

Analysis of the Induction Period of Oxidation of Edible Oils by Differential Scanning Calorimetry

P. Šimon*, L'. Kolman, I. Niklová, and Š. Schmidt

Faculty of Chemical Technology, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

ABSTRACT: Oxidation of rapeseed and sunflower oils has been studied by differential scanning calorimetry under non-isothermal conditions and by Oxidograph under isothermal conditions for various temperatures. The parameters of an Arrhenius-like equation describing the temperature dependence of induction period have been obtained. A new method for evaluation of the parameters from nonisothermal differential scanning calorimetry measurements, based on the dependence of onset temperature of the oxidation peak on heating rate, is presented. It has been shown that the method gives parameters not affected by systematic errors. These can be used in modeling the oxidation process where the effects of oxygen diffusion, heat transfer, and evolution of reaction heat are explicitly involved. The results obtained by differential scanning calorimetry are compared with the Oxidograph measurements. The discrepancies between the results obtained by the two methods are accounted for by oxygen diffusion within the samples.

Paper no. J9478 in *JAACS* 77, 639–642 (June 2000).

KEY WORDS: Differential scanning calorimetry, edible oils, induction period, kinetics, oxidation.

Rancidity is an objectionable food quality defect where oxidation of oils and fats plays the most important role (1). Characteristic changes associated with oxidative deterioration include development of unpleasant tastes and odors as well as changes in color, viscosity, density, and solubility. The generalized scheme for autooxidation of unsaturated fatty acids can be found in Reference 2.

To estimate the stability of oils and fats, one usually subjects the sample to an accelerated oxidation test under standardized conditions, where heating is the most common means of accelerating the oxidation. The induction period (IP) is measured as the time required to reach an endpoint of oxidation, corresponding to a sudden change in the rate of oxidation (3).

The physicochemical principles for most of the methods used for IP determination can crudely be divided into two groups, i.e., the determination of oxidation products and the determination of oxygen uptake (1–5). The oxidation is an exothermic process and the reaction heat evolved makes it possible to employ differential scanning calorimetry (DSC)

or differential thermal analysis (DTA) for its study. Surprisingly, we have encountered only a few papers dealing with DSC or DTA study of oxidation of edible oils or fats (6–9). That the DSC method is not widely employed is probably due to the fact that, mainly at lower temperatures, the exothermic peak of oxidation is flat and its onset, corresponding to the end of IP, cannot be determined unambiguously.

When studying oxidation at various heating rates we realized that, contrary to the isothermal measurements, the oxidation peak is distinct in these nonisothermal measurements and the onset temperature can be read accurately and unambiguously. Hence, in this paper a new method is proposed for obtaining the kinetic parameters of induction periods from the onset temperatures of nonisothermal DSC runs with linear increase of temperature. The results obtained are compared with the induction periods obtained by Oxidograph.

EXPERIMENTAL PROCEDURES

Refined high-linoleic sunflower and zero-erucic rapeseed oils were taken from an industrial semicontinuous deodorizer manufactured by Lurgi (Palma-Tumys, Bratislava). The main characteristics of the oils are summarized in Table 1. The iodine value, saponification value, acid value, peroxide value, and unsaponifiable matter were determined according to standard procedures (10). Tocopherols were determined using high-performance liquid chromatography.

Two techniques were employed to study the edible oils oxidation: (i) Differential scanning calorimeter Shimadzu DSC-60 (Kyoto, Japan). The temperature scale was calibrated

TABLE 1
Characteristics of the Oils Under Study

Parameter	Sunflower oil	Rapeseed oil
Iodine value (g I ₂ /100 g)	125.4	111.6
Saponification value (mg KOH/g)	213.9	210.9
Acid value (mg KOH/g)	0.143	0.204
Peroxide value (mmol 1/2 O ₂ /kg)	0.351	0.281
Unsaponifiable matter (%)	1.313	1.275
Tocopherols (mg/100 g)	28.07	52.42
α-Tocopherol (mg/100 g)	24.15	17.62
β- + γ-Tocopherol (mg/100 g)	3.34	33.00
δ-Tocopherol (mg/100 g)	0.58	1.80

*To whom correspondence should be addressed.
E-mail: simon@cvt.stuba.sk

using the standards In and Zn. Samples of 2–3 mg were placed in open standard aluminum pans. The purge gas, forming the reaction atmosphere, was oxygen. Exothermic peaks in the DSC records are oriented upward. The standard deviation of a single measurement of the oxidation onset temperature, determined from three measurements, was less than 1.1 K for all scans. (ii) Oxidograph (Mikrolab, Århus, Denmark). The kinetics of oxidation was followed by the decrease of oxygen pressure at constant volume under isothermal conditions within the temperature range 100–125°C. The sample size was 5 g. The standard deviation of a single measurement of the induction period, determined from five measurements, was less than 0.15 h.

THEORY

In general, the dependence of the induction period on temperature can be expressed by an Arrhenius-like relationship (12):

$$t_i = A \exp(B/T) \quad [1]$$

where A and B are constants and T is the absolute temperature. For a nonisothermal process, the induction period can be calculated according to the Equation 2 (12)

$$1 = \int_0^t \frac{dt}{t_i(T)} \quad [2]$$

where the dependence of t_i on temperature is given by Equation 1. In case of the linear increase of temperature in DSC measurements, the furnace temperature can be expressed as

$$T_f = T_0 + \beta t \quad [3]$$

where T_f is the furnace temperature, T_0 is the starting temperature of the measurement, and β stands for the coefficient of temperature increase (scan). If one assumes that the temperature of the sample equals that of the furnace, combination of Equations 1–3 gives the result (12)

$$\beta = \int_{T_0}^{T_i} \frac{dT}{A \exp(B/T)} \quad [4]$$

where T_i is the temperature of the end of induction period, i.e., the onset temperature of the oxidation peak. As Equation 4 indicates, when the rate of heating increases, the onset temperature also increases.

RESULTS AND DISCUSSION

Induction periods have been measured for rapeseed and sunflower oils. Figure 1 shows that, within range of 80–320°C, the nonisothermal DSC oxidation of the oils occurs in two

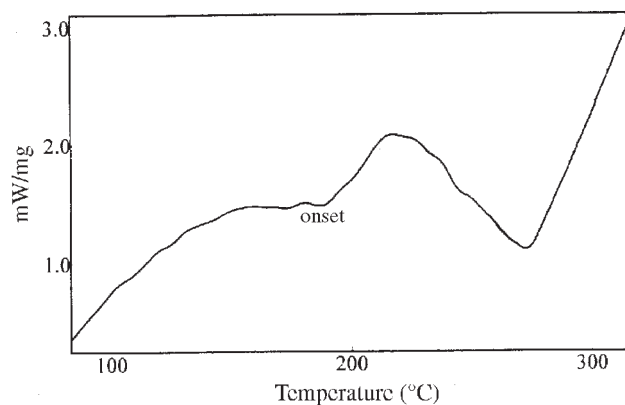


FIG. 1. Nonisothermal differential scanning calorimetry (DSC) record of sunflower oil oxidation, scan rate 20 K/min.

stages. The first stage is decisive for the study of oxidative changes, the second stage corresponds to quantitative decomposition of the oils (8,9).

The kinetic parameters describing the induction period have been obtained for nonisothermal DSC measurements and isothermal Oxidograph measurements. The onset temperatures of oxidation for DSC measurements with various scan rates are listed in Table 2. The parameters A and B in Equation 4 have been obtained by minimizing the sum of squares between experimental and theoretical values of heating rate by the simplex method (13). The integration indicated in Equation 4 has been carried out by the trapezium method. The agreement between experimental and fitted points is demonstrated in Figure 2. The standard deviations of A and B were calculated assuming a quadratic surface near the minimum (13). For the isothermal Oxidograph measurements, the kinetic parameters A and B have been obtained by a direct comparison of experimental and theoretical values of induction periods using the program ORIGIN, where the theoretical values are given by Equation 1. The values of A and B and their standard deviations obtained by both procedures are listed in Table 3.

In Table 3 the values of kinetic parameters A and B , describing the IP dependence on temperature, are almost identical for the rapeseed oil, but they differ greatly for the sunflower oil. As one can see from Figure 3, the kinetic parameters for rapeseed oil lead to identical IP values for the two techniques. For the sunflower oil, the parameters obtained by

TABLE 2
Onset Temperatures (in °C) of Oxidation for Various Scan Rates

Heating rate (K min ⁻¹)	Sunflower oil	Rapeseed oil
2	152.9	169.2
5	168.0	179.8
10	177.3	189.7
15	186.2	198.0
20	191.6	207.2
25	199.2	214.2

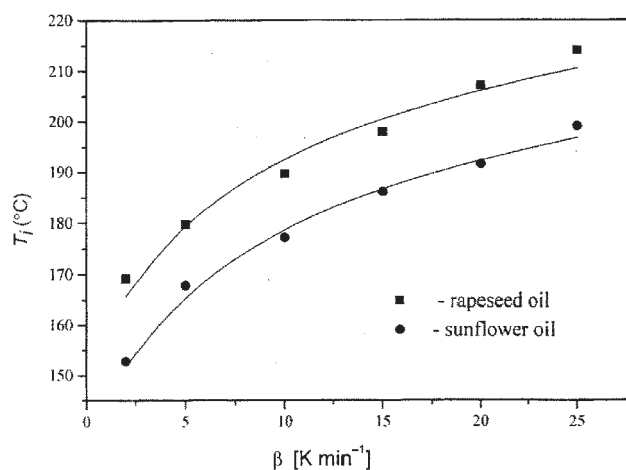


FIG. 2. Experimental and fitted dependences of the oxidation onset temperatures on the scan rates for the sunflower and rapeseed oils. T_i , temperature at the end of the induction period; β , coefficient of temperature increase.

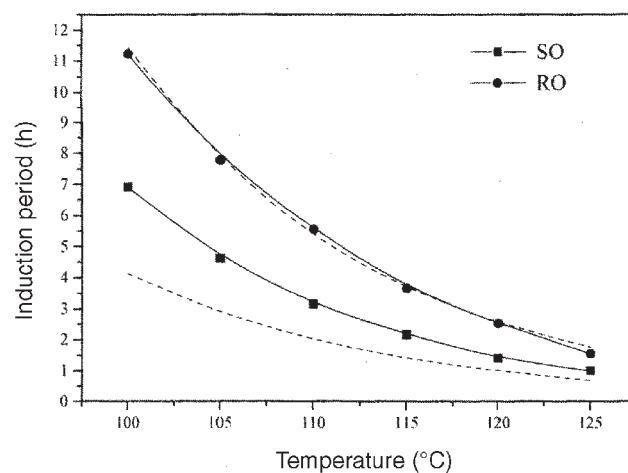


FIG. 3. Comparison of the Oxidograph (solid lines) and DSC (dashed lines) temperature dependences of the induction periods for the rapeseed (RO) and sunflower (SO) oils. For abbreviation see Figure 1.

DSC lead to much shorter induction periods than those obtained by Oxidograph. This difference can be ascribed to better oxygen saturation of the oil in DSC measurements. Oxygen is supplied to the oil by diffusion, and it is consumed in the oxidation processes taking place during the induction period. Within the framework of the diffusion film theory (14), and by assuming that a steady state is established between diffusion and oxidation, the oxygen concentration in the oil can be expressed as

$$\frac{dc}{dt} = \frac{DS}{VZ}(c_o - c) - kc = 0 \quad [5]$$

where c is the oxygen concentration, c_o is the saturated oxygen concentration, D is the diffusion coefficient, S is the oil-oxygen interphase area, V is the volume of the oil, z is the thickness of the diffusion film in the oil, and k stands for the rate constants of the oxidation processes occurring during the induction period. From Equation 5 one can obtain

$$\frac{c_o}{c} = 1 + \frac{kVz}{DS} \quad [6]$$

The IP length should be indirectly proportional to the concentration of oxygen in the oil. Hence, if the oxygen concentration in the oil is lower than the saturation concentration, IP can be expressed as

TABLE 3
Values of the Kinetic Parameters A and B and Their Standard Deviations Obtained by Various Methods

Sample	Method ^a	$10^{11} \times A/\text{min}$	$10^{-3} \times B/\text{K}$
Sunflower oil	Noniso-DSC	16.6 ± 0.7	10.5 ± 0.1
	Iso-Oxidograph	2.34 ± 0.65	11.4 ± 0.1
Rapeseed oil	Noniso-DSC	8.73 ± 0.36	11.1 ± 0.1
	Iso-Oxidograph	16.2 ± 13.6	10.9 ± 0.3

^aDSC, differential scanning calorimetry.

$$t_i = t_i^o \frac{c_o}{c} = t_i^o \left(1 + \frac{kVz}{DS} \right) \quad [7]$$

where t_i^o is the IP length for the saturated oxygen concentration in the oil. From Equation 1 it follows:

$$\frac{d \ln t_i}{dT} = -\frac{B}{T^2} \quad [8]$$

Combination of Equations 7 and 8 gives

$$B = B_o + \frac{E_d - E_a}{R[1 + (DS/kVz)]} \quad [9]$$

where B_o is the kinetic parameter B for the saturated oxygen concentration in the oil and E_d and E_a are the activation energies for the diffusion and the oxidation processes occurring during the induction period. From Equation 9 we see that the parameters B and B_o are close for the conditions $D \rightarrow \infty$, $(S/V) \rightarrow \infty$, $z \rightarrow 0$, and $k \rightarrow 0$.

For DSC, the ratio S/V is approximately 10^4 m^{-1} , for Oxidograph this ratio is about 150. Thus, the ratio S/V is almost two orders of magnitude higher for DSC, so that the kinetic parameter B obtained from DSC is much closer to the value B_o and is not affected by diffusion or by the sample size. The sample in Oxidograph is stirred by a magnetic stirrer which accelerates the oxygen diffusion since z decreases with increasing turbulence (14). However, the stirring is obviously not intense enough to make up for the large sample size. From Figure 3 we see that rapeseed oil is more stable than the sunflower oil so that the rate constant k is greater for the sunflower oil than for the rapeseed one. Consequently, oxidation of the sunflower oil in Oxidograph experiments is mostly controlled by diffusion since the rate of oxygen uptake is greater than its supply to the sample by diffusion. This is obviously the reason for lower values of induction periods measured by DSC than by Oxidograph for the sunflower oil (Fig. 3) and

also for the differences in the kinetic parameters obtained by the both methods (Table 3). The rate constant k for the rapeseed oil is obviously so low that the oxygen saturation of the sample is established in Oxidograph measurements. Therefore, for the rapeseed oil the parameters B are practically identical for both methods and the induction periods also are practically the same (Fig. 3). Equation 9 can account for most of the differences between induction periods measured by various methods (3,4).

Modeling of the processes occurring in foods has an important role in hazard analysis and ensuring quality during the food production, transport, and storage. However, it is necessary to bear in mind that the quality of the results of modeling depends on the quality of the kinetic model, i.e., whether the model involves all the essential effects, and on the reliability of the input parameters. The kinetic parameters A and B obtained by nonisothermal DSC measurements do not convey the effect of oxygen diffusion within the sample so that these parameters are free of systematic errors. Consequently, they are transferable to models of oxidation where the effects of reaction kinetics, oxygen diffusion, heat transfer, and evolution of reaction heat are explicitly involved. In practice, oxidation occurs under nonisothermal conditions: a pure isothermal regime is rare. Equation 2 makes it possible to calculate the IP for any temperature regime.

The parameters A and B obtained by the nonisothermal DSC make it possible to discriminate very sensitively between the stabilities of the oils. In Figure 4 the IP ratio for rapeseed and sunflower oils as a function of temperature is demonstrated. The curve calculated from A and B parameters is much higher than the curve obtained from Oxidograph measurements. Moreover, the DSC calculated curve is exponentially shaped as it is predicted by theory. The Oxidograph curve exhibits a maximum between 105–115°C which indicates that this temperature region is optimum for discrimination between oil stabilities. It can be expected that, for unstable oils, the rate of oxidation in the Oxidograph will be governed by the diffusion only and the induction periods will converge to a certain value. For fairly different values of diffusion coefficients of oxygen in the oils, the order of oil sta-

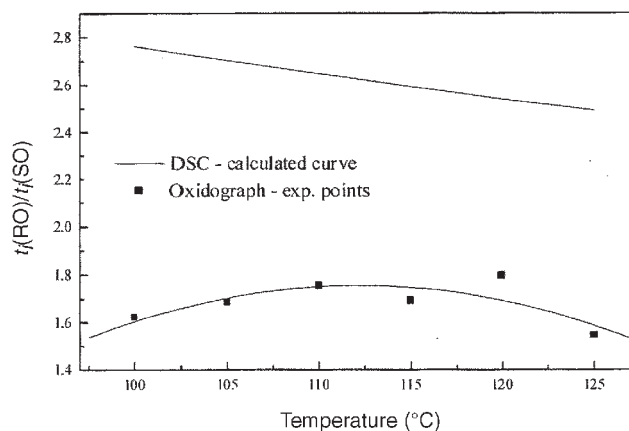


FIG. 4. Comparison of the ratio of induction periods (t_i) of rapeseed and sunflower oils determined by DSC and by Oxidograph. For abbreviation see Figure 1.

bilities determined by Oxidograph can even be erroneous. Equation 9 can also account for the differences between the results of various accelerated oxidation tests (3,4).

We believe that the method of treatment of nonisothermal DSC runs, based on the analysis of onset temperature of the oxidation in relation to heating rate, also can be employed for the study of other reactions exhibiting the induction period, such as oxidation of fat, tallow, and polymers. The value of the scan rate should not exceed 20–25 K/min since above this value the temperature T_i steeply increases, obviously owing to the existence of a temperature gradient in the sample. Then, the temperature of the sample is not equal to the temperature of the furnace which is the requisite condition for the derivation of Equation 4. For the treatment of nonisothermal DSC data, the program TIND has been written in FORTRAN-77. The DOS version of the program is available on request.

ACKNOWLEDGMENT

The financial support from the Slovak Grant Agency, grants No. 1/4208/97 and 1/6226/99, is gratefully acknowledged.

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[Received December 6, 1999; accepted April 4, 2000]