Chapter

Torrefaction of Sunflower Seed: Effect on Extracted Oil Quality

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Abstract

The aim of this work is to study the effect of heat treatment on the lipidic profile of sunflower seed oil. It determined and compared the contents of bioactive components in seed oils extracted with n-hexane (Soxhlet method) from raw and roasted sunflower. The influence of torrefaction on fatty acid composition, triglyceride composition, and peroxide value (PV) has been studied. Thermal oxidation assays were carried out, and samples were evaluated by measuring induction time. Oleic acid was the main unsaturated fatty acid. Concerning triglyceride composition, OOL + LnOO, OOO + PoPP, POP and OOO + PoPP, OOL + LnOO, POP were the main, respectively, for raw and roasted samples. The seed oil samples extracted from the roasted sample exhibited a higher peroxide value (213.68 meq.O_2/kg) than the raw sample (5.79 meq.O_2/kg). The acid values were, respectively, 3.24 and 1.81 mg of KOH/g of oil for roasted and raw samples. On the other hand, induction time for raw sample was higher (16.23 h) than the roasted sample one (2.67 h).

Keywords: torrefaction, sunflower, seed oil, oxidation

1. Introduction

Lipids are major components of a man's diet. Their high quantities may be found in plant seeds distributed in many regions of the world. They can provide oils with a high concentration of monounsaturated fatty acids that prevent cardiovascular diseases by several mechanisms [1]. Several oleaginous seeds exist in the world. Some seeds are eaten as they are, such as sunflower seeds; others are used in the extraction of oil [2]. Sunflower (*Helianthus annuus* L.) is cultivated for its seeds' high oil content. Oil represents up to 80% of its economic value [3]. Abd EL-Satar et al. [4] concluded from their works that wider plant spacing and increasing nitrogen fertilization levels in addition to cultivars with high yield potential increase the plant's ability to take the needs of nutrients and solar radiation; this leads to an increase in photosynthesis, which reflected the increasing economic yield. Solvent extraction is one of the traditional techniques of extracting vegetable oil from oil seeds. Oil seeds are put in contact with a suitable solvent, in its pure form, for extracting the oil from the solid matrix to the liquid phase [5]. In many cases, chemical studies that employ a series of chemical compounds and/or sensory descriptors are used to characterize edible oil and fats [6]. In Tunisia roasted sunflower seeds, called "glibettes," are frequently consumed. Roasting enhances the organoleptic characteristics of seeds and gives them a taste and a pleasant smell. A huge number of papers on studies of different oils and fats are published every year. However, the effect of this heat treatment on the composition and nutritional qualities has not been studied.

There is no published work. The main objective of this study was to determine the TG, total FA composition, peroxide value (PV), acid value, and oxidative stability of the sunflower seed oil before and after torrefying. This study can be used to understand the causes of certain diseases related to the consumption of oxidized fat.

2. Experimental

2.1 Sunflower seed samples

Sunflower seeds (*Helianthus annuus* L.) are grown in Beja region (latitude 36°43′32″; longitude 9°10′54″; elevation 248 m), located in the northwest of Tunisia. After harvesting the seeds are stored in a dry place at room temperature, protected from light. Then the seeds were roasted at an artisan (called Hammas). The temperature and processing time are, respectively, 180°C and 10 min. Sunflower seeds were placed in a bowl and covered with salted water. Thus, they will absorb some of the water and will not dry too much during cooking. Seeds were drained and salted water was emptied. The oven was preheated to about 180°C. The seeds were arranged in a thin layer on the plate for better cooking. Seeds were baked and broiled for about 10 min. Occasionally, seeds were stirred in order to grill them evenly. Seeds may develop a slight crack in the middle during torrefaction. The still hot seeds were cooled and stored in an airtight box.

2.2 Seed oil extraction

The fat content was measured with a Soxhlet extractor apparatus with 250 ml of hexane at 60°C for 6 h, and then the solvent was removed by evaporation. The seed oil obtained was drained under a nitrogen stream (N_2) and was then stored in a freezer at −20°C until analysis.

2.3 Fatty acid composition

Fatty acid composition was determined by the analytical methods described by the European Parliament and the European Council in EEC regulation 2568/91 (1991) [7]. Fatty acids were converted to fatty acid ethyl esters (FAMEs) before being analyzed by shaking off a solution of 0.2 g of oil and 3 ml of hexane with 0.4 ml of 2 N methanolic potassium hydroxide. The FAMEs were then analyzed in a Hewlett-Packard model 4890D gas chromatograph furnished with an HP-INNOWAX-fused silica capillary column (cross-linked PEG), 30 m × 0.25 mm × 0.25 μm, and a flame ionization detector (FID). Inlet and detector temperatures were held at 230 and 250°C, respectively. The initial oven temperature was held at 120°C for 1 min, and then it was raised to 240°C at a rate of 4.0°C/min for 4 min. The FAME-injected volume was 1 μl, and nitrogen (N_2) was used as the carrier gas at 1 ml/min with a split inlet flow system at a 1:100 split ratio. Next, heptadecanoic acid C17:0 was added as an internal standard before methylation in order to measure the amount of fatty acids. Eventually, fatty acid contents were calculated using a 4890A Hewlett-Packard integrator.

2.4 Triacylglycerol composition

Triacylglycerol in different samples were determined according the International Olive Council [8]. The chromatographic separation of TAGs was

performed using an Agilent 1100-reverse phase high-performance liquid chromatography (HPLC) system (Agilent Technologies, Waldbronn, Germany) equipped with an Inertsil ODS-C18 (5 μm, 4.5 × 250 mm) column. Elution was performed by using the mixture of acetonitrile/acetone (50:50, v/v) at a flow rate of 1 mL/min at 30°C. The working solutions of triacylglycerols (1%, w/v) were prepared in the elution mixture and injected into the column to determine their specific retention times. Identification of the peaks was carried out using a soybean oil chromatogram as reference. The mean of the data was calculated from three biological repeats obtained from three independent experiments.

2.5 Peroxide value, acid value, and thermal oxidation

Official methods of the American Oil Chemists' Society [9] were used for the determination of the peroxide value (method Cd 8-53) and the acid value (method Cd 8-53). The oxidative stability of the oils was determined using a Rancimat 743 Metrohm apparatus (Metrohm Co., Basel, Switzerland). This instrument was used for automatic determination of the oxidation stability of oils and fats. The level of stabilization was measured by the oxidative-induction time using 3.5 ± 0.01 g samples of oils. The temperature was set at 100°C, the purified airflow passing through at a rate of 10 l/h. During the oxidation process, volatile acids were formed in the deionized water and were measured conductometrically [10]. Samples of oils were placed in the apparatus and analyzed simultaneously. The samples were placed at random. The induction times were recorded automatically by the apparatus' software and taken as the break point of the plotted curves [11].

3. Results and discussions

3.1 Yield oil

The extraction yields are 43 and 52%, respectively, for raw and roasted seeds. Thus, we get a gain in yield of 9%. This gain is due to the roasting. Hydrolytic and proteolytic enzymes disrupt the structure of the cell and improve extraction yields. Oil yield depends on the cell disruption during the extraction process. Oil was located inside the cell. Various factors can influence the efficiency of the extraction process such as size of the solid particles, agitation, ratio of liquid/solid, extraction duration, pH, and temperature. Since the optimal temperature value coincides with the optimum protein degradation value, extraction of oil can be considered as a process aimed at degrading proteins which results in the release of the oil. However, the quality of the oil obtained depends on the operating conditions of extraction [12]. The yield extraction can be improved using other methods such as the Folch method. Hence, oils extracted using polar solvents such as a combination of chloroform and methanol may cause extraction of polar materials (phospholipids). In addition, neutral triacylglycerols can affect the oil yield extraction [1]. The effect of extraction time and temperature can also be significant for oil yield. However, several researchers have studied aqueous extraction of oil from sunflower. Evon et al. [3] have studied the feasibility of an aqueous process to extract sunflower seed oil using a corotating twin-screw extruder. The best oil extraction yield obtained was approximately 55%.

3.2 Fatty acid composition

Table 1 shows fatty acid composition of sunflower seed oil compared to those of literature. Oleic, linoleic, palmitic, and stearic acids were found as major fatty

acids of sunflower seed oils. Their contents are 46.64, 38.11, 8.81, and 5.48%, respectively, for the raw sunflower seed. According to the work of [14], this composition depends on the environmental conditions during grain filling. The main environmental factors driving oil fatty acid composition are temperature and solar radiation. For oil quality purposes, oleic and linoleic are the most important fatty acids because they constitute almost 85% of the total fatty acids in sunflower oil. Sunflower fatty acid composition has been modified by breeding and mutagenesis parameters for minimum and maximum oleic acid percentage [15]. The roasted sunflower seed fatty acid contents were found to be 44.91, 36.95, 9.13, and 7.26%, respectively, for oleic, linoleic, palmitic, and stearic acids. Linoleic acid is the fatty acid most susceptible to degradation in sunflower oils [16]. The high amount of linoleic acid present in sunflower seed oil can make it more susceptible to oxidation and consequently cause higher cytotoxicity due to the production of free radicals. Diminution of unsaturated fatty acid was detected, caused by thermal treatment. Two news fatty acids appear: arachidic (0.91%) and behenic acid (0.83%). These fatty acids were detected in sunflower seeds in low amount [12]. They were 0.23 and 1.35%, respectively, for arachidic and behenic acid. Authors confirmed that the amount of arachidic and behenic acid were, respectively, 0.33 and 0.52% [17].

Sunflower seed oil is very nutritional because of its oleic acid content. The oleic acid content is varied: 46.64% in our study, 85.8% in [12], and 24.86% in [13]. It showed that fatty acid composition is highly variable [16, 18]. The palmitic acid, oleic acid, and linoleic acid contents ranged, respectively, from 5.3 to 27.9%, 31.6 to 84%, and 2.4 to 56.8%. Sunflower seed oil was fully liquid at the ambient temperature, as it is very rich in monounsaturated (oleic) and polyunsaturated (linoleic) fatty acids. Sunflower seed oil gives better functional properties such as good spreadability at refrigeration temperatures because of its high content of PUFA [19].

	The present study			[12]	[13]
Fatty acid content (%)	**Symbol**	**Raw**	**Roasted**		
Myristic acid	C14:0			0.05	—
Palmitic acid	C16:0	8.81	9.13	3.48	0.068
Palmitoleic acid	C16:1	0.45	—	—	6.12
Stearic acid	C18:0	5.48	7.26	3.65	3.41
Oleic acid	C18:1	46.64	44.91	85.8	24.86
Linoleic acid	C18:2	38.11	36.95	4.96	63.18
Linolenic acid	C18:3	0.51	—	—	0.082
Arachidic acid	C20:0	—	0.91	0.23	—
Behenic acid	C22:0	—	0.83	1.46	—
Lignoceric acid	C24:0	—	—	0.30	—
SFA		**14.29**	**18.13**	**9.17**	**3.478**
MUFA		**47.09**	**44.91**	**85.80**	**30.98**
PUFA		**38.60**	**36.65**	**4.96**	**63.262**
PUFA/SFA		**2.70**	**2.03**	**0.54**	**18.18**

SFA, saturated fatty acid; MUFA, monounsaturated fatty acid; PUFA, polyunsaturated fatty acid.

Bold entries are to express the sum.

Table 1.
Fatty acid composition of sunflower seed oil.

3.3 Triglyceride composition

The compositions of triglycerides (TGs) expressed as the equivalent carbon number (ECN) found in sunflower seed oil samples are reported in **Table 2**. The main triglycerides found in the sunflower seed oil samples analyzed were OOL + LnOO, OOO + PoPP, POP and OOO + PoPP, OOL + LnOO, POP, respectively, for raw and roasted samples. These accounted for more than 62 and 66% of the total area of peaks in the chromatogram, respectively, for raw and roasted samples.

The level of OOL + LnOO, OOO + PoPP, the main TG in sunflower seed oil samples, was remarkably high, with a concentration of 25.90, 24.50 and 21.30, and 26.90%, respectively, for raw and roasted samples. The OOL + LnOO content of raw sunflower seed oil is greater than that in the roasted sample. However, the OOO + PoPP content is lower in the raw sunflower seed oil one. The next three TG fractions are POP, OOLn + PLL, and SOL with contents of 11.91, 10.80, and 10.34% and 18.17, 7, and 9.62%, respectively, for raw and roasted samples.

3.4 Peroxide value, acid value, and thermal oxidation

Peroxide value is a measure of the concentration of peroxides and hydroperoxides formed in the initial stages of lipid oxidation. Peroxide value is one of the most widely used tests for the measurement of oxidative rancidity in oils and fats [20]. The quality parameters of a crude oil included (i) the acid value, expressed in mg of KOH/g of oil, which is an indication of the free fatty acid content of the oil, and (ii) the peroxide value, expressed in terms of meq.O_2/kg of oil [21]. The results of peroxide value, acid value, and Rancimat test are shown in **Table 3**. Peroxide value increases considerably from 5.79 to 213.68 meq.O_2/kg, respectively, for raw and roasted oil samples. This is due to the high linoleic acid content, which is the fatty acid most susceptible to degradation in sunflower oils. Thermal oxidation assays of

TAG	ECN	Raw	Roasted
LLL	ECN 42	0.30	0.98
PoLL + OLLn + PoOLn	ECN 42	0.28	0.27
PLLn	ECN 42	0.51	0
OLL + PoOL	ECN 44	0.15	0.17
OOLn + PLL	ECN 44	10.80	7.00
PPLn + PPoPo	ECN 44	0.20	0
OOL + LnOO	ECN 46	25.90	21.30
PoOO	ECN 46	5.00	4.12
OOO + PoPP	ECN 48	24.50	26.90
SOL	ECN 48	10.34	9.62
POO	ECN 48	0.64	0.67
POP	ECN 50	11.91	18.17
SOO	ECN 50	4.21	3.00
POS + SLS	ECN 50	4.26	7.77

P, palmitic; Po, palmitoleic; S, stearic; O, oleic; L, linoleic; Ln, linolenic; and A, arachidic acids.

Table 2.
Triacylglycerol composition of sunflower seed oil.

Sample	Peroxide value (meq.O_2/kg)	Acid value (mg of KOH/g of oil)	Induction time (h)
Raw	5.79	1.81	16.23
Roasted	213.68	3.24	2.67

Table 3.
Peroxide value and oxidative stability of sunflower seed oil.

sunflower seed oil were carried out. The new compounds formed were evaluated [16]. Results showed that the levels of all the new compounds analyzed strongly depended on the degree of oil unsaturation and unsaturated oils with low content of linoleic acid, and high content of palmitic acid behaved exceptionally well. The linoleic acid is most susceptible to polymerization. The saturated fatty acids show a great importance in delaying oil polymerization [16].

The acid value (AV) expresses the extent of hydrolytic changes in the sunflower oils. The acid values were 1.81 mg of KOH/g of oil for the raw sample and 3.24 mg of KOH/g of oil for the roasted one. This increase of acid value indicates that TG hydrolysis occurred during the heat treatment. However, it can be consider that the operating conditions did not change oil quality significantly. The acid value remained stable at less than 3.5 mg of KOH/g of oil. The characteristic of crude sunflower oil based on specification from the American Fats and Oils Associations shall be pure with free fatty acid of 3% maximum or acid value below 6 mg of KOH/g of oil [21]. It showed that the feedstock sunflower oils possessed high free fatty acid [22]. Hydrolysis reactions of triglyceride with enzymatic and chemical pathways produce the free fatty acid (FFA). FFA is one of the important quality parameters. The formation of free fatty acid chain due to hydrolysis may lead to sensorial characterization [23]. The stability of sunflower seed oil expressed as the oxidation induction time was about 2.67 and 16.23 h, respectively, for raw and roasted seeds. This value may be justified by the high contents of MUFA and PUFA [24, 25]. Induction time values were quite different according to the oil composition (degradation), in proportion to the heat treatment. A high oxidation stability (33–45 h) of date seed oil measured by Rancimat was justified by the relatively low content of PUFA and the high content of natural antioxidants, such as phenolic compounds. Authors indicated that the species containing linoleic acid were oxidized more rapidly than those containing oleic acid [24, 26]. TAG polymers are the most characteristic compounds formed at high temperature, their rate of formation being dependent on the content of polyunsaturated fatty acids [27].

4. Conclusion

From the results and discussion of the study conducted, it can be concluded that the operating condition of torrefaction had an important influence on the oil extraction yield and the quality of oil extracted. Higher oil extraction yield was reached with increased temperature (torrefaction). The oil extraction yield of 52% was obtained under operating conditions of 180°C and 10 min. However, torrefaction process produced oil of bad quality. Changes of fatty acid composition, triglyceride composition peroxide value, acid value, and oxidative stability were observed. During torrefaction process oxide species were produced under the effect of high temperature. Thus, we can understand some diseases appeared to the customer of roasted sunflower seed (glibettes).

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