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Extraction of High Stearic High Oleic Sunflower Oil Using Eco-Friendly Solvents

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Abstract: The present work aimed to evaluate the extractive performance of three green solvents—absolute ethanol, hydrated ethanol (96%), and absolute isopropanol (AIP)—in high stearic high oleic sunflower seeds, comparing them with the conventional solvent hexane. The oil yield from exhaustive Soxhlet extraction with hydrated ethanol was significantly lower, with no significant differences being observed among the other solvents. Extraction with AIP produced the extract with the lowest non-lipid material content and the oil with the lowest concentration of crystallizable waxes, showing a 53% reduction compared to hexane. Since AIP showed a higher extraction efficiency than absolute ethanol after 4 h of processing, its oil extraction kinetics when used as a solvent were further studied. A modified Fick's diffusion model revealed that, for hexane extraction at 50 °C, the effective diffusion coefficient and the washing fraction were higher than those for AIP extraction (26% and 5.4% higher, respectively). No clear dependence of the oil extraction kinetics on the temperature was observed between the studied temperatures (50 °C and 70 °C). The results showed the feasibility of using absolute ethanol and AIP as alternatives to hexane. Additionally, isopropanol presented operational advantages, producing oil that required less dewaxing during refining than that extracted with hexane or ethanol and showing higher oil selectivity than ethanol.

Keywords: high stearic high oleic sunflower; solvent extraction; ethanol; isopropanol; kinetics

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1. Introduction

There is a growing trend in the agri-food industry of developing crops with unique characteristics that can improve their derived products' technical and functional properties. In this regard, high stearic high oleic (HSHO) sunflower is distinguished by its composition that is rich in stearic and oleic (ω-9) acids, which confer unique nutritional characteristics, a unique melting range, and oxidative stability to its oil for industrial use, while also being a healthy alternative [1]. This oil has the highest proportion and is the best natural source of stearic acid compared to other vegetable oils. Although liquid at room temperature, it can be fractionated to produce stearins which are suitable for various industrial applications [2].

The global oilseed processing industry universally employs hexane as a solvent for vegetable oil extraction. Despite its complete solubility with oil, which enables obtaining meals with low residual oil content and good sensory characteristics, it is necessary to replace it. Hexane derives from a non-renewable source, is characterized by high flammability and toxicity, and contributes to environmental contamination when not adequately

recovered [3,4]. Therefore, using environmentally friendly solvents is becoming a priority in the food industry [5]. Short-chain alcohols, mainly ethanol and isopropanol, are promising alternatives due to their greater operational safety, low toxicity, renewable production potential, and ability to extract high-quality oils while improving defatted meals' sensory and functional characteristics [6]. Several methods of extracting edible oils from seeds have also been studied for their environmental impact and economic feasibility. Ethanol and isopropanol oil extraction processes were analyzed, highlighting their effectiveness as more environmentally friendly alternatives to the more traditional solvents like hexane [7].

Due to their polar nature, alcoholic solvents can extract minor compounds of nutritional and antioxidant importance, such as tocopherols and phenolic compounds, increasing the nutritional value of the extracted oils. Additionally, vegetable oil extraction using short-chain alcohols allows for a more significant removal of sugars, saponins, phosphatides, and pigments, as well as the elimination of compounds that cause bitterness in defatted meals, resulting in higher-quality extraction meals compared to those obtained with hexane [8,9]. Therefore, the content of minor components in the oil, such as waxes which are predominantly located in the hulls [10], could also be affected by the type of solvent used during the extraction process.

Although partial dehulling of the sunflower seeds is performed before extraction due to the significant amount of waxes present in the hulls, the oil must still undergo dewaxing during a subsequent refining stage (winterization). However, during this refining stage—which is based on cooling to crystallize high-melting-point components followed by mechanical separation— not only waxes are removed, but also those products that crystallize at the temperatures at which winterizing is carried out. For this reason, the dewaxing stage in HSHO sunflower seed oil leads to losses in its stearic acid proportion. Due to its high saturated fatty acid content, HSHO sunflower oil begins to behave as a semi-solid oil below 15 °C [11].

The solubility of vegetable oils in alcoholic solvents depends on both the temperature and the water content of the solvent. Increased solubility has been reported with rising temperatures and a decreasing water content at a given temperature. Such behavior has been observed in various plant matrices using ethanol and isopropanol with different water contents [6,8]. When vegetable oil extractions are performed using alcohols instead of hexane, it is essential to consider the temperature at which a single phase is observed between the oil and alcohol (miscibility temperature). Gandhi et al. [12] evaluated the solubility of soybean oil in various solvents, reporting miscibility temperatures of 70 °C and 50 °C for ethanol and absolute isopropanol (AIP), respectively.

Kinetic studies have been extensively conducted on the extraction of oil from various materials, not only from oilseeds. Microalgae like *Chlorella vulgaris* and the seeds of *Sterculia foetida* and *Chukrasia tabularis* L. (new feedstocks) have been studied for their oil extraction kinetics using polar and non-polar solvents [13–15].

Information on using ethanol and isopropanol during the extraction of oil from sunflower seeds is scarce. Gallegos-Infante et al. [16] analyzed the oil quality obtained from three varieties of dehulled sunflower seeds using hexane and isopropanol as solvents. The authors reported that, although the oils extracted with isopropyl alcohol showed higher percentages of free fatty acids than those extracted with hexane, their overall values did not exceed official standards. Rodriguez et al. [17] investigated the use of enzymes in sunflower collet oil extraction using ethanol and isopropanol as solvents. Meanwhile, Baümler et al. [18] evaluated the oil extraction kinetics of sunflower collets using 95% ethanol compared to hexane. No previous studies have been found regarding the kinetics of oil extraction from sunflower seeds using absolute ethanol/isopropanol, nor on the effect of the solvent type on the wax content in the extracted oil.

This study aimed to analyze the influence of the solvent type during oil extraction from HSHO sunflower seeds, employing absolute ethanol, 96% ethanol, and absolute isopropanol as alternative solvents to compare them with traditional hexane. Both the extraction yields (Soxhlet) and oil quality (tocopherol content, wax content, and fatty acid composition) were evaluated, as well as the protein content in the residual extraction meal. Oil extraction studies were also performed as a function of time, to develop models to explain the oil extraction kinetics and assess the effect of the solvent type (comparing a previously selected alcohol and hexane) on the model parameters.

2. Materials and Methods

2.1. Sample Characterization

HSHO sunflower hybrid (5 kg) provided by Advanta Semillas SAIC (Balcarce, Argentina) grown under a greenhouse with drip irrigation in Orán, Salta (Argentina) was used in the assays. This type of sunflower is obtained by combining conventional breeding techniques and mutagenesis (a non-genetically modified ingredient) [19]. The grain sample was stored in hermetically sealed plastic containers and kept at 5 ± 1 °C until the assays were performed. The raw material was characterized in terms of moisture content [20], oil content [21], protein [22] (considering 6.25 as the nitrogen–protein conversion factor), crude fiber [22], and ash content [22].

2.2. Soxhlet Oil Extraction

The oil content of the sample was determined by exhaustive extraction with technical grade hexane (≥98.5%) according to standard procedure IUPAC 1.122 [21] in a Soxhlet apparatus. Similarly, the extractive capacity of alcohols was determined using absolute ethanol (99.1%), hydrated ethanol (96%, azeotropic composition), and absolute isopropanol (≥99.0%). Approximately 10 g of the sample ground to a particle size of less than 2 mm was used. The solvent was added, filling three-quarters of the 250 mL glass flasks. The process was carried out for 8 h at atmospheric pressure. The thermal cycles were carried out at 80 °C for the extraction using hexane as the solvent and at 85 °C during the extractions with alcohols. After the set extraction time, the miscella was separated from the meal using a Sorvall Legend ×1 centrifuge (Thermo Fisher Scientific, Osterode am Harz, Germany) and subsequently subjected to vacuum evaporation using aBüchi R-3000 rotary evaporator, (Büchi Labortechnic AG, Flawil, Switzerland). The extracted material obtained using the alcohols as solvents was fractionated into two phases, hexane-soluble material and other compounds, by a hexane washing step following a procedure similar to that reported by other authors [18,23]. The solvent-free concentrated extract (TE) was brought into contact with 10 mL hexane and then filtered. The procedure was repeated once, and the hexane was evaporated from the collected solution. This process resulted in two fractions: a hexane-soluble material (lipid fraction, LF) and a fraction of other compounds (hexane-insoluble material, HIM). Both fractions were quantified gravimetrically, and all assays were performed in duplicate. Therefore, due to the simultaneous extraction of other compounds, the results obtained in this work when alcohols were used as solvents are referred to as "lipid fraction" instead of "oil". Also, when the authors compare hexane and alcohols as solvents, they refer to the lipidic material extracted (oil), whereas, when comparing alcohols, they refer to the lipidic fraction extracted.

2.3. Characterization of Extracted Lipid Material

The lipid material obtained using the different solvents was characterized by determining the minor components (tocopherols and waxes) and fatty acid composition. The tocopherol concentrations and fatty acid compositions in the extracted oils were determined

using the techniques described by de Figueiredo et al. [24]. The quantification of waxes was performed by capillary gas chromatography (GC) with an on-column injector and FID detector. Thewaxes underwent previous purification by column chromatography with a double layer of silica gel and silica gel impregnated with silver nitrate for the quantification of long-chain waxes (up to C60) [25]. Column chromatography was performed using a glass column (i.d. 15 mm, length 400 mm) with hydrated silica gel (12 g, 2% water) as solid stationary phase. The waxes were eluted with hexane/ethyl ether (99:1 *v/v*) at a flow rate of 3 mL/min using Sudan I dye to control the end of the elution. The eluted wax fraction was evaporated to dryness, diluted with n-heptane, and analyzed by capillary GLC with an on-column injection system. A Perkin Elmer Clarus 580 gas chromatograph equipped with an FID detector (T = 350 °C), a temperature-programmable on-column injector, and a TotalChrom Navigator data processor version 6.3.1 (Perkin Elmer, MA, USA) was used. The capillary column was an HP5 of fused silica, 11 m length × 0.32 mm i.d., 0.52 µm film thickness (Hewlett Packard). Waxes were classified as follows: those with less than 40 carbon atoms, were considered the oil-soluble fraction; waxes from 40 to 43 carbon atoms were the partially soluble fraction, and waxes with more than 44 carbon atoms constituted the crystallized fraction. Determinations were performed in duplicate.

2.4. Characterization of Extraction By-Products (HIM and Defatted Meal)

The total carbohydrate contents of the hexane-insoluble fractions were determined by the phenol-sulfuric method described by DuBois et al. [26], with an external standard curve using glucose (99%, Merck). A solution of the sample in water was prepared, taking care that the carbohydrates were within the sensitivity range of the method (10–100 µg/mL). Both 1 mL of the aqueous sample solution and 0.6 mL of the 5% aqueous phenol solution were placed in a labeled test tube. Then, 3.6 mL of concentrated sulphuric acid was thoroughly mixed until homogenized. The sample was allowed to cool to room temperature (approximately 30 min), and the intensity of the orange color was determined against a blank prepared in the same way using water. A Mapada UV 1800 PC spectrophotometer (Mapada Instruments Co., Ltd., Shanghai, China) with a wavelength of 490 nm was used for the measurements. Assays were performed in triplicate.

After extraction with the different solvents, the meals were characterized by determination of their protein content according to the technique Ai 4-91 [22].

2.5. Time-Dependent Tests

To analyze the time-dependent oil extraction employing short-chain alcohols, experimental runs were carried out with the solvent/s that generated the best yield according to the Soxhlet test (Section 2.2). The experiments were carried out at a laboratory scale in an agitated batch system with temperature control, similar to the tests carried out using hexane as solvent [2] but with the addition of the phase-separation stage of the extracted material. The grain sample was ground in a coffee grinder (Tecnodalvo, Instrumental Pasteur, CABA, Argentina) and then screened to obtain a particle size between 0.42 and 1.00 mm. The mean diameter of the sample was determined by conducting experiments in triplicate, using a laser diffraction particle size analyzer (Malvern Mastersizer Model 2000 E, Malvern Instruments, Worcestershire, UK) with Sirocco 2000-M dry dispersion unit. Before each test, 5 g of ground sample and 90 mL of solvent were separately heated to extraction temperature and then brought into contact by adding the solvent to the vessel with the sample. The tests were carried out at 70 °C, taking into account the considerations made by Gandhi et al. [12] regarding the temperature of miscibility in soybean oil and with a sample–solvent ratio of 1:18 (g/mL) [18]. In accordance with several previous studies on oil extraction kinetics, the experiments were carried out at different times (from 300 to

64,800 s) [2,24,27,28]. The concentrated extract was brought into contact with hexane and then filtered according to the phase-separation stage described previously in Section 2.2. The hexane-soluble material constituted the lipid material (LM) that was used to study oil extraction kinetics. Subsequently, the most efficient alcoholic solvent (higher lipid fraction yield and/or lower extraction rate) was selected, and kinetic studies were carried out at 50 °C [2] to compare with the solvent hexane.

2.6. Kinetics Data Modeling

The experimental data were fitted to a mathematical model based on Fick's second law that considers a non-stationary state and two main extraction mechanisms: a quick washing stage followed by a slower stage of diffusion [24,29], shown in Equations (1) and (2).

$$\frac{M_t}{M_\infty} = 1 - \left(1 - \frac{M_0}{M_\infty}\right)\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp^{-n^2B(t-t_0)} \quad (1)$$

where Mt, M_∞, and M_0 represent the masses of oil (kg solute; kg dry defatted meal^{-1}) that diffuse at time t, infinite time, and initial time t_0 (s), respectively. M_0/M_∞ (dimensionless) and B (s^{-1}) are adjustable parameters determined by the Marquardt–Levenberg algorithm with SIGMAPLOT software v. 12.0 Systat [30]. M_0/M_∞ represents the mean value of the oil extracted during the initial washing time (t_0, tending to zero). The parameter B allows for the estimation of the effective diffusion coefficient (Deff, $m^2.s^{-1}$) by the following equation:

$$B = \frac{D_{eff.}\pi^2}{R^2} \quad (2)$$

The proposed model considers particles of spherical geometry where R (m) represents the average radius of the particles.

2.7. Statistical Analysis

In order to detect differences between yields, the experimental data were analyzed by means of analysis of variance (ANOVA) followed by Tukey's test using the Infostat software Versión 2011 [31]. Differences were considered significant at $p \leq 0.05$. All tests were performed at least in duplicate.

The regression models developed for both the extraction with hexane and the extraction with the selected alcohol, according to Section 2.3, were compared through their parameters using a procedure based on the principle of the extra sum of squares (ESS) and the "conditional error," with a significance level of 95% [27]. They were compared to determine if the coefficients M_0/M_∞ and/or B in Equation (1) were solvent-dependent. Then, for the alcohol selected according to Section 2.3, the models were compared to determine if the coefficients were temperature-dependent. The null (H_0) and alternative (H_1) hypotheses were proposed: H_0: coefficients M_0/M_∞ and/or B did not depend on solvent or temperature (global model in the case that none of them were solvent-dependent or temperature-dependent; common M_0/M_∞ model if only B varied with solvent or temperature; common B model if only M_0/M_∞ depended on solvent or temperature); H_1: both parameters M_0/M_∞ and B depended on solvent or temperature (individual parameters model). To compare the models associated with each of the hypotheses, the statistic F_0 was obtained with the ESS of each model and compared with the corresponding critical value Fc. The lack of fit was tested using a direct comparison method with the contrast statistic F_0^{dc} [27]. When F_0^{dc} is lower than the corresponding critical value at a 95% confidence level (F_c^{dc}), the lack of fit is not significant, and the chosen model is suitable for representing the oil extraction kinetics.

3. Results and Discussions

The proximate composition of the HSHO sunflower sample is presented in Table 1.

Table 1. Proximate composition of the HSHO sunflower seeds on dry basis.

Determination	Content (%db)
Oil	35.9 ± 0.1
Proteins	25.3 ± 0.4
Crude fiber	13.1 ± 0.3
Ash	4.5 ± 0.0
Carbohydrates [1]	21.2

[1] Calculated by difference.

The oil content of the HSHO sunflower sample was low compared to the values reported for conventional sunflower varieties (34–57.5%db) [32,33]. These differences would be associated with the shorter agronomic breeding time of the HSHO sunflower hybrid compared to those of other conventional sunflower hybrids. On the other hand, the sample had a similar oil content, higher protein content, and lower crude fiber content than the values reported for HSHO low lipid sunflower [24], showing satisfactory progress in the field development of the HSHO hybrid.

3.1. Extraction by Soxhlet with Different Solvents

The extraction yields (expressed as percentage on a dry basis and relative to the original sample, %db) obtained for the different fractions are shown in Table 2.

Table 2. Extraction yields of the material obtained by Soxhlet and the fractions separated, i.e., that fraction that was soluble and insoluble in hexane, and carbohydrate content of hexane-insoluble material.

Determination (%db) *	Ethanol (99.1%)	Ethanol (96%)	AIP	Hexane
TE yield	44.1 ± 1.2 ^{c}	44.3 ± 0.6 ^{c}	39.3 ± 0.2 ^{b}	35.9 ± 0.1 ^{a}
LM yield	35.1 ± 0.8 ^{b}	30.2 ± 0.8 ^{a}	34.3± 0.3 ^{b}	35.9 ± 0.1 ^{b}
HIM	9.1 ± 0.5 ^{b}	14.1 ± 0.2 ^{c}	5.0 ± 0.1 ^{a}	---------
Carbohydrate content of HIM	4.1 ± 0.1 ^{b}	6.1 ± 0.02 ^{c}	2.0 ± 0.02 ^{a}	---------

* Percentage ondry basis relative to the original sample of ground seeds. TE: total solvent-free extract. HIM: hexane-insoluble material. LM: lipid material, i.e., LF for alcoholic solvents. Different letters in the same line indicate significant differences (Tukey's test, $p \leq 0.05$).

It can be observed that the yield of extracted material was significantly higher for the three alcohols studied compared to that of hexane. The extracted lipid fraction, i.e., the fraction that was soluble in hexane, was 87.3%, 79.6%, and 68.2% of the total material extracted by AIP, ethanol (99.1%), and ethanol (96%), respectively. Due to their polar nature, alcohols extract, simultaneously with the lipid fraction, other compounds that are not soluble in hexane such as phospholipids, sugars, specific proteins, polyphenols, and pigments [17,34]. Ethanol (99.1%) and AIP did not show significant differences in the LM yield between the two, nor with hexane, showing a lipid extractive capacity similar to the latter. The significantly lower LF yield obtained with ethanol (96%) could be attributed to a decreased solubility and diffusion of oil with increasing water content in the solvent. When the alcohol concentration decreases, the solubility of the oil is sharply reduced because of the increase in the polarity of the solvent, while the extraction of other soluble components in polar solvents is increased [6,35]. The HIM yield increased significantly with the solvent polarity; in this sense, AIP obtained the lowest value, followed by absolute ethanol, and, finally, the highest value was obtained when azeotropic ethanol was used. The same

trend was observed for the amount of carbohydrates in the HIM that was extracted (%db relative to the original sample of ground seeds). Ethanol (96%) extracts more sugars due to having a higher water content than other alcohols. Baümler et al. [18] obtained 10%db of hexane-insoluble components in sunflower collets by Soxhlet extraction using ethanol 95% as the solvent, detecting that they were mainly composed of sugars and phospholipids. The carbohydrate values obtained for the extraction of HSHO sunflower grains with ethanol (96%) were 1.8 times higher than those reported by Baümler et al. [18] for extraction with ethanol 95% from conventional sunflower collets. Likewise, the values obtained when absolute ethanol was used were 30% higher than those reported for canola kernels extracted with the same solvent [28].

Table 3 shows the characterization of the lipid material (LM) extracted with the different solvents regarding its minor components (waxes and tocopherols) and fatty acid composition.

Table 3. Wax composition, tocopherol content, and fatty acid composition of the LM extracted with different solvents.

Determination		Ethanol (99.1%)	Ethanol (96%)	AIP	Hexane
Waxes	(mg/kg of grains in db)	155.1 ± 1.0 ^{c}	127.6 ± 0.2 ^{a}	138.9 ± 1.5 ^{b}	207.4 ± 0.4 ^{d}
	(mg/kg of LM)	442.0 ± 2.8 $^{a, C*}$	422.5 ± 0.7 $^{a, B*}$	405.0 ± 4.2 $^{a, A*}$	577.0 ± 9.8 ^{b}
	Oil-soluble (%)	20.5 ± 0.7 ^{b}	21.0 ± 0.0 ^{b}	21.5 ± 0.7 ^{b}	14.6 ± 0.0 ^{a}
	Partially oil-soluble (%)	30.0 ± 0.1 ^{b}	30.0± 0.0 ^{b}	34.0 ± 0.0 ^{c}	22.1 ± 0.9 ^{a}
	Crystallizable > C44 (%)	49.5 ± 0.7 ^{b}	49.0 ± 0.1 ^{b}	44.5 ± 0.7 ^{a}	63.3 ± 0.9 ^{c}
Tocopherols	(mg/kg of grains in db)	363.0 ± 12.4 ^{b}	424.8 ± 1.4 ^{c}	303.1 ± 0.3 ^{a}	316.9 ± 12.1 ^{a}
	(mg/kg of LM)	1034.3 ± 35.2 ^{b}	1406.5 ± 4.6 ^{c}	883.8 ± 0.8 ^{a}	882.8 ± 33.8 ^{a}
	Alpha (%)	96.4 ± 0.1 ^{a}	96.9 ± 0.04 ^{b}	96.7 ± 0.03 ^{ab}	97.0 ± 0.2 ^{b}
	Beta (%)	1.2 ± 0.03 ^{c}	0.8 ± 0.03 ^{a}	0.9 ± 0.02 ^{b}	0.8 ± 0.03 ^{a}
	Gamma (%)	2.5 ± 0.1 ^{a}	2.3 ± 0.01 ^{a}	2.4 ± 0.1 ^{a}	2.2 ± 0.2 ^{a}
Fatty acid composition	(% of total fatty acids)				
	Palmitic (C16:0)	4.3 ± 0.2 ^{a}	4.6 ± 0.0 ^{a}	4.4 ± 0.2 ^{a}	4.4 ± 0.1 ^{a}
	Stearic (C18:0)	16.3 ± 0.1 ^{b}	15.3 ± 0.0 ^{a}	16.3 ± 0.3 ^{b}	16.4 ± 0.1 ^{b}
	Oleic (C18:1)	73.8 ± 0.0 ^{a}	74.7 ± 0.1 ^{b}	73.5 ± 0.1 ^{a}	73.6 ± 0.4 ^{a}
	Linoleic (C18:2)	2.7 ± 0.0 ^{a}	3.0 ± 0.1 ^{a}	3.1 ± 0.1 ^{a}	2.7 ± 0.1 ^{a}
	Arachidic (C20:0)	1.2 ± 0.1 ^{a}	1.1 ± 0.1 ^{a}	1.3 ± 0.2 ^{a}	1.2 ± 0.0 ^{a}
	Behenic (C22:0)	1.9 ± 0.1 ^{a}	1.4 ± 0.1 ^{a}	1.6 ± 0.1 ^{a}	1.9 ± 0.3 ^{a}

Means in the row followed by the same letter are not significantly different (Tukey's test, $p > 0.05$).* Capital letters indicate a comparison between the different alcohols (independently of the oil obtained using hexane).

The total wax content in the HSHO sunflower oil extracted with hexane (577.0 ± 19.8 mg/kg oil, or ppm) was within the range reported for crude sunflower oils (between 200 and 3500 ppm) [36]. Likewise, this value was lower than that obtained for oils extracted from sunflower collets (between 808 and 1118 ppm) [37], and 670 ppm [18].

The total wax contents of the oils extracted with the alcoholic solvents (mg/kg LF) were significantly lower than that obtained by the extraction with hexane. When the wax concentration data from the oil obtained with hexane were excluded from the statistical comparison, significant differences were observed among the three remaining products, with the concentration of oil obtained through AIP being significantly lower.

When considering the relative compositions of the wax types, a reduction of 42%, 52%, and 53% in the crystallizable waxes extracted with absolute ethanol, hydrated ethanol, and AIP, respectively, was observed compared to those obtained with hexane. These results are consistent with those reported by Baümler et al. [18], who observed a 70% reduction in crystallizable waxes in the material extracted with 95% ethanol from sunflower collets compared to that obtained with hexane extraction. These findings suggest that oil extraction

with alcohols facilitates crude oil refining by requiring a less rigorous winterization or dewaxing step, which could translate into lower costs. In this regard, the short-chain alcohol extraction of HSHO sunflower seeds could present an additional advantage by reducing or eliminating the stearic acid losses that typically occur during winterization for this particular hybrid.

The number of tocopherols in the extracted LF was significantly higher when using absolute ethanol and 96% ethanol as solvents than with hexane, with 96% ethanol yielding the highest values. In contrast, no significant differences was detected in the lipid material extracted with AIP and hexane tocopherol content. Differences in solvent polarity may explain these results.

Tocopherols are amphipathic molecules with a hydrophobic hydrocarbon tail associated with lipid membranes and polar head groups remaining at the membrane surface [38]. The higher tocopherol yield that was obtained can be attributed to the greater polarity of alcohols compared to hexane. Ethanol (96%) is significantly more effective in extracting tocopherols, yielding 34% more than hexane. Absolute ethanol also outperforms hexane, extracting 15% more tocopherols. These results are consistent with those reported by Baümler et al. [18], who observed a 38% increase in the tocopherol yield in sunflower collet oils extracted with azeotropic ethanol. Furthermore, other authors have reported similar findings to those of the present study, as no significant differences in tocopherol content were observed between lipid materials extracted from rapeseed grains using hexane or isopropanol [39].

No statistically significant differences were detected in the fatty acid compositions of the lipid materials extracted with the different solvents, except for in the oil obtained with 96% ethanol. In this case, a significant decrease in the proportion of stearic acid and a considerable increase in the relative proportion of oleic acid were observed compared to the other solvents. However, it is worth noting that the oil extracted with 96% ethanol maintains the fatty acid proportions established by the Argentine Food Code [40] for classification as a High Stearic-High Oleic sunflower oil (oleic acid content equal to or greater than 60% and stearic acid content equal to or greater than 10% of the total fatty acids). For future studies, it would be interesting to evaluate the effect of increased water content in the solvent on the relative fatty acid composition of the extracted LF.

3.2. Proteins in Extraction Meals

Table 4 shows the crude protein contents obtained after Soxhlet extraction using the different solvents studied.

Table 4. Protein content (%b.s.) in residual meals of extraction from HSHO sunflower grains with ethanol (99.1%), ethanol (96%), AIP, and hexane as solvents.

Protein Content (%d.b.)			
Ethanol (99.1%)	**Ethanol (96%)**	**AIP**	**Hexane**
43.9 ± 0.4^{c}	37.7 ± 0.7^{a}	38.3 ± 0.2^{ab}	39.5 ± 0.6^{b}

Expressed as percentage of protein in the residual meal (dry and defatted solid). Values in the same row followed by different letters (effect of solvent type) are significantly different with $p < 0.05$, Tukey's test.

The residual meal obtained after the extraction with ethanol (99.1%) exhibited a significantly higher protein content than the other solvents. Since both the non-lipid fraction (HIM) and the carbohydrate content extracted with absolute ethanol were significantly higher than those obtained with AIP (Table 2), the results suggest that the increase in the relative concentration of proteins in the meal for the extraction with ethanol (99.1%) would be a consequence of the reduction in carbohydrates. On the other hand, the protein content in the residual meal for the extraction with ethanol (96%) was significantly lower

than those obtained for the extractions with absolute ethanol and hexane. At the same time, the amounts of carbohydrates and HIM extracted were significantly higher than those obtained with other alcohols. These results suggest that ethanol (96%) has a higher extraction capacity for sugars and proteins than the other solvents due to having a greater polarity than hexane and AIP (and a higher water content). A similar trend has been reported by different authors, who observed a less protein-rich residual meal that was attributable to increased water content in the extraction solvent [6,41]. Toxicity has been reported in pigs fed with defatted meal containing residual hexane after oil extraction [42]. Therefore, using short-chain alcohols during this process would make valorizing residual meals for industrial or food applications possible by obtaining a by-product without the harmful impact on health or the environment caused by using hexane. There could also be fewer restrictions in the desolventization stage and acceptable protein content for food use, depending on the hydration conditions of the solvent.

3.3. Batch Oil Extraction as a Function of Time

The ground sample of HSHO sunflower seeds used for the time-dependent runs presented a mean particle diameter of 585 ± 18 mm.

3.3.1. Comparative Study Between Absolute Alcohols (Ethanol (99.1%) and AIP) at 70 °C

The experimental LF extraction tests, as a function of time, were performed using AIP and absolute ethanol (ethanol (99.1%)) as solvents, as these alcohols yielded the highest LF recoveries (Table 2). Figure 1 presents the experimental data for the yields of oil or lipid fraction (LF), and the total extract (TE) as a function of time, for the extractions with absolute ethanol (a) and AIP (b). At all time points and for both solvents, the yield of TE was significantly higher than that of LF (ANOVA, Tukey's Test, $p \leq 0.05$). As previously noted, short-chain alcohols can extract compounds such as sugars, phosphatides, and pigments [17,28]. The difference between the TE and LF is attributed to the extraction of these hexane-insoluble compounds.

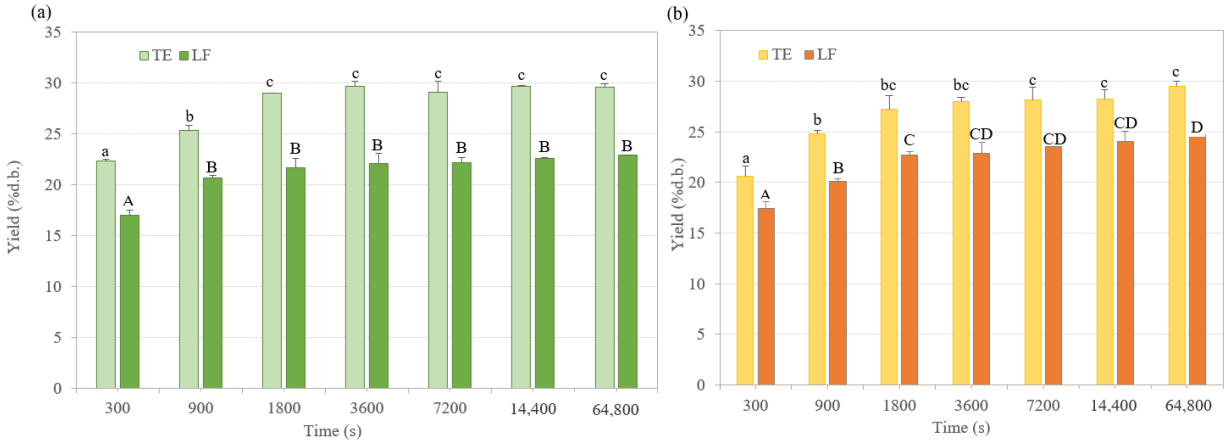


Figure 1. Yields, as a function of time, of total solvent-free extract (TE) and lipid fraction (LF) for extraction with (**a**) absolute ethanol and (**b**) isopropyl alcohol. Different capital letters indicate significant differences in LF (Tukey $p \leq 0.05$) between times. Different lowercase letters indicate significant differences in TE (Tukey $p \leq 0.05$) between times.

The yield of LF exhibited a significant increase with extraction times up to 900 and 1800 s when using absolute ethanol and AIP, respectively, with only marginal increases (Tukey's Test, $p > 0.05$) being observed for longer extraction times. When comparing the LF extraction yields between the two alcohols as a function of the extraction time (Table 5), no significant differences were observed for extraction times shorter than 4 h. However, at

4 h of extraction, an increase of 6.6% in the LF was obtained for AIP compared to absolute ethanol, with a rise of 8.3% being observed at 64,800 s (considered infinite time).

Table 5. Comparison of yields of lipid fractions as a function of time (70 °C) between absolute isopropanol (AIP) and ethanol (99.1%).

Time (s)	Lipid Fraction Yields (%db)	
	AIP	Ethanol (99.1%)
300	17.9 ± 0.6 [a]	17.0 ± 0.5 [a]
900	20.1 ± 0.2 [a]	20.7 ± 0.1 [a]
1800	22.4 ± 0.4 [a]	21.6 ± 0.9 [a]
3600	22.9 ± 0.1 [a]	22.1 ± 1.0 [a]
7200	23.5 ± 0.1 [a]	22.2± 0.5 [a]
14,400	24.1 ± 1.0 [b]	22.6 ± 0.1 [a]
64,800	24.8 ± 0.03 [b]	22.9 ± 0.01 [a]

Values in the same row followed by different letters indicate significant differences between solvents ($p < 0.05$, Tukey's test).

The corresponding alcoholic extraction efficiency values (g of oil/100 g of initial oil in the dry solid) ranged from 67.1% to 69.1% for AIP and from 62.8% to 63.8% for absolute ethanol. These results are consistent with those reported by Capellini et al. [6], who obtained 59% and 71% LF yields from rice bran using azeotropic ethanol and isopropanol, respectively, during 1 h of extraction. Similarly, ref. [43] observed 65% and 69% extraction efficiencies for ethanol and AIP during 16 h of extraction from passion fruit seeds. These results could be attributed to the different polarities of the alcoholic solvents. Capellini et al. [6] reported that ethanol performs less well than solvents of intermediate polarity, such as isopropanol. This behavior can be explained by the dielectric constant (a measure of molecular polarity), since ethanol and isopropanol present dielectric constant values of 22.29 and 17.30, respectively.

3.3.2. Comparative Study Between AIP and Hexane (50 °C)

The LF yield was significantly lower when absolute ethanol was used than when AIP was used, which led to the selection of AIP as the reference solvent for the extraction kinetics comparison with hexane in subsequent studies. Figure 2 shows the comparison of the oil yields for the batch extractions at 50 °C using AIP and hexane as solvents.

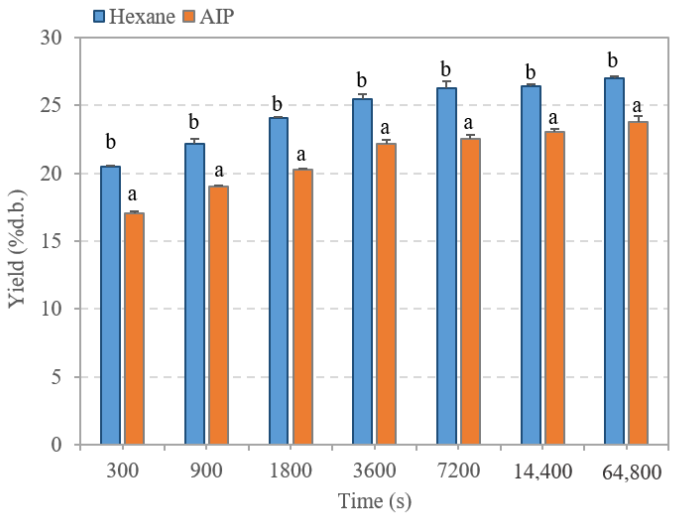


Figure 2. Yields of lipid material (LM) at 50 °C for HSHO sunflower kernels. AIP solvent: hexane-soluble extract fraction extracted with AIP (LF). Hexane solvent: oil extracted with hexane. Different letters for each time indicate significant differences between solvents (Tukey, $p \leq 0.05$).

The LM extractions with hexane were significantly higher than the corresponding LM yields extracted with AIP for all studied times. Furthermore, considering the total extraction process time, an average of 16.5 ± 2.4% more oil was obtained when using hexane compared to AIP. Sánchez et al. [28] observed the same trend when conducting batch extractions at 50 °C using ethanol (99%) to obtain oil from canola seeds. Table 6 presents the obtained coefficients and the results of the nonlinear model comparisons analyzing the effect of the solvent type on the kinetics of oil extraction from ground seeds.

Table 6. Comparison of the coefficients obtained from the different models proposed for the oil extraction kinetics using isopropyl alcohol and hexane as solvent.

Model	Solvent	$M_0/M_\infty.10^2$	$B.10^5$ (1/s)	R^2	F_0	F_c
Global (Common A and B)	--	62.6 ± 2.4	32.0 ± 4.5	0.962	4.49	4.10
Individual parameters	Hx	64.3 ± 2.1	36.0 ± 4.4	0.988	-	-
	AIP	61.0 ± 3.1	28.5 ± 5.2	0.973		
Common M_0/M_∞	Hx	62.6	39.2 ± 2.6	0.986	0.32	4.96
	AIP		26.2 ± 2.7	0.972		
Common B	Hx	65.8 ± 1.1	32.0	0.979	0.43	4.96
	AIP	59.4 ± 1.8		0.990		

Hx: hexane; AIP: absolute isopropanol.

For the solvent type analysis, comparing the global model with the individual parameter model indicates significant differences ($F_0 > F_c$), evidencing a dependence of one or both model parameters on the solvent. However, in comparing the common B model and the common M_0/M_∞ model with the individual parameter model, the corresponding contrast statistics did not detect significant differences ($F_0 < F_c$). These results suggest the existence of an interaction between the involved variables (solvent type and time), whose effect is not represented by the global model. Consequently, the individual parameter model was selected to represent the influence of the solvent type on both parameters. As F_0^{dc} (1.42) was lower than F_c^{dc} (2.48) for the selected model, this model is suitable for representing the kinetics of oil extraction from HSHO sunflower seeds using hexane and absolute isopropyl alcohol (AIP) as solvents at 50 °C. The effective diffusion coefficient (D_{eff}) associated with parameter B, obtained for hexane extraction ($3.12 \pm 0.38 \times 10^{-12}$ m^2/s), was 26% higher but of the same order of magnitude as the corresponding value for AIP extraction ($2.47 \pm 0.45 \times 10^{-12}$ $m^2/$). Additionally, M_0/M_∞ was 5.4% higher in the same direction (Table 6). An influence of the extraction solvent on the kinetic parameters has also been observed during extractions from ground canola grains. Sánchez et al. [28] reported a decrease in M_0/M_∞ and D_{eff} when using ethanol (99.1%) compared to hexane. Similarly, studies performed on sunflower collets [18] observed lower D_{eff} values for extractions conducted with 95% ethanol than those conducted with hexane.

3.3.3. Oil Extraction Kinetics Using AIP as a Solvent (50 and 70 °C)

Figure 3 shows a comparison of the LF yields extracted with AIP at 50 °C and at 70 °C for the different established extraction times.

When statistically comparing the LF yields between temperatures for each extraction time, no well-defined trend was found, with significant differences being observed at 900, 1800, and 14,400 s. While the effect of temperature on the extraction efficiency in oilseeds is well known, studies have generally used hexane as the extraction solvent. However, along with the lipid fraction, alcohols simultaneously extract other hexane-insoluble compounds (such as proteins and carbohydrates), which may affect the oil extraction depending on

the solubility of these materials. Future studies which investigate this topic by expanding the temperature range and evaluating the effect of intermediate temperatures would be desirable.

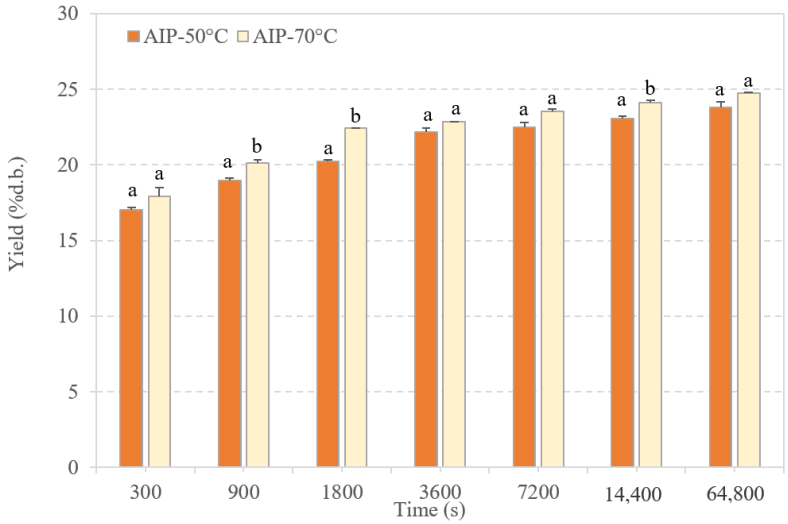


Figure 3. Extraction yields of the hexane-soluble extract fraction (LF), extracted with AIP at two temperatures: 50 °C and 70 °C. Different letters for each time indicate significant differences between temperatures (Tukey, $p \leq 0.05$).

Table 7 shows the parameters of the models used to represent the oil extraction for all the studied cases (as explained in Section 2.7), along with the ESS comparison results.

Table 7. Comparison of the coefficients obtained from the different models proposed for the oil extraction kinetics using isopropyl alcohol as solvent. (50 and 70 °C).

Model	T (°C)	$M_0/M_\infty.10^2$	$B.10^5$ (1/s)	R^2	F_0	F_c
Global (Common A and B)	--	62.1 ± 2.0	27.5 ± 3.6	0.975	0.04	4.46
Individual parameters	70	63.0 ± 2.8	26.7 ± 5.1	0.979	-	-
	50	61.0 ± 3.1	28.5 ± 5.2	0.973		
Common M_0/M_∞	70	62.1	28.2 ± 3.2	0.979	0.003	5.32
	50		26.7 ± 3.5	0.972		
Common B	70	62.7 ± 1.7	27.5	0.979	0.13	5.32
	50	61.4 ± 2.0		0.972		

There were no significant differences when statistically comparing the global and individual parameter models ($F_0 < F_c$). Additionally, comparing the individual parameter model with the common B model and the common $M_0)/M_\infty$ model did not show significant differences in either case ($F_0 < F_c$). Thus, to represent the oil extraction kinetics when using AIP as a solvent, the global model was selected. Moreover, since ($F_0^{cd} = 1.20 < F_c^{cd} = 2.69$), the global model is suitable to obtain the M_0/M_∞ and Deff when using AIP as a solvent within the temperature range studied.

Figure 4 shows the experimental data and the fitting curve of the global model for oil extraction with IPA at 50 °C and 70 °C.

The D_{eff} obtained for the LF extraction kinetics (2.38×10^{-12} m^2/s) was lower but of the same order of magnitude as that found for hexane extraction at 50 °C.

Statistical comparisons of the oil yields across operating temperatures for each extraction time revealed no well-defined trend. Nonetheless, a single model (global model) was

developed to represent the kinetics of oil extraction with AIP within the studied temperature range (50–70 °C). Gandhi et al. [12] observed that the miscibility of soybean oil was higher in ethanol (70 °C) than in AIP (50 °C). However, alcohols simultaneously extract other non-hexane-soluble compounds (such as proteins and carbohydrates) along with the lipid fraction, which could affect the oil extraction due to the solubility of these materials. Future research should aim to extend the temperature range (including lower values) and evaluate the effects of intermediate temperatures.

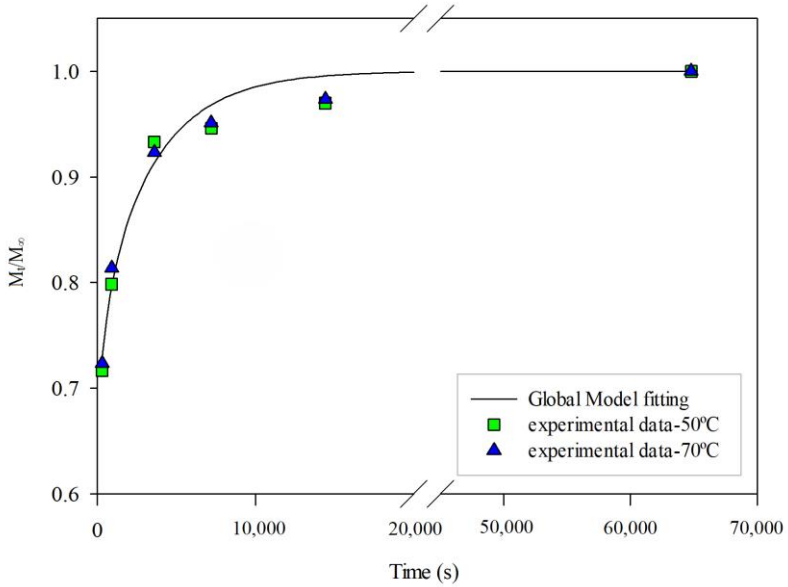


Figure 4. Experimental data (bullets) of hexane-soluble extract fraction (LF) at 50 °C and 70 °C for extraction with AIP and fitted curve according to the global model (continue line).

4. Conclusions

The extracted material obtained using alcohols as solvents (hydrated ethanol, absolute ethanol, or absolute isopropanol) consisted of two phases: a hexane-soluble material (lipid fraction—LF) and a hexane-insoluble material (HIM), separated by simple fractionation using hexane.

No significant differences were observed in the lipid material yields from exhaustive extraction (Soxhlet) between absolute alcohols and hexane. In contrast, azeotropic ethanol exhibited a significantly lower yield than the other solvents studied. The lipid fraction extracted with absolute isopropanol (AIP) showed a tocopherol composition and a residual extraction meal protein content that did not significantly differ from those obtained with hexane extraction. However, this solvent produced crude LF with a significantly lower crystallizable wax content than the other solvents, representing an additional advantage for processing HSHO sunflower oil.

No statistically significant differences were found in the fatty acid compositions of the lipid material extracted with different solvents, except for that extracted with ethanol (96%).

The modified Fick model proved suitable for describing the extraction kinetics of HSHO sunflower oil using AIP as solvent at 50 °C and 70 °C. A statistical comparison of parameters was performed to evaluate the dependence of the kinetics on the type of solvent (AIP and hexane) and temperature. The results indicated that the washing fraction and the effective diffusivity were solvent-dependent. However, these parameters were not temperature-dependent when AIP was used as the solvent (comparing 50 °C and 70 °C).

By utilizing computational tools, such as those used to fit the modified Fick's model equation employed in this study, it was possible to represent the extraction kinetics of high stearic high oleic (HSHO) sunflower oil when employing AIP as a solvent. This

approach allowed us to obtain the model parameters, which were the washing fraction Mo/M_∞ and B (associated with effective diffusivity) at two distinct temperatures (50 °C and 70 °C). These parameters could be utilized to simulate and optimize the extraction process by employing computational models to enhance the efficiency and profitability of this "green" extraction process.

The importance of using these models in the extraction of HSHO sunflower oil with isopropyl alcohol as the solvent lies in the fact that, to the best of our knowledge, no information on this specific system is available in the literature. Understanding this system is particularly relevant due to the unique characteristics of this oil and the environmental friendliness of the process, which results from the solvent used, producing oil with a low wax content, which leads to a reduced need for winterization.

The results of the present study show the feasibility of using absolute ethanol and AIP as alternative solvents to hexane. AIP emerges as a more efficient option due to its significantly higher selectivity compared to absolute ethanol (lower proportion of hexane-insoluble compounds in the extract) and its production of high-quality crude lipid fraction that would require less refining, particularly during the dewaxing stage. The final selection of the type of alcoholic solvent must be supported by economic impact studies, considering factors such as the solvent's availability, desolventization, and product purification. Furthermore, this selection will involve balancing the quality of the extracted products and the by-products, whether focusing on the production of a residual meal rich in protein and an improved oil quality (compared to hexane extraction) or opting to extract an oil with a lower wax content (particularly crystallizable waxes) to reduce costs and losses during subsequent oil purification stages. Recovering ethanol and isopropanol as solvents in oil extraction reduces the environmental pollution resulting from the process compared to the use of hexane. However, it increases operating costs due to higher energy requirements and a higher initial investment in recovery equipment being required. Therefore, the choice of solvent should also consider the process efficiency, the cost, and sustainability objectives.

It is feasible that a possible evaluation of the techno-economic-environmental impact of replacing hexane with ethanol or AIP (depending on the plant matrix used) in an industrial plant does not present the same profitability as when using hexane. However, the process would be feasible and have a lower environmental impact.

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Data Availability Statement: The data presented in this study are available at the request of the corresponding author for privacy reasons.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AIP	Absolute isopropanol
HSHO	High stearic high oleic
TE	Total solvent-free concentrated extract
LF	Hexane-soluble material (lipid fraction)
HIM	Hexane-insoluble material
LM	Lipid material

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