Research Article

Characterization of waxes and residual oil recovered from sunflower oil winterization waste

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Two filter cakes from the sunflower oil winterization process were used to recover, fractionate and characterize their oil and wax fractions. Both samples presented high lipid content (75.35 and 58.21% dry basis) composed of 88.1 and 89.1% oil and 11.9 and 8.9% waxes. Recovered oils had a very low free fatty acid content, differences in the degree of deterioration consistent with their fatty acid composition, and significant differences in their wax contents, which were in the order of crude sunflower oils (1356–604 mg/kg). Purified waxes were between 40 and 60 carbon atoms with a fatty alcohol and fatty acid distribution in the range of 18–34 and 14–34 carbon atoms, respectively. Significant differences were found between samples in their wax and fatty acid profiles according to differences between the hybrids studied. DSC thermograms presented differences in the onset temperature (71.98 and 75.15°C), melting peak (76.70 and 80.53°C), and melting enthalpies (202.77 and 204.35 J/g), with the lower values being exhibited by the sample with higher fatty acid unsaturation and lower content of waxes with more carbon atoms.

Practical applications: Results revealed the potential use of this waste, reducing oil losses and recovering waxes with an adequate quality for their application in various industries. The characterization of the purified waxes is of extreme importance for their potential use in different industries and technologies. This is also of great environmental relevance, because the waste material generated by the winterization process could be reused, and thus gain added value.

Keywords: Filter cake / Sunflower oil recovered / Sunflower waxes / Winterization

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1 Introduction

In the sunflower oil extraction process minor compounds, such as waxes, tocopherols and phospholipids, are extracted along with the oil. These minor compounds influence the quality and stability of edible oils [1], some have pro- or antioxidant properties (e.g., tocopherols, metals, and free fatty acids), and others have to be removed in the refining process (e.g., phospholipids and waxes) [2]. Waxes are considered unwanted material because they tend to crystallize at room temperature due to their low solubility, causing turbidity in refined oils. There are several technical alternatives for the separation of waxes during the refining process, all of which involve different crystallization conditions (temperature, residence time, presence or absence of soaps, phospholipids, use of solvent or no solvent, etc.). The conventional method, called winterization or dewaxing, consists of a gradual crystallization and separation by filters. It involves first an oil cooling stage using mild mechanical agitation to cause crystallization of the waxes, followed by a crystal separation from oil by filtration using a filter aid [3]. The residue of this process, which is considered an industrial waste, is called "filter cake" and it consists of a mixture of filtering aid, oil, and waxes. The filter cake resulting from the filtration process contains 50–60% oil [4], plus the filter aid and some wax. Ergonul and Nergiz [5] determined that the major part of crude sunflower waxes and corn oil waxes

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Abbreviations: **ΔH,** change in enthalpy; **AV,** p-anisidine value; **CC,** column chromatography; **d.b.,** dry basis; **DSC,** differential scanning calorimeter; **FA,** fatty acids; **FAME,** fatty acid methyl esters; **FFA,** free fatty acids; **FID,** flame ionization detector; **IOC,** International Olive Council; **LF,** lipid fraction; **PV,** peroxide value; **PW,** purified waxes; **RO,** recovered oil; **TLC,** thin layer chromatography; **T_{on},** onset temperature; **T_p,** peak temperature; **WS,** waste sample

is removed within 24 h winterization using 0.6% kieselghur, being the waxes retained in the filter cake. So, if its composition is well defined and reasonably constant, the filter cake can serve as the starting material for the isolation of the wax.

Sunflower waxes consist of long-chain saturated esters (in the range of 36–60 carbon atoms, C36–C60) derived from fatty alcohols and fatty acids [1, 6, 7]; they are mainly located on the hull surface of sunflower seeds [6] in concentrations of up to 3% depending on the hybrid and origin of the seeds [1]. Soluble waxes (<C40) are mostly retained by refined oils [1, 8], while partially soluble (C40–C42) and crystallizable waxes (>C44) are partially or totally reduced by winterization, respectively [9]. The recovery of waxes from the winterization residue would contribute to obtaining a byproduct of potential technological interest, with a great variety of possible uses in skin care cosmetics and lipsticks, paper production, food packaging, etc. [10]. Waxes have been used in the food industry as protection during storage against fruit desiccation [11], and their application in emulsion formulations for the preparation of edible food coatings has been expanding steadily [10, 12]. Uses as an ingredient in livestock feed mixed with grain and silage have also been reported [13]. Among these applications, the use of waxes in fruit dip coatings is one of the oldest preservation and protection methods [14].

As stated above, waxes can be obtained from the oil refining waste, giving the possibility of a new application and revaluation of this waste. However, there is scarce data in the literature about its composition. The characterization of the main components of this residue will allow for the evaluation of their applicability and increase their market value.

The aim of this article is to determine the composition of the filter cake from the sunflower oil winterization process, focusing on the recovery and characterization of the purified waxes. The quantity and quality of the separated oil fraction is also determined in order to measure the amount of lost oil and its potential reuse.

2 Material and methods

2.1 Samples

Waste samples or "filter cakes" from the winterization process were provided by two local factories, and they were named waste sample 1 (WS1) and waste sample 2 (WS2). Moisture and lipid contents (% d.b.) were determined according to IUPAC method 1.121 and 1.122 [15], both determinations were performed in triplicate as part of the characterization of the raw material.

2.2 Waste sample fractionation and wax recovery

The waste material consisting of waxes, oil and filter aid was fractionated in order to obtain purified waxes using n-hexane as solvent. First, the waste samples (WS1, WS2) were washed with n-hexane at 50°C for 30 min, and then the hot solution was filtered to remove the insoluble particles or filter aid. After this process, a lipid fraction (LF1, LF2) consisting of a large proportion of oil and waxes was obtained and fractionated into purified waxes (PW1, PW2) and recovered oil (RO1, RO2) by successive washings with cold n-hexane.

2.3 Analytical methods

2.3.1 Oil quality indexes and fatty acid composition

Standard IUPAC (1992) and AOCS (2009) official methods were used to determine the acidity or free fatty acids (FFA) (IUPAC 2.201) [15], peroxide value (PV) (AOCS Cd 8–53) [16], and p-anisidine value (AV) (AOCS Cd 18–90) [16]. Quality determinations were performed in duplicate. The fatty acid composition was determined by GC analysis of the methyl esters obtained by transesterification with a cold methanolic solution of potassium hydroxide (COI/T20 Doc. No33) [17]. Fatty acid methyl esters (FAME) were analyzed by GC according to AOCS method Ce 1e-91 [16]. FAME were separated using a SP2380 capillary column [stabilized poly (90% biscyanopropyl/10% cyanopropylphenyl siloxane)] (30 m length, 0.25 mm i.d., 0.25 μm film thickness; Supelco Inc., Bellefonte, PA, USA) maintained at 170°C for 15 min, then increased at 4°C/min to 210°C for 10 min using hydrogen as gas carrier. Two injections were performed for two independent analyses.

2.3.2 Wax analysis

Wax composition of RO and PW was determined by a modified International Olive Council (IOC) method for wax determination involving a double-adsorbent layer of silica gel and silver nitrate impregnated silica gel as solid phase in the column chromatography (CC) followed by GC [9]. All reagents were of analytical grade, except n-hexane, n-heptane, and ethyl ether, which were of chromatographic grade (J.T. Baker Inc., Phillipsburg). Silica gel 60, particle size 0.06–0.200 mm, 70–230 mesh (Art 7734, Merck, Darmstadt, Germany) was dried at 500°C for 4 h, hydrated with 2% of water, and stabilized for 12 h prior to use in CC. Silver nitrate impregnated silica gel was prepared by pouring a solution of silver nitrate (5 g dissolved in 240 mL of distilled water) onto 100 g of extra pure silica gel 60 (Art. 7754, Merck, Darmstadt, Germany) in a ceramic bowl, heating it from room temperature up to 170°C in an electronic oven, and activating it overnight. Then, the impregnated silica gel was allowed to cool down slowly to 50°C in the oven (in the dark) and kept in the dark in a sealed bottle. The following wax standards of 99% purity were used for chromatographic analysis: C32 = lauric acid arachidyl ester ($C_{32}H_{64}O_2$), C34 = palmitic acid stearyl ester ($C_{34}H_{68}O_2$), C36 = stearic acid stearyl ester ($C_{36}H_{72}O_2$), C38 = arachidic acid oleoyl ester ($C_{38}H_{74}O_2$),

C40 = arachidic acid arachidyl ester ($C_{40}H_{80}O_2$), C42 = arachidic acid behenyl ester ($C_{42}H_{84}O_2$), and C44 = behenic acid behenyl ester ($C_{44}H_{88}O_2$). The C32 wax standard was also used as internal standard for the quantitative analysis.

The wax fraction was isolated by CC performed in a glass column (i.d. = 15 mm, length = 400 mm) with a double solid phase of silver nitrate impregnated silica gel (3 g) placed at the bottom of the column and 2% hydrated silica gel (12 g) placed on the top [9]. The bottom of the column containing the silver nitrate impregnated silica gel was covered with aluminum foil to protect it from the light. Approximately 300 mg of RO or 3 mg of PW (weighted accurately), and two drops of a 1% solution of Sudan I dye in n-hexane were loaded into the column with the aid of two 2-mL portions of n-hexane. The waxes were eluted with n-hexane/ethyl ether (99:1 v/v) at a flow rate of 3 mL/min. The elution of wax esters was ended when the dye reached a mark made on the glass column 2 cm below the interphase between the 2% hydrated silica gel and the silver nitrate impregnated silica gel. The eluted wax fraction was evaporated to dryness and diluted with n-heptane for chromatographic analysis.

A Perkin Elmer Auto System XL gas chromatograph equipped with a flame ionization detector (FID), a temperature programmable on-column injector and a TotalChrom Workstation data processor version 6.3.1 (Perkin Elmer, MA, USA) was used for the final analysis of wax fractions. The capillary column was an HP-5 (5% diphenyl and 95% dimethyl-polysiloxane), fused-silica 15 m length × 0.32 mm i.d., 0.25 mm film thickness (Hewlett-Packard, Palo Alto, CA). The operating conditions were as follows: hydrogen at 3 mL/min as carrier gas; oven temperature programming: initial temperature, 80°C hold for 1 min, increase at 20°C/min to 240°C, increase at 5°C/min to 325°C and hold for 6 min, increase at 20°C/min to 340°C and hold for 27 min; on-column injector programmed from 80 to 320°C at 20°C/min and injection volume of 5 μL; FID at 350°C. Two injections were performed for two independent analyses.

2.3.3 Fatty acid and fatty alcohol separation

The determination of the components of PW required their saponification, extraction of both saponifiable and unsaponifiable matter, and separation of alcohols in the unsaponifiable fraction by TLC, followed by the analysis of FAME and fatty alcohol by GC [1]. The separation technique was based on the IOC method (COI/T.20/Doc.No.26/Rev1) [17] with some modifications to secure a complete saponification and a good recovery of the analytes. Waxes were saponified with 100 mL of 2N-KOH for 6 h, followed by three washings with 80 mL of ethyl ether, and a subsequent washing of these joint fractions with three 50 mL portions of distilled water. The hydro-alcoholic fraction contains fatty acids (FA) while the ethyl ether fraction contains the fatty alcohols. FA were converted to methyl esters by acid-catalyzed esterification according to IUPAC standard method 2.301 [15]. Fatty alcohols were separated from the unsaponifiable matter by TLC chromatography according to the IOC method (COI/T.20/Doc.No.26/Rev1) [17]. Determinations were performed in duplicate.

2.3.4 GC conditions for the determination of fatty acid constituents of waxes

FA composition was determined by GLC according to AOCS method Ce 1e-91 [16]. The same gas carrier and chromatographic column used for the FAME analysis of the oil (SP-2380) was used to separate the FAME components of the waxes, but in this case the oven temperature programming was as follows: initial temperature, 170°C hold for 15 min, increased at 4°C/min to 260°C and hold for 7 min. Standards of FAME with a purity of 99%, in the range of 8–30 carbon atoms, were purchased from Sigma Chemical Co. Two injections were performed for each independent sample.

2.3.5 GC conditions for the determination of fatty alcohol constituents of waxes

Standard solutions of alcohols and alcohol samples were converted into trimethylsilyl ethers and analyzed according to the IOC method (COI/T.20/Doc.No.26/Rev1) [17]. The analysis of fatty alcohols was carried out on a SE-54 fused silica capillary column (30 m x 0.25 mm i.d.) with a 0.25 μm film thickness (Supelco, Inc., Bellefonte, PA), increasing the temperature by 7°C/min from 170 to 300°C (held for 31 min), and using hydrogen as carrier gas. Fatty alcohol standards with a purity of 99%, containing 20–30 carbon atoms, were purchased from Sigma Chemical Co. Two injections were performed for each independent sample.

2.3.6 Differential scanning calorimetry (DSC)

A Perkin Elmer Pyris I apparatus (USA) was used to evaluate the melting profile of PW. Approximately 8 mg of PW were placed on an aluminum DSC pan and hermetically sealed. The samples were placed inside the DSC chamber and heated from 10°C to 120°C at 5°C/min to evaluate the melting profile. The following parameters were obtained: Onset (T_{on}) and peak temperatures (T_p), and the change in enthalpy (ΔH).

2.3.7 Color measurement

The CIE-Lab L^*, a^* and b^* values for each sample of RO and PW were measured in triplicate using a Hunter Lab Ultra Scan XE colorimeter with Universal Software (Hunter Associates Laboratory, Inc., 11491 Sunset Hills Road, Reston, VA, USA).

2.3.8 Statistical analysis

Significant differences were analyzed performing a two-way ANOVA and Fisher's test ($\alpha = 0.05$), using the statistical

analysis software InfoStat version 2011 (Group InfoStat, FCA, National University of Cordoba, Argentina).

3 Results and discussion

The two waste samples (WS1 and WS2) from the dewaxing process rendered a lipid content of $75.35 \pm 0.77\%$ (d.b.) and $58.21 \pm 1.03\%$ (d.b.), respectively, with the initial humidity being $0.14 \pm 0.01\%$ (d.b.) for WS1 and $0.20 \pm 0.02\%$ (d.b.) for WS2. As both samples exhibited high lipid content (over 50%), the recovery of the lipid material retained in them is promising.

The lipid material was fractionated into recovered oil (RO) and purified waxes (PW), as described in the experimental section. The material recovered from WS1 consisted of 88.1% oil and 11.9% waxes, whereas the wax content of the material recovered from WS2 reached 8.9%. Therefore, a high percentage of the dewaxing waste (53–66%) consists of oil that is lost, a range slightly higher than that reported in the literature (50–60%) [4]. The quality indexes of RO1 and RO2 were: FFA $= 8.46 \times 10^{-3} \pm 0.08 \times 10^{-3}$ and $2.92 \times 10^{-3} \pm 0.30 \times 10^{-3}$% oleic acid, PV $= 26.88 \pm 2.65$ and 6.91 ± 0.36 meqO_2/kg, AV $= 6.92 \pm 0.31$ and 3.11 ± 0.27, respectively. The values of FFA are within the legal limits (CODEX STAN 210–1999, [18]) for virgin oils (2.0% oleic acid) and refined oils (0.3% oleic acid). The extremely low values of FFA indicate their complete removal during neutralization (or in the previous stages of refining), but RO1 presented a PV value that was above the maximum limit established for virgin oils (PV $= 15$ meqO_2/kg) [18]. These results reflect the greater deterioration of RO1, with its higher unsaturated fatty acid content being the main factor responsible for the higher susceptibility to oxidation of the oil (Table 1). While both samples exhibited approximately 10% of saturated fatty acids, RO1 presented linoleic acid as its main unsaturated fatty acid, whereas RO2 had a significantly higher oleic acid content (Table 1). This wide difference in fatty acid composition could be due to the type of seed processed (conventional or high-oleic sunflower hybrids) [19]. As expected, the high-oleic sunflower oil (RO2) was less susceptible to oxidative changes during refining and storage. Taking into account the color of RO,

Table 1. Fatty acid composition of RO samples

Fatty acid	RO1 (%wt)	RO2 (%wt)
C14:0	0.1	Tr
C16:0	6.4	3.6
C16:1	0.1	0.1
C17:0	Tr	Tr
C17:1	Tr	0.1
C18:0	3.1	3.2
C18:1	34.0	87.9
C18:2,	54.8	3.3
C18:3	0.1	Tr
C20:0	0.2	0.3
C20:1	0.1	0.2
C22:0	0.7	0.9
C23:0	Tr	Tr
C24:0	0.2	0.3
C26:0	0.2	n.d.

n.d., detected; Tr, traces (<0.1%).

Table 2. Color settings of the RO and PW samples

	L^*	a^*	b^*
RO1	92.82[a]	−3.57[a]	19.68[b]
RO2	94.74[b]	−2.83[b]	9.03[a]
PW1	88.41[b]	8.48[a]	7.61[a]
PW2	85.49[a]	8.61[b]	9.49[b]

Values are mean of three independent samples analyzed by duplicate.
Values in the same column followed by different letters are significantly different ($p < 0.05$) by the Fisher test.

Table 3. Wax composition of recovered oils

Wax	RO1 (%wt)	RO2 (%wt)
C34	0.3	0.6
C36	1.4	2.4
C38	1.2	1.7
C40	5.5	5.0
C41	0.4	0.2
C42	8.0	2.3
C43	0.8	0.2
C44	19.5	4.8
C45	2.0	1.0
C46	20.4	16.0
C47	2.1	2.2
C48	15.6	20.6
C49	1.7	2.4
C50	8.5	14.2
C51	0.7	1.3
C52	5.9	11.9
C53	0.4	1.0
C54	2.8	5.8
C55	0.2	0.5
C56	1.3	3.0
C57	0.2	0.3
C58	0.5	1.6
C59	0.2	0.5
C60	0.2	0.8
Total Content (mg/kg)	1356	604
Soluble and partially soluble fraction (mg/kg)	240	74
Insoluble fraction (mg/kg)	1116	530

Table 4. Relative percentage of waxes, fatty alcohols, and fatty acids identified in PW samples

Wax	PW1 (%wt)	PW2 (%wt)	Fatty alcohol	PW1 (%wt)	PW2 (%wt)	Fatty acid	PW1 (%wt)	PW2 (%wt)
C40	0.3[b]	n.d.[a]	C18:0	0.2	n.d.	C14:0	1.3[b]	0.9[a]
C41	0.1[b]	n.d.[a]	C20:0	1.1[a]	1.1[a]	C16:0	16.2[b]	9.5[a]
C42	6.6[b]	Tr[a]	C21:0	0.1[a]	0.1[a]	C16:1	0.9[a]	0.9[a]
C43	1.1[b]	Tr[a]	C22:0	9.0[a]	8.6[a]	C17:0	1.1[a]	0.9[a]
C44	23.4[b]	1.9[a]	C23:0	1.0[a]	1.0[a]	C18:0	4.9[a]	5.1[a]
C45	2.2[b]	0.6[a]	C24:0	30.5[a]	29.4[a]	C18:1	20.2[a]	42.6[b]
C46	24.9[b]	13.6[a]	C25:0	2.5[a]	2.4[a]	C18:2	22.1[b]	5.9[a]
C47	1.6[a]	1.9[a]	C26:0	26.2[a]	26.3[a]	C20:0	0.4[a]	0.8[a]
C48	16.3[a]	22.3[b]	C27:0	0.8[a]	0.8[a]	C18:3	2.8[b]	0.2[a]
C49	1.1[a]	2.1[b]	C28:0	12.9[a]	13.5[a]	C20:1	0.1[a]	0.1[a]
C50	9.2[a]	18.8[b]	C29:0	0.7[a]	0.7[a]	C20:2	0.9[a]	0.9[a]
C51	0.9[a]	2.2[b]	C30:0	7.6[a]	8.1[a]	C22:0	0.6[a]	1.0[a]
C52	6.3[a]	16.1[b]	C31:0	0.5[a]	0.5[a]	C23:0	0.8[a]	0.5[a]
C53	0.5[a]	1.4[b]	C32:0	5.8[a]	6.3[a]	C24:0	0.3[a]	1.1[b]
C54	3.0[a]	9.3[b]	C33:0	0.2[a]	0.3[a]	C24:1	2.1[b]	0.3[a]
C55	0.2[a]	0.8[b]	C34:0	0.8[a]	0.8[a]	C26:0	2.5[a]	2.4[a]
C56	1.3[a]	4.7[b]				C27:0	0.7[a]	0.8[a]
C57	0.1[a]	0.4[b]				C28:0	5.5[a]	6.2[a]
C58	0.5[a]	2.3[b]				C29:0	0.5[a]	0.5[a]
C59	0.2[a]	0.3[b]				C30:0	4.6[a]	6.2[a]
C60	0.2[a]	1.1[b]				C31:0	1.6[a]	2.4[a]
						C32:0	4.7[a]	5.6[a]
						C34:0	5.1[a]	5.3[a]

Values are mean of two independent samples analyzed by duplicate.
Values for the same component in the same row followed by different letters are significantly different ($p < 0.05$) by the Fisher test.
Tr, traces (<0.1%); n.d., not detected.

significant differences were observed in lightness and yellow/blue axis (Table 2). Both samples showed high lightness and the presence of a green component (negative values of a^*), with RO1 being more yellow than RO2. Both recovered oils could be returned to the oil refining process, thus reducing oil losses.

The wax composition of the recovered oils is shown in Table 3. The methodology used for wax determination allowed for the quantification of waxes up to C60 by removing interfering substances such as steryl esters of sterols [9]. For both samples, the main fraction corresponded to crystallizable waxes (>C44), while the soluble and partially soluble fraction (C34–C43) represented less than 20%. The RO1 sample showed a higher total wax content (1356 mg/kg), while the value for RO2 was 604 mg/kg. Similar wax contents and profiles were reported by several authors for sunflower crude oils [8, 19, 20]. In contrast, it was reported that the main wax fraction in dewaxed oils corresponds to soluble waxes (C34–C43), being crystallizable waxes mostly retained by filter aid [5]. The differences between the samples (RO1 and RO2) may be due to factors such as type of hybrid, origin and conservation of the seed, percentage of hulls adhering to the seeds, temperature, and the technology used in the oil production.

Purified waxes were characterized for wax composition, and fatty acid and fatty alcohol components (Table 4). PW1 was composed mainly of waxes in the range of 40–60 carbon atoms, with higher percentages of C44, C46, C48, C50, and C52 (Fig. 1a), whereas in PW2 the predominant waxes were C46, C48, C50, C52, and C54 (Fig. 1b). In both PW samples, the waxes with over 44 carbon atoms constituted 80% of the total wax esters, the values being similar to those of previous studies [6, 9, 12]. Baümler et al. [6] found a similar wax profile when they analyzed the hull contribution to wax content in sunflower oil. They also observed that the crystallizable fraction consisted mainly of even-numbered waxes with more than 40 carbon atoms, with higher percentages of C44, C46, and C48. The fatty alcohol distribution was found to be in the range of 18–34 carbon atoms for both samples PW1 and PW2 (Table 4). The main alcohols found were C24 (30.5%), C26 (26.2%), and C28 (12.9%) for PW1, and C24 (29.4%), C26 (26.3%), and C28 (13.5%) for PW2, constituting the 70% of total fatty alcohols in both samples. Fatty acids were in the range of 14–34 carbon atoms, with the majority of the fatty acids having 16, 18, 30, 32, and 34 carbon atoms in both samples. The presence of odd waxes could be explained by the presence of small amounts of compounds with odd-carbon numbers.

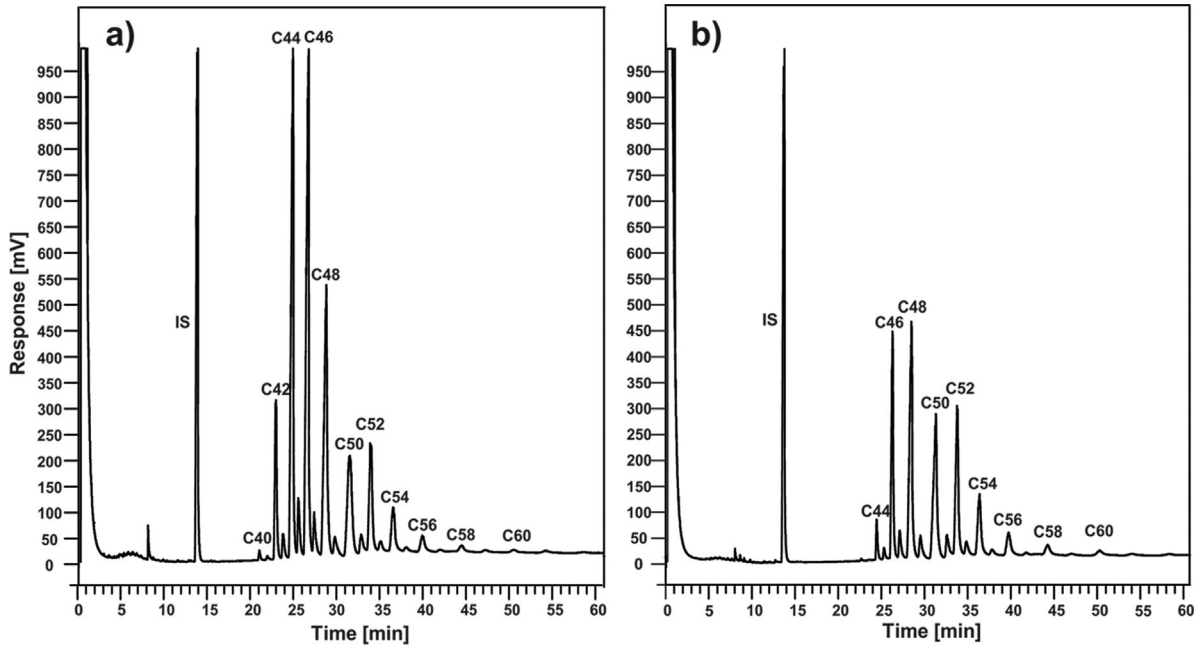

Figure 1. Chromatogram of recovered sunflower waxes. (a) PW1. (b) PW2.

These results are similar to those reported in several studies on sunflower oil sediments and wax oil fraction [1, 7, 21]. Significant differences ($\alpha = 0.05$) between samples in wax and fatty acid profiles were found, and they can be attributed to the different hybrids studied, since the wax sample from the high-oleic seed presented a higher amount of oleic acid than that from the conventional one. The fatty acid composition is also highly controlled by genetic and environmental factors, especially night temperature during grain filling [22]. Agüero et al. [23] found sunflower hybrids with high oleic acid and equal or higher grain yield and oil content than traditional hybrids.

The thermal behavior for PW1 and PW2 obtained using DSC analysis is presented in Fig. 2. Melting points ranging

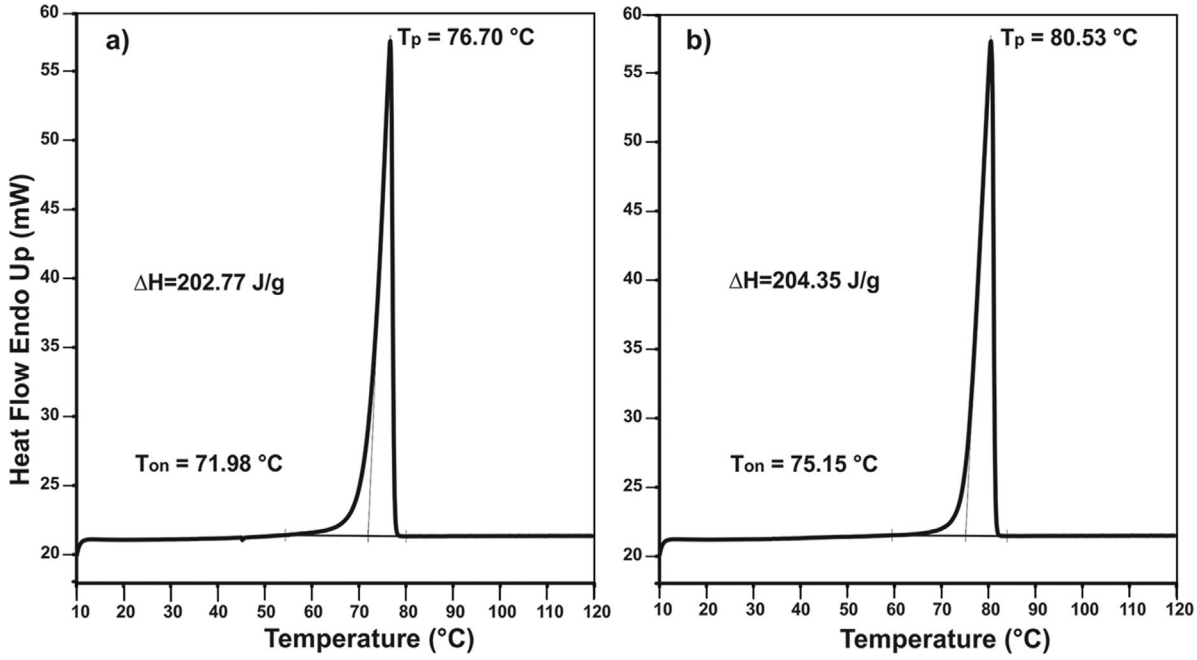

Figure 2. Thermal behavior of sunflower waxes. (a) PW1. (b) PW2.

from 76 to 77°C for purified sunflower waxes have been reported by Leibovitz and Ruckenstein [24] and by Baümler et al. [12], whereas Liu et al. [25] reported lower values (73°C). The DSC thermogram curve for PW1 showed a lower temperature range with a melting temperature peak of 76.70°C. PW2 exhibited a melting peak at a slightly higher temperature of 80.53°C. The melting enthalpy of these two samples, associated with the phase change and determined from the DSC peak areas, was of 202.77 and 204.35 J/g for PW1 and PW2, respectively. In addition, PW1 showed a lower onset temperature (T_{on}) than PW2. This can be attributed to the chain length of the waxes and to the unsaturation grade of the fatty acid components. It is known that the melting temperatures of wax esters increase with chain length, requiring more energy to melt, while unsaturated fatty acids can melt at lower temperatures with less energy. PW1 presented a smaller amount of waxes with longer chain length and higher unsaturation compared with PW2 (Table 4). The values of melting enthalpy were on the order of those reported by Baümler et al. [12], but higher than Liu et al. (190 J/g) [25], suggesting differences in the composition of the samples analyzed.

When the color of the waxes was analyzed, significant differences were found in lightness (L^*), red/green axis (a^*), and yellow/blue axis (b^*) between PW1 and PW2 (Table 2). Both waxes presented high lightness values and low yellow ($+b^*$) and red ($+a^*$) values. The PW1 waxes were less yellow ($b^* = 7.61 \pm 1.41$) than PW2 ($b^* = 9.49 \pm 0.99$), which could be beneficial in certain applications such as edible film for food applications.

4 Conclusions

This report provides important data about the composition of the filter cake from the sunflower oil winterization process and the characterization of the recovered purified waxes. In general, the waste samples presented high lipid content, which can be recovered and fractionated. The recovered oil could be returned to the oil refining process, thus reducing oil losses. The characterization of the purified waxes allowed for a deeper understanding of their composition, which is of extreme importance for their potential use in different industries and technologies. This is also of great environmental relevance, because the waste material generated by the winterization process could be reused, and thus gain added value.

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