Determination of the oxidative stability of hazelnut oils by PDSC and Rancimat methods

Hanna Ciemniewska-Żytkiewicz · Katarzyna Ratusz · Joanna Bryś · Magdalena Reder · Piotr Koczoń

Abstract The present study was conducted to determine the oxidative stability of hazelnut oil and compare it with more common and previously tested olive oil and rapeseed oil. The oxidative stability was determined by means of two independent methods, pressure differential scanning calorimetry (PDSC), and oxidative stability index (OSI) using *TA Instruments* DSC and *Metrohm* Rancimat equipment, respectively. Both the PDSC and Rancimat devices were set at five different isothermal temperatures in the range of 100–140 °C. The times to reach peak maximum (τ_{max}) obtained from PDSC exotherms were statistically related with the Rancimat induction times (τ_{on}) to obtain correlation coefficient >0.99 within linear relation. Based on the Arrhenius equation and activated complex theory, activation energies (E_a), pre-exponential factors (Z), and specific rate constants (k) for studied oils oxidations were calculated. To the best of our knowledge, this is the first study dealing with oxidative stability of hazelnut oil using PDSC technique. According to the results obtained, PDSC seems to be useful and quick method for kinetic analysis of lipid oxidation in hazelnut oil.

Keywords Hazelnut oil · Olive oil · Rapeseed oil · Oxidative stability · PDSC · Rancimat

H. Ciemniewska-Żytkiewicz (✉) · J. Bryś · M. Reder · P. Koczoń
Department of Chemistry, Faculty of Food Sciences, Warsaw University of Life Sciences, Nowoursynowska St. 159c, 02-776 Warsaw, Poland
e-mail: hanna_ciemniewska_zytkiewicz@sggw.pl

K. Ratusz
Department of Food Technology, Faculty of Food Sciences, Warsaw University of Life Sciences, Nowoursynowska St. 159c, 02-776 Warsaw, Poland

Introduction

Tree nuts, including hazelnuts (*Corylus avellana* L.), are nutritious, provide macronutrients, micronutrients, and bioactive phytochemicals, tasty, convenient, and easy snacks that contribute to healthy lifestyle. Hazelnut oil can be used for several purposed such as cooking, salad dressing, flavouring ingredient, and as well as, a component of skin moisturizers, and cosmetic products [1, 2]. To maintain the freshness of hazelnuts or its oil, it is of paramount importance to study their susceptibility to lipid oxidation in order to optimize the processing and storage conditions.

The assessment of oils and fats quality can be conducted using the oxidative stability determination. Nowadays, the Rancimat Metrohm (Europe) and the oxidative stability index (OSI) (USA) are the most commonly explored and used [3–6]. However, there are also some new methods to evaluate oxidative stability, among others, OXITEST, which enables to assess the oxidation process directly on foodstuff without fat extraction [7], or near infrared emission spectroscopy (NIRES) which allows to determine the induction time of edible oils in accelerated oxidation experiments by monitoring the intensity of a band at 2,900 nm, which corresponds to the formation of hydroperoxides [8].

The transfer of an oxygen molecule to unsaturated fatty acids requires energy. Therefore, the oxidative stability of vegetable oils can also be established by differential scanning calorimetry (DSC) technique, supported by kinetic analysis of lipid oxidation [9]. DSC technique with use of both isothermal (constant temperature) and dynamic (linear increase of temperature) conditions has been successfully applied for analysis of vegetable oils, e.g., rapeseed, olive, soybean, sunflower, and high-stability oils, as

reported in literature [4–6, 10–13]. According to Kowalski et al. [10], the isothermal pressure DSC seems to be more suitable than non-isothermal DSC for studying the oxidation of edible oils because the pressure DSC experiment is carried out at lower temperatures, and the heat of transition is more precisely defined.

Few authors [4, 5, 13, 14] who evaluated the oxidative state of oils by DSC highlighted an elevated correlation between thermal analysis and traditional oxidative tests, like oxidative stability instrument or the Rancimat. However, to the best of our knowledge, this is the first study dealing with pressure differential scanning calorimetry (PDSC) and Rancimat in the context of hazelnut oil.

We presumed that PDSC technique alike other methods currently applied for hazelnut oils assessment is fairly useful while have another advantages, e.g., simplicity, quickness and requires quite small amounts of samples for analysis [15]. The main aim of this study was to compare and relate the oxidative stability of hazelnut oils determined by PDSC and the Rancimat at a wide temperature range (100–140 °C). Hence, pave the way for development of PDSC as reliable technique for routine evaluation of oxidative stability of hazelnuts oil and therefore quality of hazelnuts.

Materials and methods

Chemicals

All the solvents (*n*-hexane, diethyl ether, methanol, ethanol, and chloroform) and reagents (acetic acid, potassium iodide, sodium thiosulfate, potassium hydroxide, starch soluble, and phenolphthalein) used were of analytical grade and purchased from P.O.Ch Co. (Gliwice, Poland).

Materials

Three samples of cold–pressed hazelnut oil (HO), three samples of extra virgin olive oil (OO), and two samples of refined rapeseed oil (RO) were purchased on local market as a food grade commercial products.

Chemical analyses

Peroxide value (PV) of oils was determined by iodometric technique, free fatty acids (% FFA) by titration with 0.1 M ethanolic potassium hydroxide in accordance with Standards ISO 3960:2007 [16], ISO 660:2009 [17], respectively.

Fatty acid analysis

The fatty acid composition of oil samples presented in Table 1 was determined as FAMEs by capillary gas chromatography analysis after alkaline treatment as described by Christie [18]. The chromatographic conditions were the same as reported by Bryś et al. [19].

Pressure differential scanning calorimetry (PDSC)

The oxidative stability of tested oils was determined using DSC (Q20, TA Instruments) coupled with a high-pressure cell (Q20P). The equipment was calibrated using high-purity indium as a standard. Oil samples of 3–4 mg were weighted into an aluminium pan and placed in the sample chamber under oxygen atmosphere with an initial pressure of 1,400 kPa and with the 100 mL min^{-1} oxygen flow rate. The isothermal temperature for each sample was programmed at five different temperatures (100, 110, 120, 130 and 140 °C). Obtained diagrams were analyzed using TA Universal Analysis 2000 software. For each sample, the output was automatically recalculated and presented as amount of energy per 1 g. The maximum PDSC oxidation time (τ_{max}) was determined based on the maximum rate of oxidation (maximum rate of heat flow) with the accuracy of 0.005.

Oxidative stability test

The oxidative stability was determined in 743 Rancimat apparatus from Metrohm according to ISO 6886:1997 [20], utilizing a sample of 2.5 ± 0.01 g. All samples were studied in five temperatures (100, 110, 120, 130, and 140 °C), under a constant air flow (20 L h^{-1}). The induction times were printed automatically by apparatus software with the accuracy of 0.005.

Statistical analysis

Relative standard deviation was obtained, where appropriate, for all data collected. All chemical analyses were carried out in triplicate ($n = 3$) for each sample. In case of oxidation stability determination, for each oil at each temperature, three experiments were performed and the average τ_{max} (PDSC maximum induction time) and τ_{on} (Rancimat induction time) values were calculated. The data were statistically processed with use of Statgraphics Plus for Windows software, version 4.1 (Statistical Graphics Corporation, Warrenton, VA, USA). Pearson's linear correlations were calculated at the $p < 0.05$ level.

Table 1 Parameters of hazelnut (HO), olive (OO), and rapeseed (RO) oil samples

Parameters	Hazelnut oil			Olive oil			Rapeseed oil	
	HO1	HO2	HO3	OO1	OO2	OO3	RO1	RO2
Free fatty acids (FFA/%)	0.08 ± 0.01	0.09 ± 0.01	0.08 ± 0.02	0.76 ± 0.04	0.34 ± 0.09	0.43 ± 0.02	0.23 ± 0.03	0.45 ± 0.06
Peroxide value/meqO$_2$/kg	0.28 ± 0.03	1.16 ± 0.12	0.37 ± 0.02	12.01 ± 0.22	9.01 ± 0.34	6.88 ± 0.18	4.38 ± 0.31	8.28 ± 0.11
Main fatty acids/%								
Palmitic (C16:0)	7.1 ± 0.7	7.0 ± 0.5	6.1 ± 0.4	12.7 ± 0.6	11.7 ± 0.7	11.8 ± 0.5	4.9 ± 0.2	4.5 ± 0.2
Oleopalmitic (C16:1)	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.0	1.1 ± 0.2	0.8 ± 0.1	0.9 ± 0.0	0.2 ± 0.0	0.2 ± 0.0
Staeric (C18:0)	3.0 ± 0.1	3.1 ± 0.1	2.9 ± 0.1	2.9 ± 0.3	2.8 ± 0.2	2.9 ± 0.1	1.6 ± 0.1	1.8 ± 0.1
Oleic (C18:1)	81.0 ± 0.8	81.2 ± 0.7	82.1 ± 0.9	72.9 ± 1.0	74.9 ± 0.9	74.9 ± 0.8	63.7 ± 0.4	64.2 ± 0.6
Linoleic (18:2n3c)	7.9 ± 0.1	8.0 ± 0.2	8.2 ± 0.4	8.5 ± 0.4	6.9 ± 0.3	7.4 ± 0.6	19.5 ± 0.3	19.7 ± 0.2
Linolenic (18:3n3c)	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.7 ± 0.1	0.7 ± 0.0	0.8 ± 0.1	8.2 ± 0.2	7.4 ± 0.1
Σ SFA/%	10.5 ± 0.9	10.4 ± 0.9	9.2 ± 0.7	16.5 ± 0.8	15.3 ± 0.9	15.0 ± 0.8	7.1 ± 0.6	6.9 ± 0.7
Σ UFA/%	89.5 ± 0.9	89.6 ± 1.2	90.8 ± 1.1	83.5 ± 0.9	84.7 ± 1.2	85.0 ± 0.9	92.9 ± 0.8	93.1 ± 1.1

Data expressed as mean ± standard deviation ($n = 3$)

SFA saturated fatty acids, *UFA* unsaturated fatty acids

Results and discussion

The quality assessment of studied oils

The quality parameters (FFA %, PV) and fatty acids characteristics of the tested oils are gathered in Table 1. The initial characteristics of studied oils show that the oils were of quality with the fatty acids composition of each type of oil within the acceptance range stated in the Codex Alimentarius with regard to fats and oils [21]. The PVs and free fatty acids for HO were significantly lower than for OOs and ROs which suggest that even though HO contains a high amount of unsaturated fatty acids (89.5–90.8 %), the antioxidant (mainly tocopherols) protection works very efficiently. However, the oxidation depends not only on the number of double bonds but also if these bonds are conjugated or not. Unfortunately, it was not measured in present study because not the throughout quality characteristic of studied oils, but the correlation between two methods was the main aim of this paper.

The high tocopherols content with α-tocopherol as a predominant isomer have been reported in hazelnut oils by several authors before [22–25]. Generally, higher level of unsaturation favors oxidation process. The autooxidation rates of oleic, linoleic, and linolenic fatty acids relate to degree of unsaturation and are 1:40:100, respectively [26, 27]. However, the misleading oxidation stability values may be caused by oxidation/hydrolysis products on the one hand, and by endogenous antioxidants present in vegetable oils on the other. It could explain why HOs, which is of higher oleic acid (81.0, 81.2, and 82.1 %), and high tocopherols content [22–25], exhibits significantly higher oxidative stability. Therefore, the chemical composition significantly influences oxidative stability of given oil, which in turn appears to be comprehensive tool in an assessment of the multifaceted oil quality.

PDSC (τ_{max}) and Rancimat (τ_{on}) correlation for hazelnut oil

The results of Rancimat and PDSC measurements for HO, OO, and RO are given in Table 2. For the experiments conducted in the same temperature induction time values obtained with use of PDSC were 50–78 % lower compared to that obtained with the use of Rancimat method. The differences could be related to the smaller sample size used in PDSC measurement (3–4 mg) in comparison to the Rancimat quantity of the sample (2.5 g). According to Tan et al. [14], higher surface-volume ratio of PDSC oil sample also plays an important role leading to shorten the analysis time. Moreover, in contrast to Rancimat, where the air (~21 % O$_2$) and ambient pressure is used, the PDSC analysis is conducted under increased pressure conditions (1,400 kPa) and with the pure oxygen as a gas flow. Therefore, PDSC instrument used to determine oxidative stability works faster than Rancimat which is considerably beneficial in new methodology development.
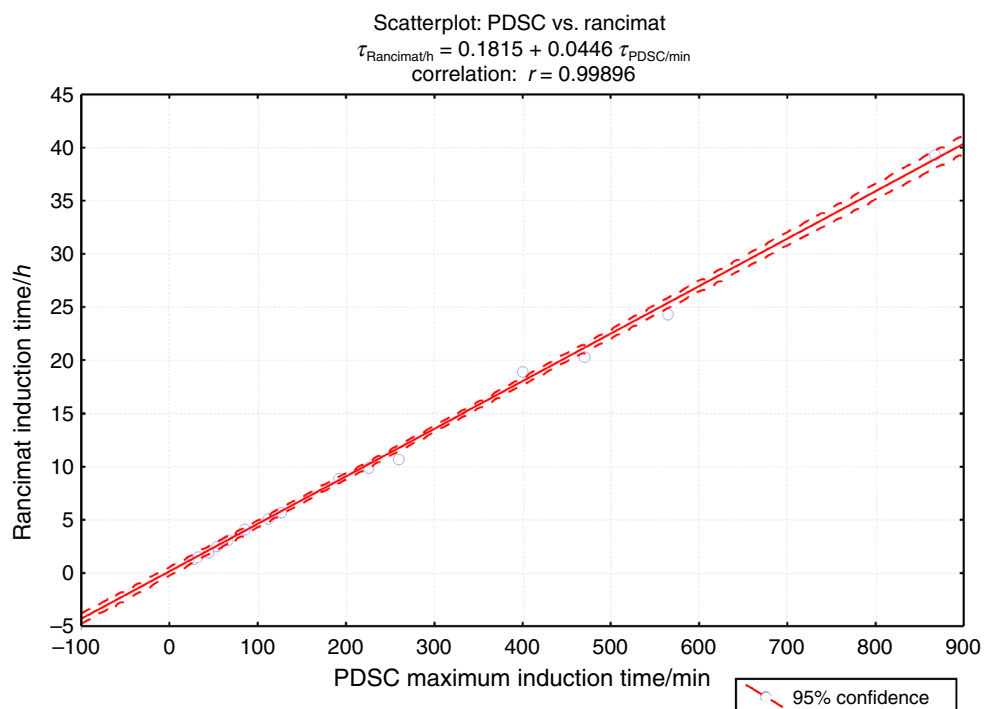
In order to verify the correlation degree between the two different analytical techniques for hazelnut oil, PDSC and Rancimat, the Pearson linear correlation index was extrapolated for samples tested in five different isothermal temperatures in range of 100–140 °C. The obtained Pearson correlation coefficient value, $R > 0.99$ for HO samples (Fig. 1), denotes a statistically significant correlation between the two analytical techniques, independent of the temperatures applied (100–140 °C), where the reaction was

Table 2 PDSC and Rancimat induction times for oxidation of HO, OO, and RO

Induction times	Temperature/°C	HO1	HO2	HO3	OO1	OO2	OO3	RO1	RO2
PDSC τ_{max}/min	100	865.56	468.33	562.61	590.58	647.00	876.83	457.12	414.34
	110	399.87	224.09	257.36	278.71	291.28	390.66	182.67	189.97
	120	191.06	119.95	125.19	134.47	134.15	180.07	98.46	82.41
	130	83.14	52.08	63.96	65.69	61.02	83.36	48.77	38.75
	140	44.21	26.44	30.76	32.99	27.47	39.20	22.85	17.66
Rancimat τ_{on}/h	100	39.49	20.41	24.44	22.93	28.32	45.74	22.05	17.40
	110	18.96	10.05	10.84	10.61	12.34	21.63	11.81	9.45
	120	8.94	5.19	5.80	4.79	5.26	9.66	5.84	4.76
	130	4.18	2.69	3.14	2.14	2.40	4.40	2.80	2.42
	140	2.00	1.39	1.61	1.10	1.23	2.17	1.54	1.32

Data expressed as means ($n = 3$)

Fig. 1 Pearson linear correlation between the τ_{max} PDSC and τ_{on} Rancimat measurements for HO

Scatterplot: PDSC vs. rancimat
$\tau_{Rancimat/h} = 0.1815 + 0.0446\,\tau_{PDSC/min}$
correlation: $r = 0.99896$

still of first order. The following correlation Eq. (1) was determined:

$$\tau_{Racimat[h]} = 0.0446\,\tau_{PDSC[min]} + 0.1815. \tag{1}$$

In addition to the statistically significant correlation with a well-founded technology as the Rancimat method, the PDSC technique presents several advantages, among which short time of analysis is most important, while some other, such as, smaller size of sample (3–4 mg) compared to Rancimat instrument (2.5 g), and no reagents needed also occur. On the other hand, evident disadvantage of PDSC is use of pure oxygen instead of air.

Kinetic analysis of PDSC and Rancimat data

Kinetic data are essential for prediction the oxidative stability of fats and oils under various heat processing, storage, and distribution conditions [28]. The results of PDSC (τ_{max}) and Rancimat (τ_{on}) were measured as a function of temperature (100–140 °C). For each type of oil studied, the dependence between logarithm of τ_{max} and τ_{on} and temperature was linear with the determination coefficients $R^2 > 0.99$, while correlation equations were as follows:

$$\log \tau_{on} \quad \text{or} \quad \log \tau_{max} = at + b, \tag{2}$$

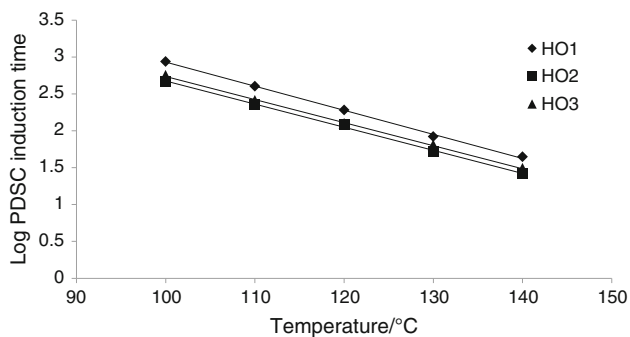$$\log \tau_{on} \quad \text{or} \quad \log \tau_{max} = AT^{-1} + B, \tag{3}$$

Fig. 2 Log PDSC induction time versus temperature for oxidation of HO
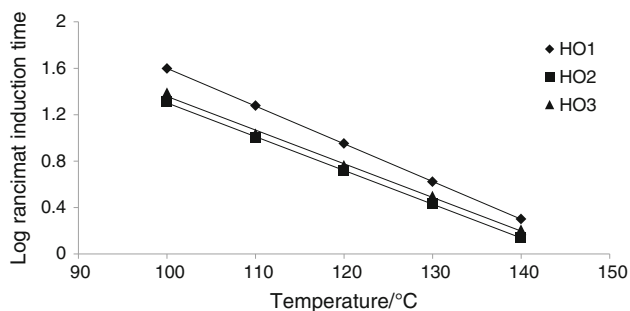

Fig. 3 Log Rancimat induction time versus temperature for oxidation of HO

where a, b and A, B are adjustable coefficients and t and T are the temperatures expressed in °C, and in K, respectively. From Eq. (2), the average induction times can be calculated for given temperatures for each type of oil separately.

As presented in Figs. 2 and 3, one can notice that three hazelnut oils tested revealed disparate correlations between logarithms of τ_{max} and τ_{on} temperatures. In terms of parameters are listed in Table 1, among the hazelnut oil samples, level of PV for HO1 was significantly lower compared to HO2 and HO3. Low PV together with not examined parameters herein, such as, secondary oxidation products or tocopherols content, in turn could have reflected in higher resistance towards thermo-oxidation of HO1 oil.

Assuming that lipid oxidation of oils in an excess of oxygen is a first-order exothermic process [5, 29, 30], the kinetic parameters, such as, pre-exponential factors (Z) and activation energies (E_a) for studied oxidation reactions can be calculated based on the Eq. (3) using A and B coefficients and the Arrhenius equation:

$$k = Ze^{-E_a/RT} \tag{4}$$

where k is the specific rate constant and R is the gas constant [4, 10]. The results of such calculations along with specific rate constants for HO, OO, and RO are gathered in Table 3.

It was observed that E_a varied in the range of 80.99–94.59 and 89.06–92.81 kJ mol^{-1} for Rancimat and PDSC measurements, respectively. The E_a value is affected by the degree of unsaturation of vegetable oil [11, 30]. Adhvaryu et al. [30] reported that a high PUFA content would lower, while high MUFA and SFA content would increase the E_a value for lipid oxidation. However, in the present study, no conclusively correlation between fatty

Table 3 Regression analysis of τ_{max} PDSC and τ_{on} Rancimat data (a, b, R^2 and A, B, R^2), activation energies/kJ mol^{-1}, pre-exponential factors and rate constants/min^{-1} or h^{-1} (PDSC or Rancimat) for oxidation of HO, OO, and RO

Parameters	Isothermal PDSC calculation based on τ_{max} measurements			Rancimat calculation based on τ_{on} measurements		
	Hazelnut oil	Olive oil	Rapeseed oil	Hazelnut oil	Olive oil	Rapeseed oil
Eq. 2						
$-a$	0.0318	0.0331	0.033	0.0302	0.0337	0.0289
b	5.9553	6.1448	5.9251	4.4385	4.8536	4.1864
R^2	0.9996	0.9999	0.9992	0.9996	0.999	0.9992
Eq. 3						
A	4.8939	5.0998	5.0929	4.6541	5.1978	4.4501
$-B$	10.319	10.814	11.010	11.083	12.429	10.613
R^2	0.9992	0.9995	0.9994	0.9996	0.9996	0.9984
E_a	89.0636	92.8108	92.6852	84.6995	94.5942	80.9869
Z	2.08×10^{10}	6.5×10^{10}	1.02×10^{11}	1.21×10^{11}	2.69×10^{12}	4.1×10^{10}
k at 100 °C	0.0071	0.0066	0.0108	0.1682	0.1541	0.1886
k at 110 °C	0.0150	0.0144	0.0236	0.3430	0.3414	0.3728
k at 120 °C	0.0305	0.0303	0.0494	0.6746	0.7267	0.7117
k at 130 °C	0.0600	0.0613	0.0998	1.2829	1.4897	1.3159
k at 140 °C	0.1141	0.1198	0.1950	2.3650	2.9496	2.3617

acids composition and E_a values was observed. The oil oxidation is multifaceted reaction which depends on many factors including fatty acid composition, endogenous antioxidants, catalysts, primary, and secondary oxidation products especially in case of cold-pressed oils.

Considering the rates of lipid oxidation (Table 3) as a function of temperature, an increasing rate of oxidation can be observed when set temperature increases [31]. For example, the rates for HO under the PDSC and Rancimat tests conditions, were 16.1 and 14.1 times higher, respectively, at 140 °C than at 100 °C, what is in a good relation with kinetic theory and data presented previously [4, 9, 10, 28, 31, 32].

Conclusions

To sum up, the preliminary results of PDSC (τ_{max}) and Rancimat (τ_{on}) showed that the oxidative stability of hazelnut oil is similar to the value of olive oil, while higher stability was observed compared to rapeseed oil. Statistically significant linear correlations between PDSC τ_{max} and the Rancimat values imply that PDSC can be recommended as an appropriate objective method for assessing the oxidative stability of hazelnut oils. Additionally, because of the short time of analysis, smaller size of sample, and no reagents needed, the PDSC method has a great potential to be successfully applied and competitive as routine quality control analysis of hazelnut oils.

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