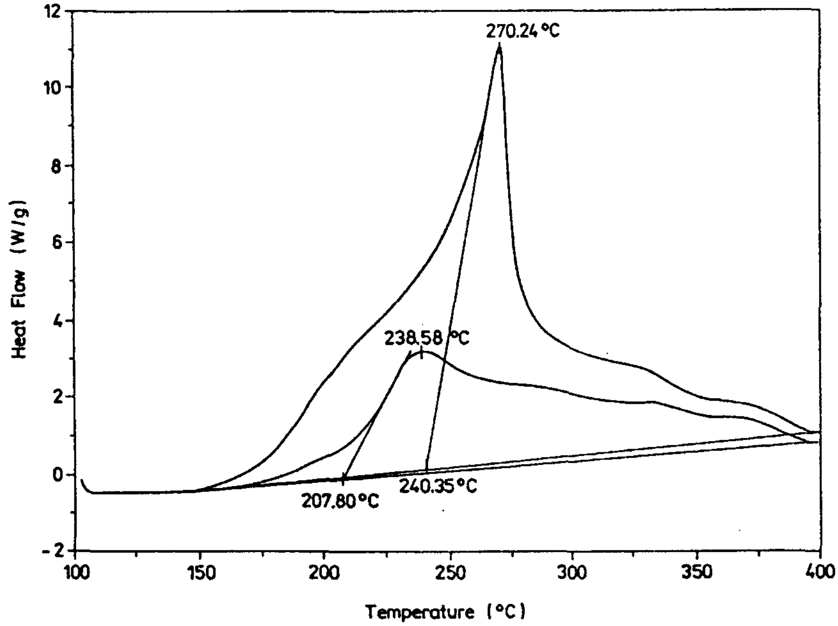

Fig. 2 The comparison of DSC curves for fresh and aged peanut oil; aged oil-bottom line; fresh oil-top line

Table 2 Data obtained from DSC curves for ASTM method

Oil	β/ deg·min^{-1}	T_{MP}/ K	a	b	δ	E/ kJ·mol^{-1}	Z/ min^{-1}	k/ min^{-1}
RSO	17.5	561.8	–2984.0	6.5	0.03	48.3	$9.8\cdot10^{3}$	0.1573
	10.0	540.5						
	7.5	526.3						
	5.0	515.5						
	4.0	500.0						
SBO	12.5	454.5	–3871.1	9.6	0.05	66.7	$2.5\cdot10^{7}$	0.3101
	10.0	448.4						
	7.5	440.5						
	5.0	434.8						
CRO	17.5	465.1	–5823.3	13.8	0.05	104.0	$6.1\cdot10^{11}$	0.4666
	10.0	456.6						
	7.5	448.4						
	4.0	444.4						
PO	12.5	551.8	–3420.0	7.3	0.04	62.3	$2.1\cdot10^{5}$	0.1934
	10.0	542.4						
	7.5	538.7						
	5.0	524.2						
	4.0	510.2						

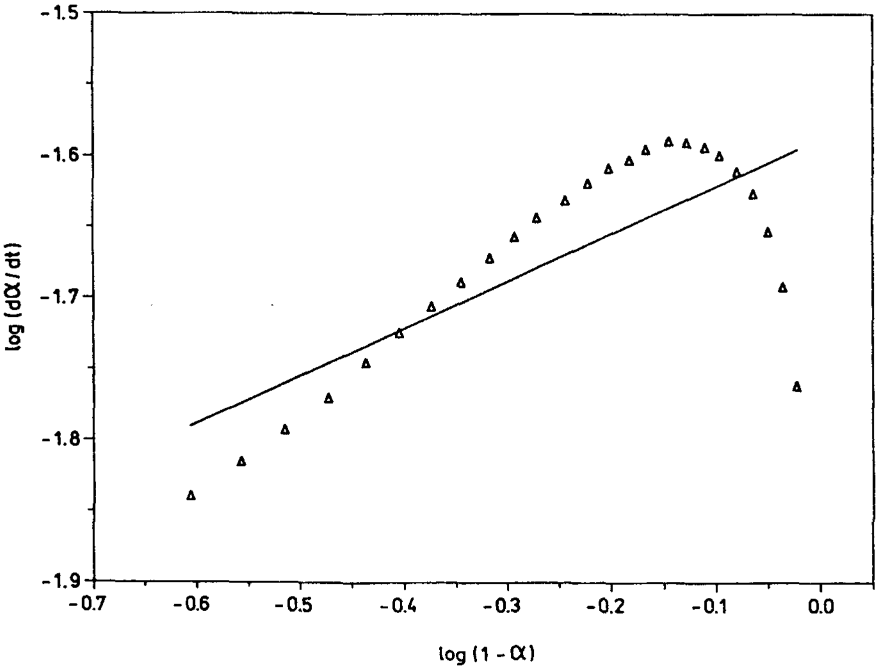

Fig. 3 Plot of log(dα/dt) *vs.* log(1−α) for n-th order model of isothermal oxidation of peanut oil

Isothermal method

From the recorded peaks of oxidation of investigating oils for each constant temperature were extrapolated induction time τ_{ON} and maximum point τ_{MP}. These values and calculated coefficients A, B from Eq. (6) and also obtained from Eq. (7) activation energies are shown in Table 3.

Thermograms of differential heat flow *vs.* time were used for the calculation of α_i and dα_i/dt_i at a given constant temperature. Selection of kinetic model of reaction depends on combining Eqs (1) with (8) or (9), and plotting log(dα/dt) *vs.* log(1−α) for n-th order model and log(dα/dt) *vs.* log[(1−α) $\alpha_{m/n}$] for autocatalytic course of reaction. Results obtained for assumed models are shown in Figs 3 and 4.

Results and discussion

Comparing the data from Tables 2 and 3 for all investigated oils we have found that the experimental values of activation energies from the dynamic method are different than from the isothermal experiments for the same oil and the average difference amounts to 20 kJ·mol^{-1} (for CRO 26.5 kJ·mol^{-1}). For

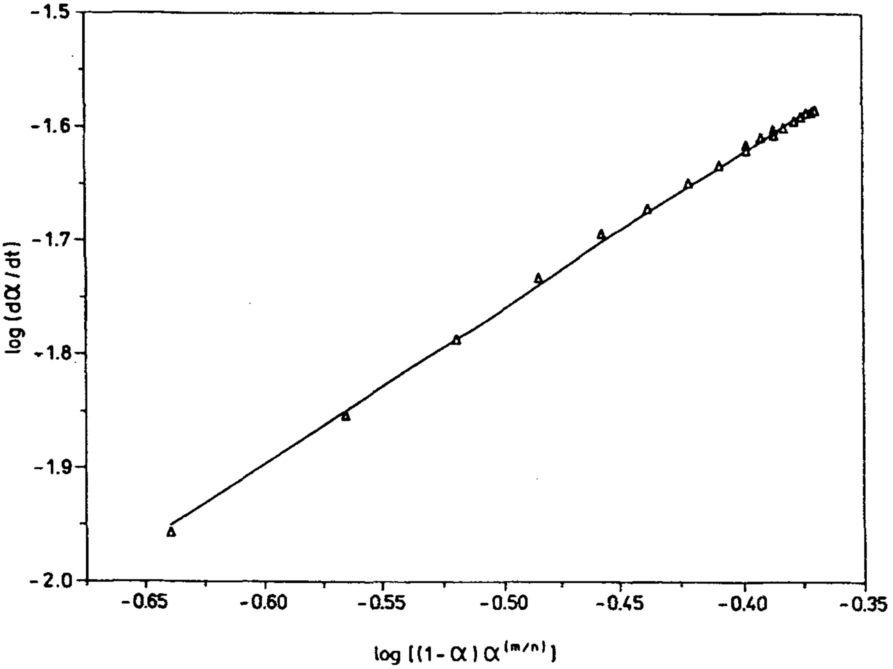

Fig. 4 Plot of log(dα/d*t*) *vs.* log[(1–α) $\alpha^{m/n}$] in autocatalytic model of reaction (for peanut oil)

rapeseed and peanut oil the 'isothermal' activation energy is higher then calculated from ASTM method while for soybean and corn oil the isothermal data give the lower energies. Such kind of differences may correspond with fatty acids compositions of investigated oils. There are similar iodic number and contents of oleic and linoleic acids (Table 1) for RSO and PO ($E_{\mathrm{ASTM}} < E_{\mathrm{ISOTHERMAL}}$). On the other hand the similar iodic number for CRO and SBO, the similar amounts of saturated fatty acids, lower contents of oleic acid and high participation of linoleic acid correlate with the opposite differences in values of activation energy for both of them ($E_{\mathrm{ISOTHERMAL}} < E_{\mathrm{ASTM}}$). However the kinetics of thermal oxidation of oils is first order reaction during the non-isothermal experiment what is in opposition to results calculated from isothermal data. The comparison Figs 3 and 4 indicates the very poor correlation the DSC data with *n*-th order model and the autocatalytic character of oxidation in constant temperature can be described as:

$$\frac{d\alpha}{dt} = k\alpha^{m}(1-\alpha)^{n} \tag{10}$$

Table 3 Data obtained from DSC curves from isothermal method

Oil	T/ K	τ_{ON}/ min	τ_{MP}/ min	A	B	δ	E/ J·mol^{-1}
RSO	405	33.9	54.9	3536.0	– 6.9	0.03	64.4
	410	26.3	41.7				
	422	15.5	26.9				
	425	11.2	19.6				
SBO	413	8.9	19.5	2819.0	– 5.5	0.05	51.3
	431	5.8	12.6				
	437	2.3	7.5				
CRO	422	13.5	23.9	4259.5	– 8.7	0.03	77.5
	429	11.7	19.0				
	431	8.5	14.7				
	435	5.7	12.0				
PO	383	24	44.4	4520	–10.2	0.02	82.3
	387	16.2	33.1				
	393	7.8	20.2				
	396	6.5	19.0				

It seems most likely that there are the different mechanisms of reaction at these various conditions and the shape of the curve (Fig. 1) shows the multiple peaks of dynamic reaction what is the sequence of multiple reactions. These peaks depend on the rates of individual reactions and the heating rate [5] but the heat flow is a function of the Arrhenius parameters of all reactions at observed moment. The first peak is smaller and too near by the second peak so it is difficult to obtain the complete information about this maximum (and activation energy) because this peak probably is made by low amount of adequate ingredients.

Conclusions

1. The different character of thermo-oxidation corresponds with observed differences of acitvation energy from both methods and it may be caused by other substances oxidated in isothermal and non-isothermal experiment.

2. The oils cannot be treated as homogeneous substance for investigate the kinetics of thermo-oxidation althought this method is successfully applied for assessment of their thermal stability. The DSC investigations of oils need a new attitude towards the role of different kind of experiment on respective components of mixture.

3. It is logical that the initial composition of the reaction mixture takes major part in course of DSC experiment and in different conditions (or different methods) we can obtain complementary informations.

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Zusammenfassung — Auf zwei verschiedene Arten wurde die Kinetik der Thermooxidation von Speiseölen (Sojabohnenöl, Rapsöl, Weizenöl und Erdmußöl) untersucht. Zur Messung unter isothermen und nichtisothermen Bedingungen in einer Sauerstoffatmosphäre wurden DSC und deren Druckvariante (PDSC) eingesetzt. Im Vergleich dieser beiden Methoden wurden für jede Ölsorte die Unterschiede bei den Werten für die Aktivierungsenergien beobachtet. Der Oxidationsmechanismus ist in beiden Methoden unterschiedlich.