PAPER

KINETICS PARAMETERS OF REFINED AND COLD-PRESSED RAPESEED OILS AFTER OXIDATION BY RANCIMAT

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ABSTRACT

This works summarizes results of quality assessment of five labelled as refined and five labelled as cold-pressed rapeseed oils. The analyzed oils were characterized by a good quality that meet requirements of the Codex Alimentarius standard. Oxidative stability of the oils was determined by Rancimat test at five temperatures (90, 100, 110, 120, 130 °C). The oxidation rate constant (k) was observed to increase along with increasing process temperature. The Arrhenius equation and active complex theory were used to compute the exponential factor (Z), activation energy (Ea), reaction rate constant at various temperatures (k) as well as enthalpy ($\Delta H^{\leftrightarrow}$) and entropy ($\Delta S^{\leftrightarrow}$) of the oxidation reaction of the analyzed oils. The Ea, $\Delta H^{\leftrightarrow}$and $\Delta S^{\leftrightarrow}$ values ranged from 76.43 to 82.44 kJ/mol, from 72.12 to 79.26 kJ/mol and from –48.35 to –68.45 J/molK for the refined oils as well from 74.24 to 77.56 kJ/mol, from 71.04 to 75.47 kJ/mol and from –56.40 to –69.99 J/molK for the cold-pressed oils, respectively.

Keywords: oxidation kinetics, oxidative stability, Rancimat, rapeseed oil

1. INTRODUCTION

Today, rapeseed (*Brassica napsus L.*) oil is produced mainly from double zero "00" cultivar. Double zero cultivar compared to first rapeseed cultivars is characterised by low content of eruic acid (0-2%), whose decomposition products are harmful to human health and glucosinolate (8-15 μM/g of seeds), which did not allow for full use of the protein contained in the seeds. Rapeseed are used mainly for edible oil production, but also as an important feedstock for biodiesel production. Rapeseed may be manufactured with the cold- or hot-pressing method or via extraction and purified by refining. The refined oil, also referred to as universal cooking oil, is the most popular on the market and used for various culinary purposes. However, in last years has been observed a growing interest in the cold-pressed oil. Compared to crude oil, the refined oil contains less free fatty acids, phospho- and glycolipids and metal ions, it has also a brighter color and higher oxidative stability. A negative effect of refining is an increase in the number of trans isomers and a decrease in the content of natural antioxidants, e.g. tocopherols (ČMOLIK *et al*., 2000; TASAN and DEMIRCI, 2003; KARABULUT *et al*., 2005). One of the key reactions proceeding in edible oils during storage and heat treatment is oxidation. The oxidation products formed contribute to the development of unpleasant odor, to deterioration of oil quality and nutritive value, and may also induce toxic effects on a human body (JACOBSEN and NIELSEN, 2008; MATTHÄUS *et al*., 2010; SHAHIDI and ZHONG, 2010).
The process of oxidation is linked with the notion of oxidative stability, namely resistance to oxidation under specified conditions. Lipid oxidation may be analyzed with various methods. The most reliable one is a shelf test that consists in placing a sample of oil at a room temperature and periodical measurements of the peroxide and anisidine values (RATUSZ *et al*., 2002; VELASCO *et al*., 2003; FARHOOSH, 2007; KOWALSKA *et al*., 2014). Owing to a long duration of this test (a few months), an increasing interest is expressed today in the so-called accelerated tests: they are significantly faster, more precise and unbiased (OSTROWSKA – LIGĘZA *et al*., 2010).
Today, the following accelerated tests are found applicable for the evaluation of the oxidative stability of fresh edible oils: electron spin resonance (ESR), magnetic spectroscopy (NMR), Furier transform (FT), active oxygen method (AOM) and differential scanning calorimetry (DSC) (WANASUNDARA *et al*., 1995; ANDERSEN and SKIBSTED, 2002; ROHN and KROHN, 2005). However, the most popular method of edible and nonedible oil stability assessment in the Metrohm Rancimat (PAWAR *et al*., 2013).
The method of oxidative stability evaluation in the Rancimat test consists in the measurement of the concentration of volatile products of oxidation, e.g. short-chain fatty acids formed as a result of accelerated oxidation of the sample. The accelerated oxidation of fat in a reaction vessel is induced by sample heating and blowing through with air. The volatile products of oxidation formed in this process are blown away to water in a measuring vessel, the electrode is immersed in. The electrode allows measuring conductivity of water with oxidation reaction products dissolving in it. A rapid increase of conductivity is tantamount to the formation of secondary products of oxidation that are well soluble in water. Results of conductivity measurements in time are presented in the form of a graph. The time preceding the process of accelerated oxidation, the moment of sudden increase of conductivity, is a measure of sample resistance to oxidation and is referred to as inductive time, induction time or oxidative stability index (OSI) (MATTHÄUS, 1996; ANWAR *et al*., 2003; JAIN and SHARMA, 2011).
Many kinetic parameters of the oxidation process may be determined based on results of the Rancimat test. They may be applied to differentiate the origin of oils and to identify differences or similarities between them. These parameters may be very useful in predicting oxidative stability of oils during their heat treatment, storage and distribution

(TAN *et al*., 2001). Many studies were conducted to determine kinetic parameters of edible oils, however they mainly concerned refined oils, whereas investigations are missing that would address a comparison of oxidation kinetics of oils produced with various methods. Considering the above, the objective of this study was to determine and compare kinetic parameters of refined and cold-pressed rapeseed oils.

2. MATERIALS AND METHODS

2.1. Chemical reagents

All the solvents and chemical reagents used in the study were of analytical grade and were purchased from POCH S.A. (Gliwice, Poland). The Supelco 37 Component Fatty Acid Methyl Esters (FAME) mix was from Sigma - Aldrich Gmbh (Schnelldorf, Germany). Deionized water (0.05 μS) was obtained using an HLP Smart 2000 apparatus (Hydrolab, Poland).

2.2. Material

The experimental material included ten oils labelled as rapeseed oils: five refined (R) and five cold-pressed (C). The oils were purchased on the local market within their shelf-life. The cold-pressed oils were packed in bottles made of dark-green glass, whereas the refined ones were in ethylene polyterephthalate (PET) bottles. Once purchased, the oils were transported to the laboratory and subjected to analyses.

2.3. Chemical analysis

The physicochemical quality of oils was determined based on the lipid values. The extent of hydrolytic changes in the analyzed oils, expressed as the acid value (AV), was determined according to the AOCS Cd 3d-63 (AOCS, 2000). The content of peroxides, expressed as the peroxide value (PV), was determined according to the AOCS 965.33 (AOCS, 1999). The extent of oxidative changes, expressed as the anisidine value (AnV), was determined according to the AOCS Cd 18-90 (AOCS, 2002). The total oxidation index (TOTOX) was computed based on results achieved for the peroxide value and anisidine value (TOTOX = 2PV + AnV).
Fatty acid composition of the analyzed oils was determined using gas chromatography according to the AOCS Ce 1h-05 (AOCS, 2005) with small modifications. Methyl esters of fatty acids were prepared according to the AOCS 2-66 (AOCS, 1997). Determinations were conducted in a Hewlett – Packard model 5890 II gas chromatograph (Agilent Technologies, Avondale, PA, USA) with a flame ionization detector, equipped in a Supelcowax 10 column (30 m x 0.25 mm x 0.25 μm). Injection temperature was 240 °C, and injection was at 1:25. Assay conditions were as follows: helium flow rate 1mL/min and oven temperature 240 °C. Detector's temperature was set at 240 °C. Peaks were identified by comparing their retention times with that of FEME mix standard.

2.4. Rancimat Test - oxidative stability

Oxidative stability of the oils was determined using a Rancimat 743 Metrohm apparatus (Herisau, Switzerland). The Rancimat test was conducted on 2.50 ± 0.01 g samples of oils that were oxidized at five temperatures: 90 °C, 100 °C, 110 °C, 120 °C and 130 °C, at a

constant air flow of 20 L/h. The volatile products formed from the oxidation reaction were soluble in 0.06 L of deionized water.
Eight samples of oils were placed in the apparatus and analyzed simultaneously. The samples were placed at random. The induction times were recorded automatically by the apparatus' software and taken as the break point of the plotted curves with the accuracy of 0.01 h.

2.5. Kinetic analysis

Based on the results obtained for the oxidative stability of the oils assayed at different temperatures, graphs were plotted and regression lines were determined according to the following equations:

$$\ln(\tau\text{Rancimat}) = a(T) + b \quad (1)$$

$$\ln(\tau\text{Rancimat}) = A(1/T) + B \quad (2)$$

Activation energy - *Ea* (kJ/mol) of the oxidation reaction, exponential factor *Z* (h^{-1}) and oxidation reaction rate constants at different temperatures were determined for individual rapeseed oils using the Arrhenius equation, according to a method by KOWALSKI *et al*. (2004):

$$k = Ze^{-Ea/RT} \quad (3)$$

Values of reaction enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) were calculated based on the equation derived from the activated complex theory:

$$\ln(k/T) = \ln(k_B/h) + (\Delta S/R) - (\Delta H/RT) \quad (4)$$

2.6. Statistical analysis

All Rancimat measurements were conducted in three replications for each oil sample, then results were averaged and presented in tables. Data were subject to analysis of variance (one-way ANOVA). Statistical differences were determined with the Tukey's multiple comparison test at a significance level of $p = 0.05$. Pearson's linear correlations were calculated at the $p<0.05$ level. All statistical analyses were performed using the Statistica 10.0 software (2010, StatSoft, Tulsa, OK, USA).

3. RESULTS AND DISCUSSION

Results of the evaluation of the initial quality of the analyzed oils were collected and presented in Table 1. The refined oils were characterized by lower acid value (0.09 – 0.27 mg KOH/ g oil) and peroxide value (0.97 – 2.02 mEq O_2/ kg oil) compared to the cold-pressed oils. In turn, they showed higher anisidine values (1.10 – 2.42), which may be due to high temperatures applied during one of the stages of the refining process – deodorization, that cause the formation of secondary products of oxidation (ČMOLIK and POKORNÝ, 2000). Similar values of the above indices were reported for refined rapeseed oils by RATUSZ *et al*. (2005).

The cold-pressed oils were characterized by higher acid value (1.03 – 1.47 mg KOH/ g oil) and peroxide value (2.12 – 8.28 mEq O_2/ kg oil). In addition, they exhibited a higher degree of oxidation expressed as TOTOX index (4.75 – 17.25) compared to the refined oils (3.04 – 5.56). The peroxide values of the cold-pressed oils differed statistically significantly. Great differences in the value of this index were also determined by MATTHÄUS and BRÜHL (2003). Higher values of these quality indices are linked with the fact that the cold-pressed oils are subjected only to mechanical treatment (filtration, centrifugation) and not to the complete refining process (degumming, deacidification, bleaching, deodorization) as in the case of the refined oils. Higher contents of free fatty acids and primary oxidation products depend on the quality of raw materials used for oil manufacturing. The anisidine values of the cold-pressed oils ranged from 0.18 to 0.69.
Values of particular lipid indices of the analyzed refined and cold-pressed rapeseed oils did not exceed the values recommended in Codex Alimentarius standard (2013). According to this standard, the threshold value of the acid value reaches 0.6 for refined oils and 4.0 mg KOH/ g oil for cold-pressed oils, whereas that of the peroxide value reaches 10 and 15 mEq O_2/ kg oil, respectively.

Table 1. Characteristics of the initial quality of the analyzed rapeseed oils.

Oil	AV (mg KOH/g)	PV (mEq O_2/kg)	AnV (absorbance x 1000)	TOTOX
R1	0.13 ± 0.01^{ab}	2.02 ± 0.03^{b}	1.32 ± 0.05^{e}	5.36 ± 0.16^{d}
R2	0.27 ± 0.03^{c}	0.98 ± 0.02^{a}	1.61 ± 0.04^{f}	3.57 ± 0.10^{b}
R3	0.25 ± 0.02^{bc}	1.02 ± 0.03^{a}	1.54 ± 0.05^{f}	3.58 ± 0.16^{b}
R4	0.09 ± 0.03^{a}	0.97 ± 0.04^{a}	1.10 ± 0.03^{d}	3.04 ± 0.07^{a}
R5	0.19 ± 0.01^{abc}	1.57 ± 0.05^{c}	2.42 ± 0.02^{g}	5.56 ± 0.11^{d}
CA*	**0.6**	**10.0**	**-**	**-**
C1	1.25 ± 0.02^{e}	4.38 ± 0.02^{e}	0.31 ± 0.05^{ab}	9.07 ± 0.02^{f}
C2	1.03 ± 0.03^{d}	5.85 ± 0.02^{f}	$0.18\pm0.04a^{b}$	11.88 ± 0.02^{g}
C3	1.09 ± 0.04^{d}	2.12 ± 0.03^{b}	0.51 ± 0.02^{bc}	4.75 ± 0.11^{c}
C4	1.47 ± 0.04^{f}	3.24 ± 0.03^{d}	0.57 ± 0.03^{b}	7.05 ± 0.04^{e}
C5	1.27 ± 0.01^{e}	8.28 ± 0.03^{g}	0.69 ± 0.02^{b}	17.25 ± 0.05^{h}
CA**	**4.0**	**15.0**	**-**	**-**

^{a,b,c,d,e,f,g,h}mean values in columns are statistically significantly different at a significance level of p=0.05
*threshold values for refined oils according to Codex Alimentarius (2013)
**threshold values for cold-pressed oils according to Codex Alimentarius (2013)

The composition of selected fatty acids of the analyzed oil was summarized in Table 2. The investigated rapeseed oils were characterized by a low content of saturated fatty acids (6.49 – 8.48 %). As indicated by literature data, the fatty acid composition of rapeseed oils is predominated by monounsaturated fatty acids, including mainly oleic acid, which was also confirmed in our study (59.31 – 63.22 %). The analyzed oils were characterized by ca. 30% content of polyunsaturated fatty acids. The fatty acid composition of the analyzed oils was typical of rapeseed oil (ROSZKOWSKA *et al*., 2014).
Differences in fatty acid composition of refined and cold-pressed oils were small and depended, most of all, on the raw materials used to produce the oils (RAMOS *et al*., 2009).
Oxidative stability of the investigated oils was examined with Rancimat test at different temperatures and respective results were presented in Table 3.

Table 2. Fatty acid composition of the analyzed rapeseed oils [%].

Fatty acid	Oil sample									
	R1	R2	R3	R4	R5	C1	C2	C3	C4	C5
Palmitic (16:0)	4.85±0.03^{b}	4.54±0.02^{a}	4.95±0.03^{b}	4.61±0.02^{a}	5.89±0.01^{e}	5.00±0.01^{cd}	5.07±0.01^{d}	5.89±0.02^{e}	5.85±0.02^{e}	4.98±0.02^{cd}
Palmitoleic (16:1)	0.23±0.01^{ab}	0.24±0.01^{ab}	0.22±0.01^{a}	0.25±0.02^{ab}	0.28±0.01^{ab}	0.28±0.01^{ab}	0.30±0.01^{b}	0.28±0.02^{ab}	0.26±0.01^{ab}	0.29±0.01^{ab}
Stearic (18:0)	1.65±0.02^{c}	1.53±0.02^{ab}	1.45±0.01^{a}	1.52±0.00^{ab}	2.13±0.00^{e}	1.68±0.01^{c}	1.51±0.01^{ab}	1.54±0.00^{b}	1.92±0.02^{d}	1.56±0.01^{b}
Oleic (18:1)	62.14±0.04^{b}	62.87±0.05^{c}	63.22±0.08^{c}	63.21±0.06^{c}	59.34±0.08^{a}	61.15±0.05^{b}	62.16±0.07^{b}	61.26±0.05^{b}	59.31±0.04^{a}	62.21±0.09^{b}
Linoleic n-6 (18:2)	19.72±0.02^{c}	19.26±0.02^{a}	19.10±0.04^{a}	19.15±0.03^{a}	19.15±0.02^{a}	19.69±0.04^{c}	19.54±0.04^{b}	19.14±0.03^{a}	19.22±0.03^{a}	19.58±0.03^{bcd}
Linolenic n-3 (18:3)	9.12±0.01^{a}	9.56±0.02^{b}	9.23±0.03^{a}	9.43±0.04^{b}	10.92±0.02^{d}	9.75±0.03^{c}	9.57±0.03^{b}	10.15±0.02^{d}	11.25±0.03^{e}	9.73±0.02^{c}
Arachidonic (20:0)	0.48±0.01^{de}	0.42±0.00^{b}	0.52±0.00^{f}	0.50±0.00^{ef}	0.46±0.00^{cd}	0.37±0.00^{a}	0.45±0.00^{c}	0.45±0.01^{c}	0.47±0.00^{cd}	0.39±0.00^{a}
Eicosenoic (20:1)	1.21±0.01^{cd}	1.26±0.02^{ce}	1.31±0.01^{e}	1.27±0.01^{ce}	1.02±0.00^{ab}	1.06±0.01^{b}	1.18±0.02^{c}	0.96±0.01^{a}	0.98±0.00^{a}	1.05±0.01^{b}
Other	0.60^{bc}	0.32^{ab}	0.10^{a}	0.16^{a}	0.81^{cd}	1.02^{d}	0.22^{a}	0.32^{ab}	0.74^{c}	0.21^{a}
Σ SFA	6.98^{b}	6.49^{a}	6.92^{b}	6.63^{a}	8.48^{d}	7.05^{b}	7.03^{b}	7.89^{c}	8.24^{d}	6.93^{b}
Σ MUFA	63.58^{c}	64.37^{d}	64.65^{d}	64.63^{d}	60.64^{a}	62.49^{b}	63.64^{c}	62.50^{b}	60.55^{a}	63.55^{c}
Σ PUFA	28.84^{c}	28.82^{c}	28.33^{a}	28.58^{b}	30.07^{f}	29.44^{e}	29.11^{d}	29.29^{de}	30.47^{g}	29.31^{de}

^{a,b,c,d,e,f,g}mean values in columns are statistically significantly different at a significance level of p=0.05.

Table 3. Induction time [h] of the analyzed rapeseed oils at 90, 100, 110, 120, 130 °C in Rancimat test.

Temperature		Oil sample									
T[K]	T[°C]	R1	R2	R3	R4	R5	C1	C2	C3	C4	C5
		Induction time [h]									
403	130	3.02±0.15^{b}	2.65±0.17^{ab}	2.42±0.11^{ab}	2.63±0.16^{ab}	2.95±0.12^{b}	1.93±0.10^{a}	1.92±0.12^{a}	2.28±0.15^{ab}	2.09±0.16^{a}	1.89±0.10^{a}
393	120	5.72±0.20^{g}	5.08±0.13^{efg}	4.56±0.14^{cde}	4.98±0.12^{def}	5.65±0.14^{fg}	3.77±0.06^{ab}	3.54±0.12^{b}	4.27±0.011^{bcd}	3.87±0.10^{abc}	3.46±0.11^{a}
383	110	11.36±0.21^{e}	10.48±0.19^{cde}	9.97±0.16^{c}	10.35±0.22^{cd}	11.25±0.18^{de}	7.28±0.11^{ab}	6.66±0.15^{a}	7.94±0.18^{b}	7.57±0.21^{ab}	7.19±0.14^{ab}
373	100	22.21±0.31^{e}	21.32±0.24^{de}	20.76±0.25^{d}	21.26±0.21^{de}	21.63±0.30^{de}	13.56±0.24^{ab}	12.99±0.22^{a}	16.03±0.27^{c}	14.80±0.25^{bc}	13.56±0.23^{ab}
363	90	42.55±0.28^{f}	40.89±0.22^{e}	40.78±0.22^{e}	40.78±0.22^{e}	41.12±0.25^{e}	26.21±0.27^{b}	25.18±0.25^{b}	33.46±0.22^{d}	28.57±0.21^{c}	23.67±0.26^{a}

^{a,b,c,d,e,f,g}mean values in columns are statistically significantly different at a significance level of p=0.05.

The induction time of rapeseed oil oxidation recorded by Rancimat depends on process temperature. Stability of the oils was decreasing along with temperature increase. The highest oxidative stability of the analyzed rapeseed oils was determined at a temperature of 90 °C, whereas the lowest one – at 130 °C. Compared to the cold-pressed oils, the refined oils were characterized by longer induction times in the Rancimat test at all temperatures.

Rancimat is the most commonly used method to determinate the oxidative stability of oils for edible and nonedible purpose (ANWAR *et al*., 2007; CASAL, 2010; FARHOOSH, 2010; GIUFFRÈ, 2016; GIUFFRÈ, 2016a, GIUFFRÈ, 2016b). The requirements for "rapeseed fuel for Diesel engines" were published in the official DIN standard where oxidation stability at 110 °C is one of the most important parameters and the value has to be less than 6h (DIN 51605, 2010).Our paper shows that the oxidative stability of analyzed rapeseed oils at 110°C varied, and ranged from 9.97– 11.36 h for refined oils, and from 6.66 to 7.94 for cold-pressed oils. In the case of edible oils the most commonly used temperature of measuring the oxidative stability for refined oil is 120 °C, but in the case of cold-pressed oils is 100 °C. The induction time of analyzed refined rapeseed oils at 120 °C were between 4.56 to 5.72 h. On the other hand, cold-pressed rapeseed oils were characterized by induction time at 100 °C between 12.99 - 16.03 h. The induction times were higher than those presented by SZTERK *et al*. (2010) in their study of cold-pressed rapeseed – (7.07 h), camelina (6.12 h), primrose (6.14 h), amaranth (6.14 h). The obtained induction times were also lower than those for hazelnut oil (22.44 h) in CIEMNIEWSKA-ŻYTKIEWICZ *et al*. (2014).

Oil oxidation at oxygen (air) excess is the first order reaction. Therefore, kinetic analysis may be carried out for the oil oxidative transformation constant (KOWALSKI *et al*., 2004). Based on the determined induction times (Table 3) and Arrhenius equation (3), the following kinetic parameters were calculated acc. to the method by KOWALSKI *et al*. (2004): activation energy of oxidation reaction - *Ea*, pre-exponential factor - *Z*, reaction rate constants - *k* for particular temperatures of the Rancimat test, as well as enthalpy $\Delta H^{\neq}$ and entropy $\Delta S^{\neq}$ of oxidation activation.

Correlations between logarithm induction time $\tau Rancimat$ and temperature and the reverse of temperature were determined for each type of oil (Figs. 1 and 2). The character of these correlations was linear with a correlation coefficient of R>0.99 and they may be determined using equations 1 and 2.

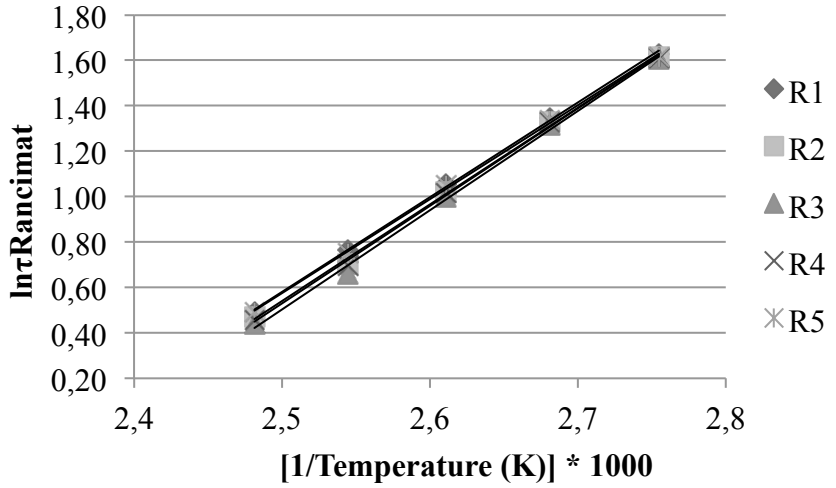

Figure 1. Semi-logarithmic correlation between lnτRancimat and (1/T) for oxidation of refined rapeseed oils.

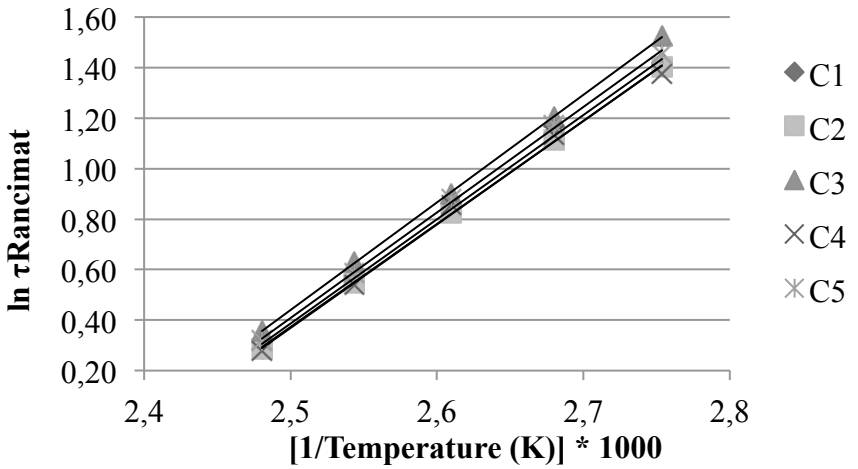

Figure 2. Semi-logarithmic correlation between lnτRancimat and (1/T) for oxidation of cold-pressed rapeseed oils.

Table 4 presents values of particular kinetic parameters of rapeseed oil oxidation. The refined rapeseed oils were characterized by generally higher values of activation energy (*Ea*) – a minimal energy of molecules needed to initiate the oxidation reaction, compared to the cold-pressed oils. The *Ea* values of oxidation reaction ranged from 76.43 to 82.44 kJ/mol for the refined oils as well as from 74.24 to 77.56 kJ/mol for the cold-pressed oils. The smaller load of energy required to initiate the oxidation reaction in the case of the cold-pressed oils may depend on many factors like, e.g., fatty acid composition, presence of endogenous antioxidants and prooxidants, e.g. primary and secondary products of oxidation, and metal ions. The cold-pressed oils were characterized by a higher TOTOX indicator than the refined ones (Table 1), which may affect a reduction in activation energy. The *Ea* values obtained for the refined oils in this study were lower than the values reported by KOWALSKI *et al*. (2004) – 85.3 kJ/mol and by FARHOOSH *et al*. (2008) – 89.94 kJ/mol, and similar to the value achieved by CIEMIENIEWSKA–ŻYTKIEWICZ *et al*. (2014) – 80.99 kJ/mol which fitted within the range obtained in our study. Differences in the values of this kinetic parameter between investigations of various authors may result from the biological variability of the raw material (ripening stage of a variety) (ADHVARYU *et al*., 2000).

In the case of the analyzed rapeseed oils, the value of a reaction rate constant *k* was increasing along with increasing temperature of oxidation. The rate of oxidation reaction was the highest at a temperature of 130 °C. The cold-pressed oils were characterized by a higher value of oxidation reaction rate constant at all temperatures compared to the refined oils. The same dependency was noted by KOWALSKI *et al*. (2004) and FARHOOSH *et al*. (2008) for rapeseed oils as well as by OSTROWSKA–LIGĘZA *et al*. (2010) for olive oil and by CIEMIENIEWSKA-ŻYTKIEWICZ *et al*. (2014) for hazel nuts. The oxidation rate constant of the cold-pressed oil was 2-3-fold higher than that of the refined oils despite small differences in the values of activation energy. It may be due to the fact that the cold-pressed oils contain more pro-oxidants that are removed from the refined oils in the refining process. The prediction of oil oxidation rate at low temperatures is limited based on data obtained. The course of oxidation process of oils differs at low and high temperatures (TAN *et al*., 2001).

Table 4. Kinetics parameters of refined and cold-pressed rapeseed oils oxidation.

Parameter	Rancimat calculation based on induction time									
	R1	R2	R3	R4	R5	C1	C2	C3	C4	C5
Equation 1										
a	0.0289	0.0300	0.0310	0.0301	0.0287	0.0282	0.028	0.0291	0.0285	0.0279
b	4.2293	4.3176	4.3990	4.3265	4.2030	3.9593	3.9145	4.122	4.022	3.9033
R^2	0.9999	0.9996	0.9989	0.9994	0.9999	0.9999	0.9997	0.9985	0.9998	0.9981
Equation 2										
A	4.2210	4.3855	4.5279	4.5279	4.1975	4.1283	4.0998	4.26	4.1778	4.0775
B	9.9824	10.4480	10.8460	10.8460	9.9301	9.9344	9.8809	10.21	10.036	9.8208
R^2	0.9990	0.9985	0.9979	0.9979	0.9985	0.9984	0.9998	0.9999	0.9995	0.9956
Ea [kJ/mol]	76.85	79.85	82.44	82.44	76.43	75.17	74.65	77.56	76.07	74.24
$Z^{\dagger}$	$9.6x10^9$	$2.81x10^{10}$	$7.01x10^{10}$	$7.01x10^{10}$	$8.51x10^9$	$8.60x10^9$	$7.60x10^9$	$1.61x10^{10}$	$1.09x10^{10}$	$6.62x10^9$
$k^{\dagger}$ at 130 °C	0.7611	0.5538	0.5438	0.5438	0.7233	1.5670	1.6167	1.0435	1.5178	1.5896
$k^{\dagger}$ at 120 °C	0.4246	0.3020	0.2908	0.2908	0.4048	0.8858	0.7828	0.7962	0.8522	0.9049
$k^{\dagger}$ at 110 °C	0.2297	0.1596	0.1505	0.1505	0.2198	0.4861	0.4295	0.4286	0.4642	0.5002
$k^{\dagger}$ at 100 °C	0.1203	0.0815	0.0752	0.0752	0.1155	0.2583	0.2282	0.2232	0.2448	0.2679
$k^{\dagger}$ at 90 °C	0.0608	0.0401	0.0361	0.0361	0.0586	0.1325	0.1171	0.1121	0.1246	0.1386
$\Delta H^{\dagger\dagger}$ [kJ/mol]	73.67	76.67	79.23	79.26	72.12	71.98	71.46	74.38	75.47	71.04
$\Delta S^{\dagger\dagger}$[J/molK]	-64.42	-55.84	-48.43	-48.35	-68.45	-67.47	-69.60	-62.33	-56.40	-69.99

†Z and k from Rancimat in h^{-1}

In addition, temperature increase is linked with increased solubility of oxygen – an increase in temperature by 10°C causes oxygen solubility increase by 25% (ROBERTSON, 2000).
Enthalpy and entropy were computed based on the active complex theory and results of linear regression from Tables 4. A high correlation ($R > 0.99$) is indicative of a very good fit and characterizes the effect of temperature on lipid oxidation using the active complex theory. The $\Delta H^{\neq}$ value determined for the analyzed refined rapeseed oils ranged from 72.12 to 79.26 kJ/mol, and that for the cold pressed oils from 71.04 to 75.47 kJ/mol. In turn, the $\Delta S^{\neq}$ value ranged from -48.35 to -68.45 J/molK for refined oils and from -56.40 to -69.99 J/molK for cold-pressed oils. KOWALSKI *et al*. (2004) obtained $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values at 82.0 kJ/mol and – 52.7J/molK for refined rapeseed oil, whereas FARHOOSH *et al*. (2008) at 86.79 kJ/mol and 112.99 J/molK, respectively. The negative $\Delta S^{\neq}$ values indicate that the active complexes are more ordered than molecules of reagents. Higher negative values point to a lesser probability of the formation of an active complex and to a slower rate of lipid oxidation (FARHOOSH *et al*., 2008). Results of our study confirm that the above statement is true for the samples of both refined and cold-pressed rapeseed oils.

4. CONCLUSIONS

In summary, the oxidative stability of the refined rapeseed oils determined with the Rancimat test is higher than that of the cold-pressed rapeseed oils. In turn, the cold-pressed oils are characterized by higher values of oxidation rate constant than the refined oils. In addition, they show slightly lower values of activation energy – *Ea*, which is linked, among other things, with a higher extent of oxidation of a fresh sample (a higher content of primary oxidation products) that accelerates the process of oxidation. Results obtained in this study seem to be consistent with findings and conclusions reported by other authors. The evaluation of oils stability at high temperatures based on this method should lead to similar conclusions and recommendations.

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