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

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The thermooxidative decompositions of some edible oils were investigated. Isothermal measurements of converxion were made with a Du Pont differential scanning calorimeter. Linseed oil, castor oil, olive oil and cod-liver oil were investigated.

Keywords: DSC, edible oils, isothermal method, kinetics

Introduction [1–5]

Fractional conversion can be assumed to be equal to

$$C = \frac{\Delta H_1}{\Delta H_2} \tag{1}$$

where ΔH_1 is the heat evolved at a given point of time, and
ΔH_2 is the total heat evolved in the process.
ΔH_1 and ΔH_2 are equal to the area under the DSC curve up to the given point of time and the total area under the DSC curve, respectively (Fig. 1).

The fractional conversion can be determined for different times: $t_1 ... t_n$ as can be the rate of conversion: $\mathrm{d}C_1/\mathrm{d}t_1 ... \mathrm{d}C_n/\mathrm{d}t_n$. Because of the lack of knowledge concerning the exact course of the oil oxidation process, two models were tested:

1. the *n*th-order model,
2. the general autocatalytic model.

The *n*th-order model assumes that the reaction behaves in accordance with Eq. (2):

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$$dC/dt = k\,(1 - C)^n \tag{2}$$

where k is the rate constant, and
n is the reaction order.

In logarithmic form, Eq. (2) becomes

$$\log(dC/dt) = \log k + n(1 - C) \tag{3}$$

By plotting $\log(dC/dt)$ *vs.* $(1 - C)$, we can obtain a straight line with slope n and intecept $\log k$.

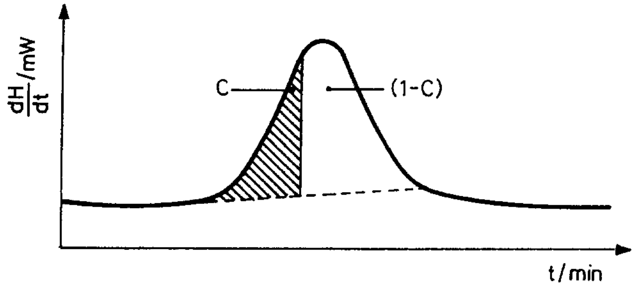

Fig. 1 Differential heat flow *vs.* time

The general atuocatalytic model is much more complicated in calculations. This model uses Eq. (4):

$$dC/dt = \log k\, C^{\mathrm{m}}(1 - C)^n \tag{4}$$

where m and n parameters.

The logarithmic form of Eq. (4) is

$$\log(dC/dt) = \log\ k + n\log[(1 - C)C^{\mathrm{m}/\mathrm{n}}] \tag{5}$$

Solving this equation yields $\log k$, m and n.

Experimental

The present investigation relates to oils with the physicochemical parameters listed in Table 1. All measurements were carried out with a Du Pont differential scanning calorimeter [6] equipped with a pressure cell, supplied with oxygen at 3 atm and flow of 6 l/h.

Thermograms of differential heat flow *vs.* time were used for the calculation of C_{i} and $dC_{\mathrm{i}}/dt_{\mathrm{i}}$ at a given constant temperature, where C_{i} is the fractional conversion as in Eq. (1). Results obtained for the nth-order model are shown in Fig. 2.

Table 1 Physical properties of investigated oils

Oil	Density/ g·cm^{-3}	Freezing-point/ °C	Iodic number/ gJ·100g^{-1}	n_D^{20}
linseed	0.9382	–15/–28	188/196	1.480
castor	0.962	–10/–18	81/189	1.453
olive	0.917	0/–5	189/196	1.467
cod-liver	0.932	–	120/146	1.475

The general autocatalytic model appeared to be much better as far as the correlation of the data with the model is concerned (Fig. 3). This model was used for the calculation of k, m and n on the basis of Eq. (5). The values are listed in Table 2.

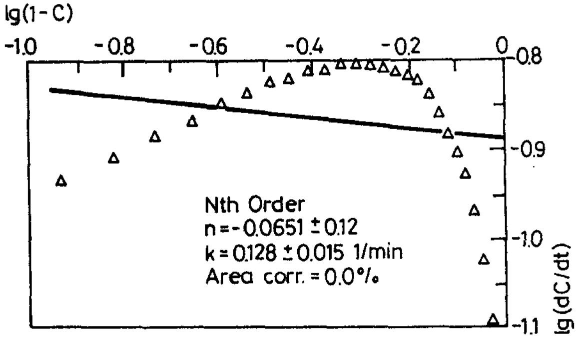

Fig. 2 Log(dC/dt) *vs.* log(1 – C) for nth model

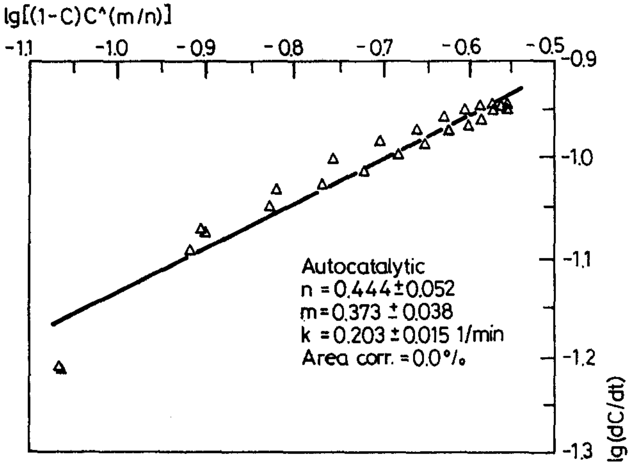

Fig. 3 Log(dC/dt) *vs.* log[(1 – C)$C^{m/n}$] in general autocatalytic model

Activation energy values (Table 2) were calculated by means of the Arrhenius equation:

$$k = Z\,e^{-E/RT} \tag{6}$$

Table 2 The values of activation energy E/kJ·mol^{-1} calculated using computer program-isothermal kinetics

Oil	E/kJ·mol^{-1}
olive	59.8
linseed	57.2
castor	89.7
cod-liver	75.2

using rate constants obtained at various temperatures.

Results and discussion

The investigations of the two models of thermooxidative decomposition for linseed oil, olive oil, castor oil and cod-liver oil led to the following conclusions:

1. The nth-model should be rejected, because of the very poor correlation of the DSC data with this model.

2. The thermooxidative decomposition can be described by the following kinetic equation:

$$\mathrm{d}C/\mathrm{d}t = k(1-C)^{n}C^{m} \tag{4}$$

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Zusammenfassung — Unter Einsatz der isothermen Methode wurden kinetische Untersuchungen der thermooxidativen Zersetzung einiger Speiseöle durchgeführt. Zur Bestimmung des Umwandlungsgrades wurde ein DS-Kalorimeter von DuPont eingesetzt. Grundlage der Untersuchung bildeten Leinöl, Rizinusöl und Olivenöl.