Assessing the Extent of Oxidation in the Thermally Stressed Safflower Oil. Part II: Two Variants of Photopyroelectric Method, Differential Scanning Calorimetry and Gas Chromatography

Dane Bicanic[1†], Otto Dнka[2], Zoltan Kantor[3], Gabriela Nagy[4], Jan Cozijnsen[5], Fulvio Mercuri[6], Juergen Gibkes[7], Dorin Dadarlat[4], Edo Gerkema[1], Jan Thoen[8], Guido Pitsi[8]

[1]Laser Photoacoustic Laboratory, Department of Agrotechnology and Food Sciences, Wageningen University and Research Centre, Bomenweg 4, 6703 HD Wageningen, The Netherlands and Faculty of Food Sciences and Biotechnology, University of Zagreb, Pierottijeva 6, Zagreb, Croatia, [2]Department of Physics, University of West Hungary, Deak F. sq. 1, 9200 Mosonmagyarovar, Hungary, [3]Department of Physics, Jozef Atilla University, Dom Ter 9, Szeged, Hungary, [4]Institute for Isotopes and Molecular Technology, P.O.B. 700, Cluj-Napoca 5, Romania , [5]Departement of Food Chemistry, Wageningen University and Research Centre, Bomenweg 2, 6703 HD Wageningen, The Netherlands, [6]Department of Mechanical Engineering, Tor Vergata University, Rome, Italy, [7]Department of Physics, Ruhr University, Bochum, Germany, [8]Laboratory for Acoustic and Thermal Physics, Catholic University Leuven, Celestijnenlaan 200, Leuven, Belgium

Differential scanning calorimetry (DSC), and the standard and inverse variant of the photopyroelectric technique (PPE) were applied to monitor the progress of oxidation induced in thermally stressed safflower oil. The results obtained by these thermal characterization methods were compared to those acquired by the gas chromatography (GC) and Rancimeter apparatus. Analytical indices were compared and the correlation coefficients calculated.

Keywords: safflower oil, oxidation,thermal stress, thermal characterization

(Received on June 29, 2000 accepted on October 27, 2000)

As stated in Part I of these two back-to-back publications, stability of edible oils toward oxidation is considered one of important properties as it determines their shelf life. However, measuring the extent of the oxidative stability is a difficult task. Since oils are generally stored around the ambient temperatures (at which the oxidation is slow), the majority of characterization methods is based on studying samples that were deliberately subjected to induced accelerated oxidation. Unlike in Part I, where emphasis placed was on the optical characterization methods, this paper is concerned with the application of thermal characterization methods (differential scanning calorimetry (DSC), standard and inverse variants of the photopyroelectric (PPE) methods) and the gaschromatography (GC) to study changes in a thermally stressed safflower oil.

Experimental

Cold pressed, unrefined safflower oil (Reform Natufood) with linoleic acid being a major constituent, was purchased from a local supermarket. Ten hours long accelerated oxidation[1,2] was achieved at 130^{o} C (403 K) and 300 ml/min flow of pressurized air. Oil samples were taken for the analysis at the beginning of the process, as well as 2, 4, 6, 8 and 10 hours from onset of the treatment.

The DSC measurements were performed on a Perkin-Elmer DSC7 instrument. For heating scans, temperature scale was calibrated using known values for the melting points of water and chlorobenzene. Calibration for cooling scans was performed by extrapolating heating data obtained at different scan speeds. Oil samples (approximately 10 mg) were poured into stainless steel DSC sample pans at a room temperature and then rapidly heated to 353 K. Cooling and heating scans (between 353 K and 153 K) were performed at 10 K/min scanning rate in both directions.

The front configuration variant of the PPE was applied to determine thermal diffusivity [3-5]. The 35 μm thick layer of oil (optically and thermally thick) was accommodated between the bottom section of the PPE cell and one surface of the PPE transducer. The opposite sensor's surface was by means of the silicone paste thermally coupled to a cryo-cooled cold finger unit. The entire system was maintained under vacuum (~10^2 mbar); both, heating and cooling rates were 0.5 K/min respectively. The oil was initially cooled down to 240 K and kept at this temperature for 15 min. The cryo-cooler was then switched off and heating initiated. The sample was heated up to 290 K; both the amplitude A and the phase Φ of the PPE signal were analyzed by a lock-in amplifier. For given experimental conditions, phase Φ is given by $\Phi=C-(\alpha f/D)^{1/2}L$, where f is modulation frequency, L is sample's thickness (assumed known), D is thermal diffusivity of the sample and C is the instrumental constant. The absolute value for D can be found from a slope in Φ versus $f^{1/2}$ plots that were constructed from data obtained by the frequency scans performed at the room temperature.

Thermal effusivity was measured by means of the IPPE (inverse variant of the PPE method) using a 9 μm PVDF foil (thermally

† To whom correspondence should be addressed.

thin. and optically thick sensor).The oil was pipetted directly on PVDF foil; the 780 nm diode laser (output 30 mW) served as a heating source[6,7].

The GC analysis of polar and non-polar volatiles was performed on a GCL-90 gas chromatograph (2 m x 3 mm i.d. glass column with packing material consisting of 10% diethylene glycol succinate on Chromosorb WAW 80-100 mesh) provided with a FID detector. The temperature of injector, detector and the column were 573 K, 523 K and 463 K respectively; argon served as a carrier gas (18 ml/min). Majority of peaks cold be identified by matching their GC retention times with those of authentic compounds.

Results and discussion

The DSC cooling curves show three exothermal peaks found at approximately –89°C, –44°C and –17 °C (Fig. 1).

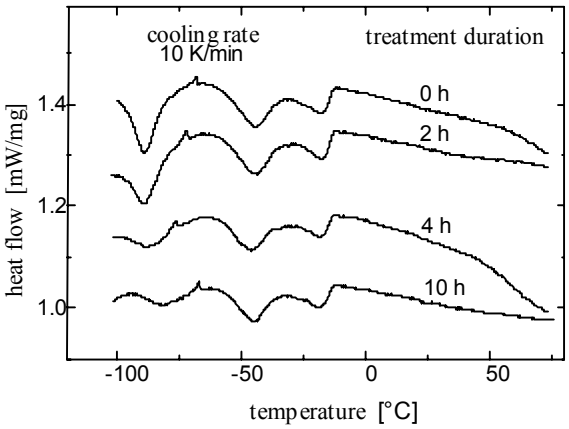


Fig. 1. DSC cooling curves for fresh (uppermost trace) and thermally stressed (2, 4 and 10 hours) safflower oil, as a function of temperature. For each curve, recorded raw heat flow values were divided by a mass of the corresponding sample. For clarity reasons, the traces were deliberately displaced in a vertical direction.

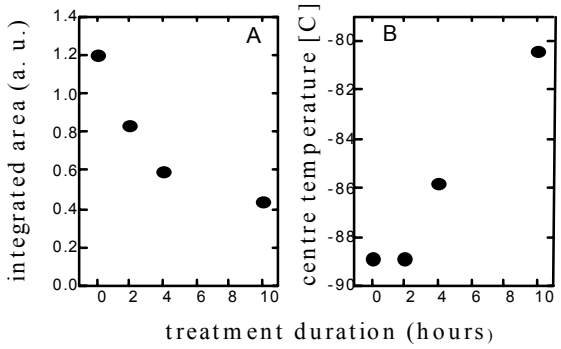


Fig. 2 Gaussian fit parameters to a low-temperature exothermal peak (at –89° C) of DSC cooling plots (10 K/min) obtained from the fresh and oxidized safflower oils. A: the integral area below baseline; B: center temperature.

The peak found in fresh oil at –89°C shows a gradual shift toward higher temperatures. Parallel to such a shift, the "strength" of the peak (i.e. the integral of the heat flow below the actual baseline) tends to decrease. It should be noted that two other features appearing at –44°C and –17 °C neither change their shape nor their position as the oxidative process proceeds. To numerically characterize the above mentioned peak at –89°, one has subtracted the baseline and determined relevant analytical indices such as the integral area of the peak, its center position and width of the best-fit Gaussian (Fig. 2).

It is worth mentioning that appropriate unit for integral area is WK/g; however the actual value of this quantity depends on a cooling rate. For the purpose of standardization, cooling rates must therefore be consistently the same. While measured values for a center temperature may depend on the accuracy, as well as on the care taken when calibrating the temperature scale for cooling scans, the peak area is the invariant of a temperature and hence a more reliable analytical index.

Within the limits of absolute error ($0.5x10^{-4}$ cm^2/s) values for D obtained by means of the PPE measurements were practically the same. i.e. $D=7.5x10^{-4}cm^2/s$ for all samples. The above value was used for normalization and to calculate (from the phase of the signal) the temperature dependence of D. None of the samples exhibited the evidence for obvious critical behavior within the selected temperature range (250-290 K). At about 260 K all samples show (Figs. 3 and 4) the change of a slope in plots for phase Φ and D (the curves in Fig. 3 were deliberately shifted in vertical direction to overlap below 260 K).

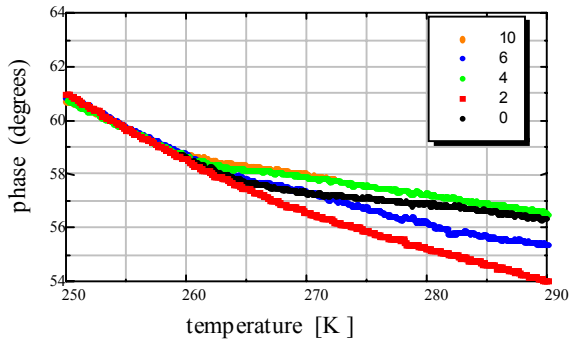


Fig. 3 Signal phase as a function of temperature. The curves were deliberately shifted in a vertical direction to overlap below 260 K.

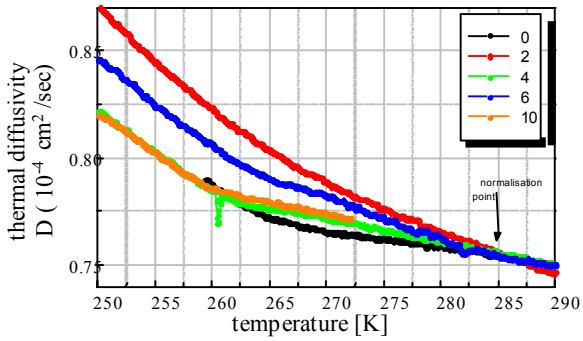


Fig. 4 Temperature dependent thermal diffusivity D of fresh and treated oils. The curves were normalized to the value ($D=7.5x10^{-4}cm^2/s$) at 285 K (see text above).

It should be pointed out however that observed (slight) dependence of a phase on a temperature variation rate suggests that the system might have not been at the equilibrium during the measurement. One possible reason for this could be a too fast temperature variation rate; under such conditions some phase transitions might have not been detected. Moreover, if during measurement, the samples were indeed not at the equilibrium, the obtained phase behavior depends on sample's thermal history. Finally, reader is aware of the fact that a model used here to calculate D from the measured phase Φ is valid only for homogeneous samples that were in equilibrium.

Table 1: The result of the analysis for variance performed for analytical indices used for thermal characterization.

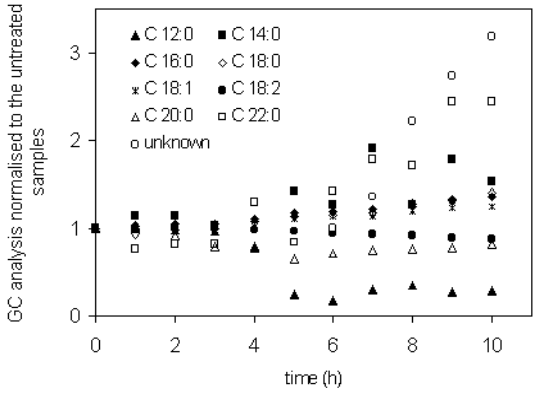
	analytical index	1	2	3	4	5	6	7	8	9	10	11	12	13
1	C 12:0 lauric acid	-	*	*	*	*		*		*	*			
2	C 14:0 myristic acid	-	-					*	*		*		*	
3	C 16:0 palmitic acid	-	-	-				*			*			
4	C 18:0 stearic acid	-	-	-	-			*			*			
5	C 18:1 oleic acid	-	-	-	-	-		*			*			
6	C 18:2 linoleic acid	-	-	-	-	-	-	*			*			
7	unidentified compound	-	-	-	-	-	-	-	*	*	*	*	*	*
8	C 20:0 arachidic acid		-	-	-	-	-	-	-	*	*			
9	C 22:0 behenic acid	-	-	-	-	-	-	-	-	-	*		*	
10	unidentified compound	-	-	-	-	-	-	-	-	-	-	*	*	*
11	thermal effusivity	-	-	-	-	-	-	-	-	-	-	-		
12	DSC signal peak area	-	-	-	-	-	-	-	-	-	-	-	-	
13	DSC (heat-flow)-(baseline)	-	-	-	-	-	-	-	-	-	-	-	-	-

*: The mean difference is significant at the 0.05 level.

Consequently, in the absence of equilibrium, the behavior for D described above is not anymore correct.

Room temperature effusivity values of distilled water (1590 W $s^{1/2}$ m^{-2} K^{-1}) and ethanol (596 W $s^{1/2}$ m^{-2} K^{-1}) served to calibrate the response of the IPPE system. Results of the IPPE measurements indicate only a slight increase in thermal effusivity of safflower oil (600 W $s^{1/2}$ m^{-2} K^{-1} for fresh safflower oil and 617 W $s^{1/2}$ m^{-2} K^{-1} for a sample treated ten hours long).

Figure 5 shows how does the composition of fatty acids profile of investigated sample change in time (values shown along y-axis were normalized to those obtained from the untreated sample). The most significant changes are observed after three



hours of oxidative treatment.

Fig. 5 Relative changes in fatty acids profile of safflower oil plotted as a function of treatment duration.

The results of the analysis of the variance for thirteen analytical indices used in this study for thermal characterization are displayed in Table 1. The correlation coefficients between the specific analytical index and treatment duration are shown in Table 2. The mathematical procedure followed and the meaning of symbols used in Tables 1 and 2, are the same as discussed in Part I (paper concerned with the optical characterization of safflower oil).

In conclusion, the integral of a DSC peak area appears sensitive to the treatment length, in particular the two initial hours. Thermal diffusivity is not a suitable parameter for monitoring changes in thermally stressed oil. Highest degree of correlation was observed for the two thus far unidentified GC components. Future GC experiment will concentrate on the detection of hydrocarbons and aldehydes; this might provide markers for studying early changes in oil, the induction time of which was found (via Rancimeter approach) to be approximately two hours (under given experimental conditions). In addition, attempt will be made to find out how the results collected under the conditions of accelerated oxidation could be related to those encountered for oils under normal storage circumstances.

Table 2. The correlation between analytical indices and duration of oxidative treatment.

	analytical index	correlation coefficient
1	C:12:O lauric acid	0.86
2	C 14:0 myristic acid	0.56
3	C 16:0 palmitic acid	0.98
4	C 18:0 stearic acid	0.96
5	C 18:1 oleic acid	0.98
6	C 18:2 linoleic acid	0.96
7	unidentified compound	0.98
8	C 20:0 arachidic acid	0.65
9	C 22:0 behenic acid	0.89
10	unidentified compound	0.99
11	thermal effusivity	0.93
12	DSC (peak area)	0.89
13	DSC (substraction of the baseline)	0.71

Acknowledgements-Partial support received from European Commission DG XII Research and Development, Brussels within the frame of Inco-Copernicus (IC15-CT96-1003) and Euram Brite (BRRT-CT98-5041) projects is being acknowledged.

References

1. J.B. Rossell, "Measurement of Rancidity" , Chapter 2 in "Rancidity in Foods", J.C. Allen and R.J. Hamilton (eds.), **1994**, Blackie Academic & Professional, Glasgow.

2. E.N. Frenkel, "Methods to Determine Extent of Oxidation", Chapter 5 in "Lipid Oxidation", **1998**, The Oily Press Ltd., Dundee, Scotland.

3. D. Dadarlat, D. Bicanic, H. Visser, F. Mercuri, A. Frandas, *J. of Amer Oil Chem Soc (JACOCS),* **1995**, *72*, 273.

4. A. Frandas, D. Bicanic, *J. of Sci Food and Agric,* **1999**, 79, 1361.

5. D. Dadarlat, D. Bicanic, J. Gibkes, W. Kloek, I. van den Dries, E. Gerkema, *Chem and Phys of Lipids,* **1996**, 82, 15.

6. D. Dadarlat, H. Visser, D. Bicanic, *Meas Sci and Tech,* **1995**, 6, 1215.

7. D. Dadarlat, D. Bicanic, J. Gibkes, A. Pasca, *J. of Food Eng,* **1996,** 30, 155.