Monitoring of rapeseed oil autoxidation with a pressure differential scanning calorimeter

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Abstract

Samples of rapeseed oils stored at room conditions were used for determination of peroxides values (PV) by iodometric titration and for thermoanalytical parameters (t_{ON} and t_{max}) determined with a pressure differential scanning calorimeter when used in the isothermal mode. The assessment of oxidative stabilities and the anticipation of the oxidative fate of oils based on a single PV or on t_{ON} and t_{max} determination is rather uncertain. The linear correlation of t_{ON} and t_{max} vs. PVs makes possible a comparative assessment of the oxidative stabilities of the oils studied. Such assessments can be performed only for oils not reprocessed which show PV$\leq$30 mmol O_2^{2-}/kg of oil. The use of pressure differential isothermal calorimetry enables a more rapid stability assessment than the use of PV measurements alone. © 1997 Elsevier Science B.V.

Keywords: Autoxidation of oils; Isothermal calorimetry; Oxidative stability; Pressure differential scanning calorimetry; Rapeseed oil

1. Introduction

Autoxidation of lipids proceeds by radical reactions. The process consists of initiation, propagation and termination steps. Independent of the way the initiation occurs, the primary products of the autoxidation are hydroperoxides. They are unstable products and are involved not only in secondary reactions but also in the free-radical chain mechanism as they can be decomposed forming new radicals which can initiate and propagate new reaction chains. One of the primary concerns among food chemists is the onset of rancidity of fat-containing foods initiated by lipid peroxidation. Thus, monitoring of peroxides is one of the earliest methods for studying of fat autoxidation [1]. Determination of peroxides in fats is widely used and various standard procedures for natural or accelerated tests of fat autoxidation have been established [2]. Various physical methods such as absorption spectroscopy, chromatography, electrochemistry, and p–V relationships for oxygen are widely used in elucidating autoxidation mechanisms and identifying reactions products. Based on these physical methods, many accelerated instrumental tests for assessment of the oxidative stabilities of fats have been developed.

As oxidation and thermal-oxidative decomposition of oils and fats are exothermal reactions, measurements of enthalpy changes by calorimetry or thermal analysis can be applied for the determination of oxidative stabilities or thermal-oxidative resistance

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of fat-based products. The most promising techniques are differential scanning calorimetry (DSC) and pressure differential scanning calorimetry (PDSC). A number of studies have been performed with the use of DSC [3–6] and PDSC [7–11] both, in dynamic and isothermal modes.

The purpose of this work was to investigate the influence of the chemical state of rapeseed oils, as determined by PV measurements, on the results of PDSC measurements of oxidative stabilities of these oils. The relationships between PVs, t_{ON} and t_{max} and the possibility of monitoring of vegetable oil autoxidation by PDSC measurements were also studied.

2. Experimental

2.1. Rapeseed oils

Fresh samples of rapeseed oils labelled as RSO-1, RSO-2, and RSO-3 were obtained from a local factory. Their peroxide values were 0.1 mmol O_2^{2-}/kg for RSO-1 and RSO-3 and 0.4 mmol O_2^{2-}/kg for RSO-2. The fatty-acid composition of the oils listed in Table 1. Organoleptic tests for smell and taste showed these properties were typical of fresh samples. Qualitative tests with 2,4-dinitrophenylhydrazine showed no presence of aldehydes in the samples.

2.2. Procedure and measurements

RSO-1, RSO-2 and RSO-3 oils (600 g of each) were stored in open 1 l beakers in the laboratory at 19±1°C.

Periodically, aliquots were taken and the peroxide value determined by iodometric titration [12]. Thermoanalytical measurements were performed at the same time.

For thermoanalytical measurements a Du Pont 1090 B thermal analyzer with 1091 disc memory and a Du Pont 910 differential scanning calorimeter equipped with a pressure cell (PDSC, model no. 900830-902) were used in isothermal mode. The instrument was calibrated with high-purity indium. Weighed samples of oil were placed in open aluminium pans. The reference pan was left empty. Experiments were performed under 1400 kPa of oxygen at 120°C. Data were recorded on 8-inch floppy discs and then plotted. From the resulting PDSC exotherms, times for the extrapolated onset of oxidation t_{ON} (obtained with the Du Pont OXIDATIVE STABILITY V 2.0 program) and the maximum of the peak t_{max} (obtained from plots) were determined, as in [8]. For each sample, 3–4 PDSC exotherms were recorded. If the reproducibility was better than 4% as judged from t_{ON} and t_{max} values, the PDSC exotherm which showed the best fit was selected and used for further mathematical analysis.

3. Results and discussion

Results of PV and PDSC measurements as a function of storage time are shown in Figs. 1 and 2. Peroxide values increase with time and the plot is characteristic of oil autoxidation, showing induction and acceleration periods. Generally, induction times

Table 1
Fatty acid compositions of oils studied

Fatty acid $C_{m:n}$[a]	Percentage content		
	RSO-1	RSO-2	RSO-3
$C_{16:0}$	5.1	5.2	4.7
$C_{16:1}$	0.2	0.2	0.3
$C_{18:0}$	1.8	2.0	1.8
$C_{18:1}$	59.6	56.4	59.9
$C_{18:2}$	19.9	23.8	19.8
$C_{18:3}$	8.5	7.9	8.4
$C_{20:0}$	0.6	0.6	0.6
$C_{20:1}$	2.1	1.9	2.3
$C_{22:0}$	0.3	0.4	0.3
$C_{22:1}$	1.9	1.6	1.9

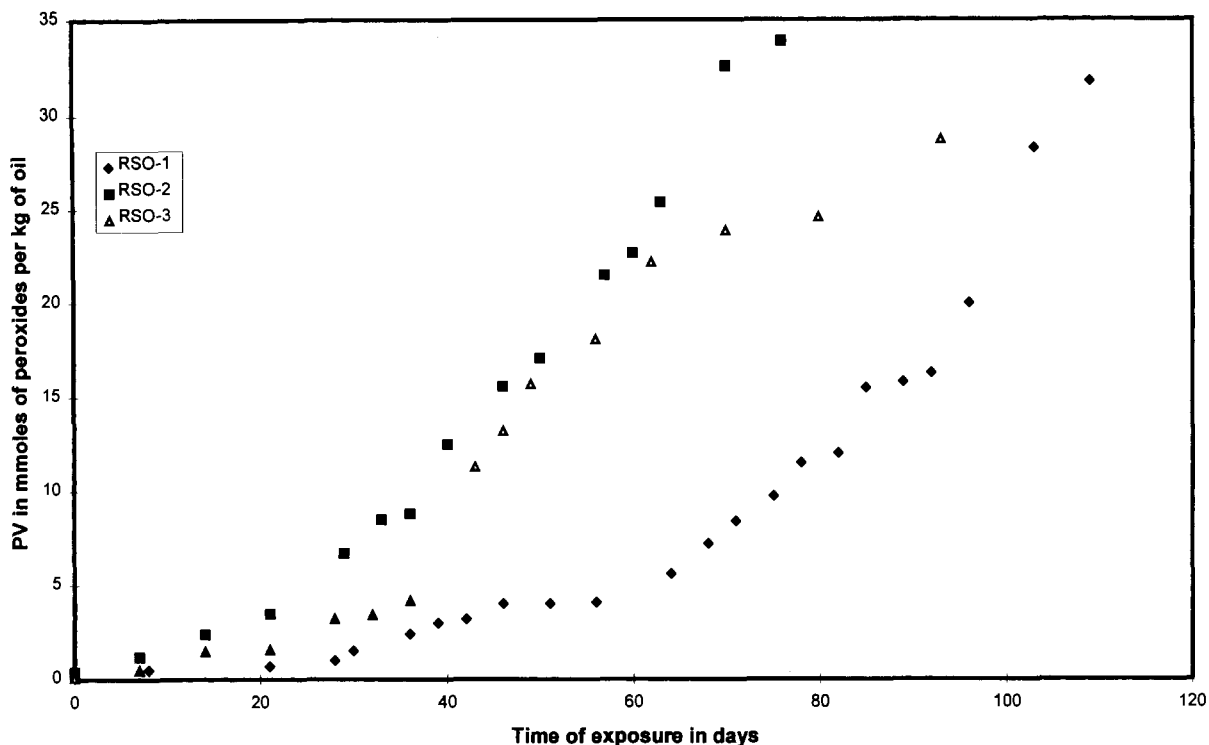[a] m=number of carbon atoms; n=number of double bonds.

Fig. 1. Peroxide values (PV) vs. time of exposure for rapeseed oils studied.

(induction periods) are determined as the intersection of tangents to the PV=$f_{(time)}$ curves and used for assessment of oil stabilities in accordance with the rule "the longer the induction time, the more stable is the oil". When the PV=$f_{(time)}$ curve is smooth, there is no problem with this determination of induction period. But for situation where experimental points are scattered, there are difficulties with such determinations (Fig. 1), and based on a single determination of PV, it is practically impossible to predict the oil oxidative stability.

Measured by PDSC, t_{max} and t_{ON} values decrease with storage time (Fig. 2). As there are no official regulations on the use of PDSC/DSC measurements for the assessment of oxidative stability of oils, only comparative studies can be performed [5,9–11]. Based on a single PDSC measurement, it is also impossible to predict oxidative stability of oil during storage. The results of PDSC measurements (t_{max} and t_{ON}) were thus correlated with PV values. The correlations appear to be linear if PV≤30 mmol O_2^{2-}/kg of oil, so they were described by Eqs. (1)

Table 2
Parameters of Eqs. (1) and (2) and coefficients of determinations (R^2)

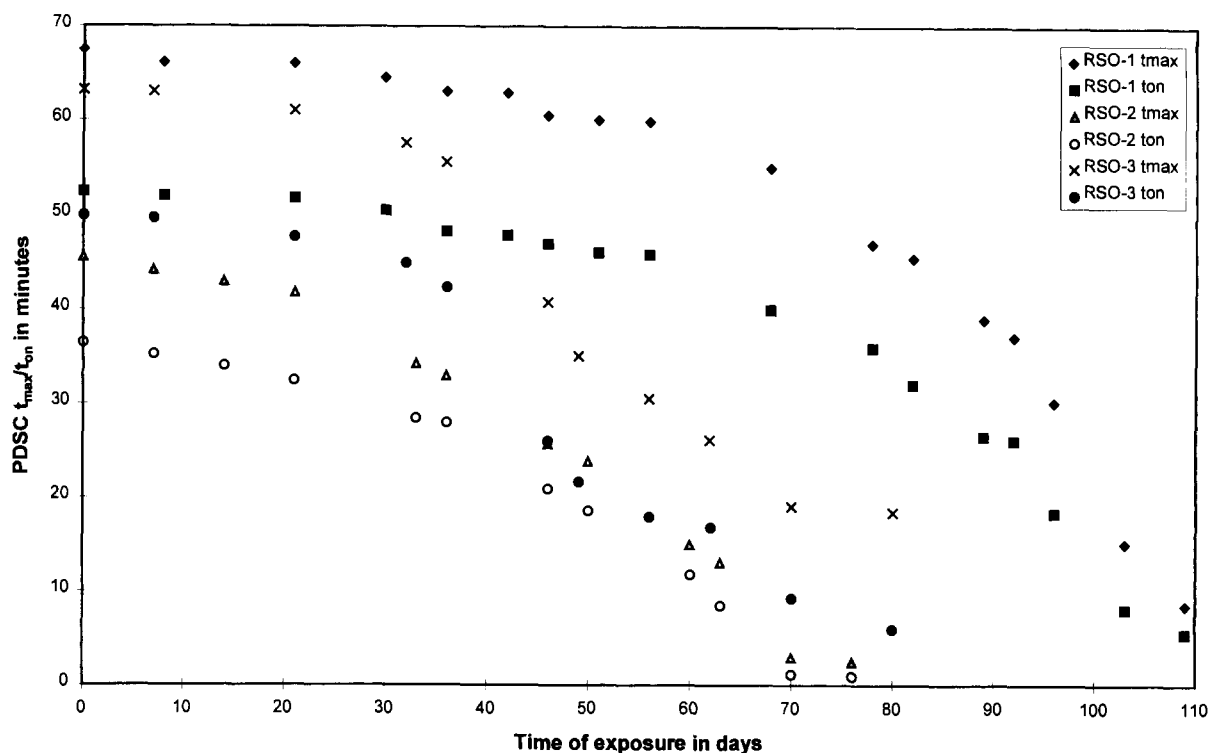| Parameters of equations	RSO-1	RSO-2	RSO-3
A	−1.857	−1.301	−1.805
B	67.74	45.76	63.72
R^2	0.999	0.998	0.996
a	−1.561	−1.082	−1.722
b	52.37	36.92	50.14
R^2	0.993	0.997	0.991

Fig. 2. Relationship between t_{max} and t_{ON} measured by PDSC and time of exposure for rapeseed oils.

and (2):

$$t_{max} = A(\mathrm{PV}) + B \qquad (1)$$

and

$$t_{ON} = a(\mathrm{PV}) + b \qquad (2)$$

Calculated parameters of these equations and suitable coefficients of determinations (R^2) for the oils studied are listed in Table 2.

4. Conclusion

Periodic measurements of PVs and T_{max}/t_{ON} values can be performed for oil stored at given conditions. After about 1 week the results of such measurements can be presented as linear correlations of PDSC parameters vs. PVs, and t_{max} or t_{ON} can be used for monitoring oxidative stability of the oil. If the temperature of stored oils is increased some 20–30°C above the room temperature, the correlation can be

obtained much more quickly. This procedure cannot be used for reprocessed oils. Heating of oxidized oils (often in N_2 atmosphere) reduces their PV values. Such oils are called "reprocessed" and cannot be used as edible oils. PDSC measurements such oils show short t_{ON} and t_{max} times that are not linearly related to PV values.

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