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The effect of commercial refining steps on the rancidity measures of soybean and canola oils

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ABSTRACT

The effect of commercial refining steps on the peroxide value (PV), acid value (AV), carbonyl value (CV), total polar compounds (TPC) content, polar compounds distribution, and oil/oxidative stability index (OSI) of soybean and canola oils was studied. The PVs were changed during the different refining steps. The AVs significantly decreased after the neutralisation step. The CVs continuously increased during the refining steps. The marked decrease observed in the TPC contents after the neutralisation step was mainly due to the decrease in the content of free fatty acids (FFA) and oxidised triglyceride monomers (oxTGM) than in the content of the other polar compounds. On the contrary, the study showed more significant changes in diglycerides (DG) and triglyceride dimers (TGD) contents than in the FFA and oxTGM contents during the deodorisation step. The OSIs significantly decreased after the neutralisation step and indicated no considerable changes during the further refining steps.

1. Introduction

Among the 17 commodity fats and oils, soybean and canola oils are the first and third (after palm oil) most produced vegetable oils in the world, respectively (Gunstone, 2001). Their crude oils contain varying amounts of substances that may impart undesirable flavour, colour, or keeping quality. Several chemical and physical refining processes, including degumming, neutralisation, bleaching and deodorisation, have been designed to remove these materials and to obtain odourless, bland and oxidatively stable oils, which are acceptable to consumers.

Lipid oxidation is an important deteriorative reaction, which has significant implications in terms of the quality and value of fats and oils, specifically in relation to the off-flavours that develop as a result of autoxidation. During the initial stages of the oxidation process, hydroperoxides accumulate as primary oxidation products, subsequently breaking down to form low molecular weight oxygenated constituents, such as alcohols, aldehydes, free fatty acids, and ketones, ultimately leading to rancidity. The accumulation of hydroperoxides is commonly monitored using the measurement of peroxide value (PV). The PV, along with acid value (AV), which is a measure of hydrolytic rancidity, are two of the most frequently determined quality indices during oil production, storage and marketing (Lovaas, 1992). Carbonyl compounds are more stable than hydroperoxides and their measurement is a good index of oxidative changes in lipids (Farhoosh & Moosavi, 2008). Endo, Li, Tagiri-Endo, and Fugimoto (2001) have developed a modified method for estimating total carbonyl compounds (known as carbonyl value, CV) in edible fats and oils. This method has been critically reconsidered in another paper (Farhoosh & Moosavi, 2006).

Polar compounds are a complex mixture of compounds, which are principally produced as a result of the action of atmospheric oxygen, the water in the medium, and the high temperature at which the process takes place. These compounds are classified into free fatty acids (FFA), diglycerides (DG), oxidised triglyceride monomers (oxTGM), triglyceride dimers (TGD), and higher oligomeric structured compounds named as triglyceride polymers (TGP) (Dobarganes, Perez-Camino, & Marquez-Ruiz, 1988). The origin of deterioration can be evaluated from polar compound distribution. The content of DG and FFA is related to hydrolytic alteration; the oxTGM content is an indicator of oxidative alteration; and the TGD and TGP are used to assess thermal alteration (Marquez-Ruiz & Dobarganes, 1997). Due to the catalytic effect of the carboxyl groups on the formation of free radicals by the decomposition of hydroperoxides, the FFA have a higher oxidative rate than their esters, and therefore, the FFA content negatively affects the oxidative stability of oils (Miyashita & Takagi, 1986). Mistry and Min (1988) proved the pro-oxidant effect of the DG in soybean oil. The oxTGM and the high-molecular weight autoxidised products also act as pro-oxidants in oils (Yoon, Jung, & Min, 1988) and are precursors of volatile autoxidation products (Frankel, Neff, Selke, & Brooks, 1988). Thus, the level of polar compounds and their distributions can be used to predict the storage and processing stability of an oil and to estimate its autoxidative quality (Hopia, 1993).

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In this study, the PV, AV, CV, and total polar compounds (TPC) content were monitored during the commercial refining steps of soybean and canola oils. Special interest was focused on changes in polar compounds' distribution after each refining step. Also, oil/oxidative stability index (OSI) of the oils during the refining steps was determined using the Rancimat method.

2. Materials and methods

2.1. Materials

Crude, degummed–neutralised, bleached and deodorised oils processed from the same batch were obtained from a commercial refinery. No additives were used. The oil samples were stored in the dark at −18 °C until analysis. The crude oils were degummed at 87–90 °C (H_3PO_4 75%, 1 kg/tonne) and promptly mixed with NaOH (16 °Be′, 5.2 kg/tonne, 18% excess) at 85–90 °C; afterwards, the neutralised oils were washed (two times, 10% v/v). In the next step, the oils were bleached at 100 °C using bleaching earth (2–3 kg Tonsil/tonne), and filtered. The bleached oils were deodorised at 210 °C.

Fatty acid methyl ester (FAME) standards, and analytical- and HPLC-grade chemicals and solvents were the products of Merck (Darmstadt, Germany) and Sigma–Aldrich (St. Louis, MO).

2.2. Fatty acid composition

The fatty acid composition of the oils was determined by gas chromatography and was reported in relative area percentages. Fatty acids were transesterified into their corresponding fatty acid methyl esters (FAMEs) by vigorous shaking of a solution of oil in hexane (0.3 g in 7 ml) with 2 ml of 7 N methanolic potassium hydroxide at 50 °C for 10 min. The FAMEs were identified using an HP-5890 chromatograph (Hewlett-Packard, Palo Alto, CA) equipped with a CP-Sil 88 (Varian, Palo Alto, CA) capillary column (60 m × 0.22 mm i.d., 0.2 μm film thickness) and a flame ionisation detector. Nitrogen was used as carrier gas with a flow rate of 0.75 ml/min. The oven temperature was maintained at 198 °C, and that of the injector and the detector at 250 °C (Farhoosh, Niazmand, Rezaei, & Sarabi, 2008).

2.3. Calculated oxidisability (Cox) value

The Cox value of the oils was calculated based on the percentage of unsaturated C_{18} fatty acids, applying the formula proposed by Fatemi and Hammond (1980):

$$\mathrm{Cox} = (1(18:1\%) + 10.3(18:2\%) + 21.6(18:3\%))/100 \quad (1)$$

2.4. Peroxide value (PV)

The spectrophotometric method of the International Dairy Federation, as described by Shantha and Decker (1994), was used to determine the PV.

2.5. Acid value (AV)

The AV was determined according to the AOCS Official Method Cd 3d-63 (1993).

2.6. Carbonyl value (CV)

The CV of the oils was measured according to the method developed by Endo et al. (2001), using 2-propanol and 2,4-decadienal as solvent and standard, respectively (Farhoosh & Moosavi, 2006).

2.7. Total tocopherols (TT)

The TT content was determined according to the colorimetric method described by Wong, Timms, and Goh (1988).

2.8. Total phenolics (TP)

The TP content was determined spectrophotometrically using Folin-Ciocalteau's reagent, according to the method described by Capannesi, Palchetti, Mascini, and Parenti (2000). A calibration curve of gallic acid in methanol was performed over the concentration range 0.04–0.40 mg ml^{-1}.

2.9. Total polar compounds (TPC)

The TPC content was determined according to the economical micromethod developed by Schulte (2004). The altered compounds that constitute the polar fraction were separated into FFA, DG, oxTGM, and TGD by high-performance size exclusion chromatography (HPSEC), according to Dobarganes et al. (1988). An Agilent 1100 Series GPC-SEC chromatograph equipped with a refractive index detector (Agilent, Waldbronn, Germany), a 10 μl sample loop and three Ultrastyragel columns (Waters Associates, Milford, MA) of 500-, 1000-, and 10,000-Å connected in series were used. The columns were 30 × 0.75 cm i.d., packed with a porous, highly cross-linked styrene-divinylbenzene copolymer (<10 μm). HPLC-grade tetrahydrofuran served as the mobile phase with a flow of 1 ml/min.

2.10. Oil/oxidative stability index (OSI)

A Metrohm Rancimat model 743 (Herisau, Switzerland) was used for the OSI analysis. The tests were done with 3 g oil samples at temperatures of 120 °C and an airflow rate of 15 l/h (Farhoosh, 2007).

3. Results and discussion

Soybean and canola oils lie in a group of vegetable oils containing substantial amounts of linolenic acid (C18:3), which is responsible for the development of an off-flavour problem known as flavour reversion (Fennema, 1996). As Table 1 shows, their fatty acid composition was quite different. Due to the higher levels of palmitic acid (C16:0) and also to some extent of stearic acid (C18:0), the percentage of SFA in the soybean oil was about two times that in the canola oil. The canola oil had a %MUFA 2.5 times higher than that of the soybean oil, mainly due to the considerably higher level of oleic acid (C18:1). There was a marked difference between the levels of linoleic acid (C18:2) in the oils studied, so that the %PUFA in the soybean oil was two times higher than that of the canola oil. Accordingly, the PUFA/SFA ratio and Cox value of the canola oil were significantly lower than those of the soybean oil. This means that the soybean oil was more prone to oxidation than the canola oil. The soybean oil had a tocopherols content higher than that of the canola oil (983 vs. 852 ppm). In contrast, a considerably higher amount of phenolic compounds was found in the canola oil (124 vs. 79.1 ppm) (Table 1). Previous research on canola, soybean, sunflower, corn, and olive oils indicated the antioxidative potential of their phenolic compounds (Farhoosh et al., 2008).

The PV, AV, and CV of the soybean and canola oils after each processing step are shown in Table 2. The PV of the crude oils was lower than 2 meq O_2/kg oil and its levels after neutralisation did not differ significantly. Hopia (1993) and Zacchi and Eggers (2008) showed that after degumming, which decreased the PV of

Table 1
Fatty acid composition and the content of phenolic compounds and tocopherols of the crude soybean and canola oils.[a]

	Soybean oil	Canola oil
Fatty acid (%)		
C14:0	0.24 ± 0.05	0.17 ± 0.00
C16:0	11.9 ± 0.49	4.77 ± 0.09
C16:1	–	0.39 ± 0.07
C18:0	4.15 ± 0.35	2.61 ± 0.07
C18:1	25.8 ± 0.30	62.4 ± 0.22
C18:2	51.1 ± 0.17	19.2 ± 0.23
C18:3	5.96 ± 0.08	7.02 ± 0.12
C20:0	–	0.96 ± 0.03
C20:1	–	0.88 ± 0.11
C22:0	0.25 ± 0.06	–
C22:1	–	2.28 ± 0.20
SFA[b]	16.5 ± 0.25	8.51 ± 0.18
MUFA[c]	25.8 ± 0.30	65.9 ± 0.06
PUFA[d]	57.0 ± 0.09	26.3 ± 0.12
PUFA/SFA	3.46 ± 0.06	3.09 ± 0.08
Cox[e] value	6.81 ±0.00	4.12 ± 0.00
TT[f] content (ppm)	983 ± 4.03	852 ± 9.53
TP[g] content (ppm)	79.1 ± 0.02	124 ± 0.16

[a] Mean ± standard deviation of triplicate determinations.
[b] Saturated fatty acids.
[c] Monounsaturated fatty acids.
[d] Polyunsaturated fatty acids.
[e] Calculated oxidisability.
[f] Total tocopherols (mg α-tocopherol/kg oil).
[g] Total phenolics (mg gallic acid/kg oil).

Table 2
Chemical indices of the oils studied during the different steps of refining.[a]

Oil	PV[b]	AV[c]	CV[d]
Soybean			
Crude	1.89 ± 0.19	2.09 ± 0.06	2.77 ± 0.38
Neutralised	1.95 ± 0.13	0.09 ± 0.03	3.23 ± 0.35
Bleached	1.35 ± 0.03	0.09 ± 0.03	5.25 ± 0.15
Deodorised	0.64 ± 0.13	0.09 ± 0.03	6.36 ± 0.27
Canola			
Crude	1.94 ± 0.12	3.22 ± 0.16	19.9 ± 0.37
Neutralised	1.94 ± 0.04	0.05 ± 0.03	21.0 ± 1.99
Bleached	1.27 ± 0.08	0.10 ± 0.03	25.6 ± 1.11
Deodorised	1.78 ± 0.07	0.14 ± 0.00	26.9 ± 1.64

[a] Mean ± standard deviation of triplicate determinations.
[b] Peroxide value (meq O_2/kg oil).
[c] Acid value (mg KOH/g oil).
[d] Carbonyl value (μmol 2,4-decadienal/g oil).

the vegetable oils studied, neutralisation increased its level. A relatively similar decrease (31–35%) in the PV of the soybean and canola oils was observed after bleaching, but their PV after deodorisation decreased (~53%) and increased (~40%), respectively. Jung, Yoon, and Min (1989) showed that bleaching considerably increases the PV of neutralised soybean oil. Increase or decrease in the PV during the bleaching step depends upon the type and amount of bleaching earth used. King and Wharton (1949) reported that there is usually an increase in the PV at low concentrations of bleaching earth, while at high concentrations there is a reduction in the PV. Hopia (1993) showed that the PV of vegetable oils practically reaches zero after bleaching, and deodorisation has no effect on the PV of bleached oils. The study of Zacchi and Eggers (2008) indicated that bleaching considerably improves the PV of the oil, and the effectiveness of deodorisation (hydroperoxide decomposition content) is affected by the intensity of the operational parameters, e.g., temperature, time and steam-stripping rate. Our results in the present study indicate that the commercial bleaching and deodorisation processes used, especially regarding the canola oil, did not act appropriately.

The AV of the crude soybean (2.09 mg KOH/g oil) and canola (3.22 mg KOH/g oil) oils reached the lowest possible level after neutralisation (0.09 and 0.05 mg KOH/g oil, respectively); afterwards, its level underwent no very obvious change, although it was observed some increase in the AV of the canola oil by the end of the processing steps (Table 2). The level of the AV is an important determinant of oil quality. The Indian Standards specification for refined oils allows a maximum AV of 0.5 mg KOH/g oil (1984). The AV for the deodorised oils was within the permitted level.

The estimation of the CV is a useful approach for the determination of the extent of lipid oxidation, because carbonyl compounds formed by the degradation of hydroperoxides possess rancid and unpleasant flavours greater than those of the other secondary products of lipid oxidation (Endo et al., 2001). A literature review provided no information about the effect of the commercial refining steps on the CV of vegetable oils. As can be seen in Table 2, the CVs of the two oils after each refining step were quite different, ranging from 2.77 to 6.36 μmol/g in the soybean oil and from 19.9 to 26.9 μmol/g in the canola oil. A similar trend was observed for the CV changes of the oils during the refining steps. There was no significant difference between the CV of the crude oils and that of the neutralised oils. The CVs considerably increased after the bleaching step, probably due to the decomposition of hydroperoxides, and slightly increased after the deodorisation step. It is expected that the CV generally decreases after a well-controlled deodorisation step, owing to the removal of volatile decomposition products.

Table 3 shows the TPC content and polar compounds' distribution of the soybean and canola oils during the different steps of refining. An HPSEC representative chromatogram indicating the efficacy of the method is presented in Fig. 1. Four main peaks, eluting in inverse order of molecular weight, were resolved: the TGD, oxTGM, DG, and FFA.

In general, refining of the oils studied led to a decrease in the TPC contents from 8.10% and 7.33% to 6.06% and 5.33% in the soybean and canola oils, respectively. However, depending on the fatty acid composition, initial quality and technology used, crude oils may undergo decreases or even increases in their TPC contents during refining (Ruiz-Mendez, Marquez-Ruiz, & Dobarganes, 1997). The TPC contents of the soybean and canola oils after each refining step were not very different (Table 3). The most marked change in the TPC contents was observed after the neutralisation step, with decreases from 8.10% and 7.33% to 5.85% and 4.76% in the soybean and canola oils, respectively. Considering that the polar fraction is composed of essentially alteration compounds, the higher the TPC content is, the lower the expected quality of the oils is. Hence, the soybean and canola oils would be oils of nearly the same quality. However, the quantitative results of the HPSEC analyses could provide a better explanation for the changes observed in the TPC contents of the oils after each refining step. As can be seen in Table 3, the marked decrease observed in the TPC contents after the neutralisation step was mainly due to the decrease in the contents of the FFA and oxTGM than in the contents of the other polar compounds. On the contrary, the study showed changes more significant in the DG and TGD contents than in the FFA and oxTGM contents during the deodorisation step.

The canola oil contained a FFA content higher than that of the soybean oil throughout the refining steps (Table 3). This may be due to the fact that the canola oil had been exposed to less suitable conditions of storage and/or oil extraction. Although it has been reported that there is some decrease in the FFA content after the degumming step, its major change is observed after the neutralisation step, when they are saponified with sodium hydroxide and separated in soapstock (Jung et al., 1989). The neutralisation

Table 3
Total polar compounds (TPC) content and polar compounds' distribution of the oils studied during the different steps of refining.[a]

	TPC content (%)	Polar compounds distribution (mg/g oil)			
		FFA[b]	DG[c]	oxTGM[d]	TGD[e]
Soybean					
Crude	8.10 ± 0.28	17.5 ± 0.52	16.6 ± 0.40	42.2 ± 1.09	4.74 ± 0.17
Neutralised	5.85 ± 0.49	8.93 ± 0.53	13.5 ± 0.36	32.3 ± 1.88	3.71 ± 0.17
Bleached	5.92 ± 0.37	8.18 ± 0.15	14.8 ± 0.60	31.2 ± 1.31	4.93 ± 0.26
Deodorised	6.06 ± 0.51	7.54 ± 0.39	17.7 ± 0.81	28.0 ± 0.53	7.38 ± 0.69
Canola					
Crude	7.33 ± 0.20	24.2 ± 1.71	16.5 ± 1.17	28.1 ± 0.75	4.62 ± 0.58
Neutralised	4.76 ± 0.18	10.3 ± 0.42	13.4 ± 0.98	19.1 ± 0.25	4.80 ± 0.81
Bleached	4.12 ± 0.04	9.20 ± 0.66	10.3 ± 0.75	18.6 ± 1.53	3.13 ± 0.70
Deodorised	5.33 ± 0.19	10.2 ± 0.43	14.7 ± 0.31	20.4 ± 0.77	7.97 ± 0.64

[a] Mean ± standard deviation of duplicate determinations.
[b] Free fatty acids.
[c] Diglycerides.
[d] Oxidised triglyceride monomers.
[e] Triglyceride dimers.

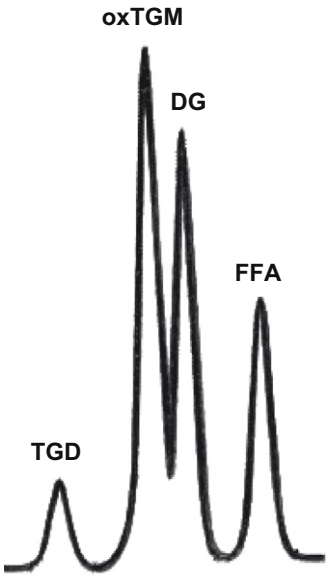

Fig. 1. A high-performance size exclusion chromatography (HPSEC) representative chromatogram of polar compounds. Retention times: 23.977 min, triglyceride dimers (TGD); 25.252 min, oxidised triglyceride monomers (oxTGM); 26.017 min, diglycerides (DG); 27.383 min, free fatty acids (FFA).

step effectively decreased the FFA content from 17.5 mg/g in the crude soybean oil to 8.93 mg/g, and from 24.2 mg/g in the crude canola oil to 10.3 mg/g. The bleaching and deodorisation steps caused no significant change in the FFA contents of the oils. However, the bleaching step caused a slight decrease of the FFA content from 8.93 mg/g in the soybean oil to 8.18 mg/g and from 10.3 mg/g in the canola oil to 9.20 mg/g. These decreases can be attributed to the adsorption caused by Tonsil bleaching earth. Furthermore, the deodorisation step had a performance slightly better for the soybean oil (from 8.18 to 7.54 mg/g) than for the canola oil (from 9.20 to 10.2 mg/g). Sarkadi (1959) reported that the FFA are formed by the hydrolysis of triglycerides and removed simultaneously during the deodorisation step. It was interesting to find that the trend in the changes of the FFA content during the refining steps was almost comparable to that of the AV (Table 2). It should be mentioned that the complete oil refining removed about 57% of the FFA in the crude oils. In fact, the FFA and a part of the polar unsaponifiable fraction, essentially free sterols, elute as one peak in HPSEC analysis (Hopia, 1993). Reliable quantitation of this fraction is not possible since the response of FFAs is significantly lower in the ELS detector (Hopia, Piironen, Koivistoinen, & Hyvonen, 1992). After the neutralisation step, the level of this fraction decreased significantly (Table 3), however, owing to the removal of FFA present in the crude oils, and therefore, the remaining HPSEC fraction represents the total amount of free sterols (Hopia, 1993).

In their study on the physical and chemical refinings of a number of vegetable oils, Ruiz-Mendez et al. (1997) concluded that higher DG contents in the physically refined oils were due to the lack of the neutralisation step. Our results in this study practically showed marked decreases in the DG contents after the neutralisation step (from 16.6 and 16.5 mg/g to 13.5 and 13.4 mg/g in soybean and canola oils, respectively); (Table 3). Depending on the oil type, the bleaching step changed the DG contents differently. After the deodorisation step, the DG contents increased and reached around the starting amount in the crude oils. This was in accordance with the results of Ruiz-Mendez et al. (1997), who indicated that the DG content of the crude oils remained without any change at the end of refining. Hopia (1993) reported no change in the DG content throughout the refining steps, indicating no hydrolytic alteration during these processes.

The contents of oxTGM in the crude soybean and canola oils were 42.2 and 28.1 mg/g, respectively (Table 3). The oxTGM content of the soybean and canola oils after the deodorisation step by losses of 34% and 27% reached 28.0 and 20.4 mg/g, respectively. As can be seen, the level of the oxTGM in the refined oils was a function of its level in the crude oils. The higher the oxTGM content in the crude oils was, the higher the oxTGM content in the refined oils was. With an exception of the slight decrease after the bleaching step (some probable adsorption of the oxTGM to the bleaching earth), Hopia (1993) found no clear trend in the oxTGM content during the refining steps, and also reported that the content of oxTGM in refined oil is comparable to that of crude oil. However, our results showed that the content of the oxTGM in the oils studied significantly decreased after the neutralisation step, and then remains nearly constant by the end of refining. Some decreases in the oxTGM content of the oils chemically refined by Ruiz-Mendez et al. (1997) could be observed as well.

No clear trend in the TGD content of the oils was observed during the neutralisation and bleaching steps, whereas deodorisation

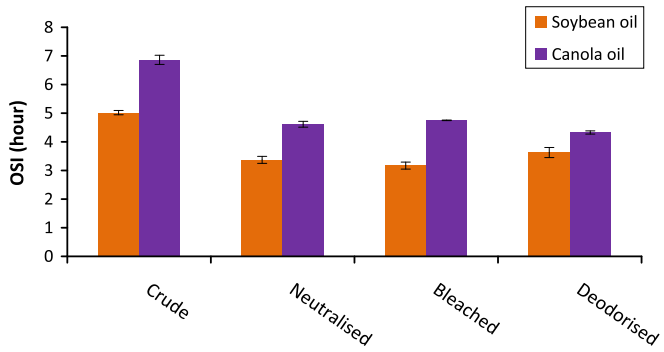

Fig. 2. The oil/oxidative stability index (OSI) of the oils studied during the different steps of refining as the mean ± standard deviation of triplicate determinations.

considerably increased it. This result was expected, since polymerisation occurs particularly at high temperatures. In total, the TGD contents increased from 4.74 mg/g in the soybean oil to 7.37 mg/g (56%) and from 4.62 mg/g in the canola oil to 7.97 mg/g (82%). Von Eder (1982) reported that the amount of TGD compounds increases during the deodorisation step (1–5 h) and depends markedly on the deodorisation temperature (190–270 °C) and the unsaturation degree of the oils. The higher increase percentage of the TGD content for the canola oil can be attributed to the higher content of its unsaturated fatty acids (92.2% vs. 82.9% for the soybean oil) (Table 1). Ruiz-Mendez et al. (1997) showed that the formation of TGD in the oils was parallel to a decrease in the amount of the oxTGM. In fact, the oxTGM is a complex group of monomeric triglycerides containing at least one oxygenated function (hydroperoxides, epoxides, ketones, etc.) (Frankel, 1985), some of which can be more susceptible to polymerisation at high temperatures through oxygenated linkages than the non-polar fatty acids through C–C linkages (Ruiz-Mendez et al., 1997).

The canola oil generally showed OSIs (6.86, 4.61, 4.75, and 4.33 h, respectively) higher than those (5.02, 3.37, 3.17, and 3.63 h, respectively) of the soybean oil during the refining steps (Fig. 2). This indicated a higher oxidative stability for the canola oil, due to its fatty acid composition being more resistant to oxidation (the PUFA/SFA ratio and Cox value) and higher amount of antioxidative phenolic compounds (Table 1). The OSIs significantly decreased after neutralisation and exhibited no considerable changes during the further refining steps. Zacchi and Eggers (2008) showed that the OSI of the rapeseed oil decreases very significantly after the degumming and neutralisation steps and little change occurs during the bleaching and deodorisation steps. During the neutralisation step, phenolic compounds are almost completely removed, which has a strong negative influence on the oxidative stability of the oils (Zacchi & Eggers, 2008).

4. Conclusions

The results obtained in this study indicated that: (a) among the commercial refining steps, the neutralisation step had the highest effect on the TPC content and polar compounds' distribution, did not markedly change the content of the primary (PV) and secondary (CV) products of lipid oxidation, and effectively decreased the oxidative stability of the oils, due to the almost complete removal of the indigenous phenolic compounds; (b) the content of carbonyl compounds, which are considered to be one of the most important secondary oxidation products influencing the sensory properties of edible oils, was a function of the fatty acid composition and the initial quality of the oils, and continuously increased during the commercial refining steps; (c) the changes trend of the TPC content during the refining steps was nearly consistent with that of the FFA and oxTGM contents, since the amount of DG remained close to the levels found in the crude oils and the amount of TGD showed an increase trend. Thus, high levels of the DG in refined oils would indicate higher percentages of the TPC in crude oils. Furthermore, high levels of the oxTGM in refined oils would indicate its higher levels in crude oils and also higher potential of the corresponding oil to produce higher levels of the TGD; and (d) the consistent changes in the AV and the FFA peak of HPSEC analysis indicated that free fatty acids are almost completely removed during the refining steps, and the remaining HPSEC fraction represents the total amount of free sterols.

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