Effect of torrefaction on the lipidic profile of sunflower seed oil

J. Mejri[a, b*]
Y. Zarrouk[c]
M. Hammami[d]

[a]Département Génie Mécanique et Agro-Industriel, Ecole Supérieure des Ingénieurs de Medjez el Bab (ESIM) Medjez el Bab, Tunisia.

[b]Unité de recherche: Les énergies renouvelables en agriculture et agro-industrie, Ecole Supérieure des Ingénieurs de Medjez el Bab (ESIM) Medjez el Bab, Tunisia

[c]Unité de Recherche en Sciences et Technologies des Aliments Ecole Supérieure des Industries Alimentaires de Tunis (ESIAT) Tunis, Tunisia

[d]Laboratoire des Plantes Aromatiques et Médicinales, Centre de Biotechnologie de Borj-Cedria Hammam-Lif, Tunisia

(*) CORRESPONDING AUTHOR:
Prof. Jamel Mejri
Tel: +216 97 577 532
Fax: + 216 78 561 700
E-mail: jmejri2001@yahoo.fr

The scope 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 has been studied. Thermal oxidation assays were carried out and samples were evaluated by measuring induction time.
Oleic acid dominated among unsaturated fatty acids. 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 roasted sample exhibited a higher peroxide value (213.68 meq. O_2/kg) compared to 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 the roasted and raw sample. On the other hand, induction time for the raw sample was higher (16.23 h) than the roasted sample (2.67 h).

Keywords: Torrefaction, sunflower, seed oil, oxidation

1. INTRODUCTION

Lipids are major components of a man 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 with several mechanisms [1]. Several oleaginous seeds exist in the world. Some seeds are eaten as they are, like sunflower seeds; others are used in the extraction of oil [2]. Sunflower (*Helianthus annuus* L.) is cultivated for its the high oil content of the seeds. Oil represents up to 80% of its economic value [3]. Abd EL-Satar *et al*. [4] concluded with their works that wider plant spacing, increasing nitrogen fertilisation levels in addition to cultivars with high yield potential increases the plant's ability to take the needs of nutrients and solar radiation, this leads to an increase in photosynthesis that 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, chemometric that employ series of chemical compounds and/or sensory descriptors are used to characterise 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, acid value and the oxidative stability of the of sunflower seed oil before and after torrefaction. This study can be used to understand the causes of certain diseases related to the consumption of oxidised fat.

2. EXPERIMENTAL

2.1. SUNFLOWER SEED SAMPLES

Sunflower seeds are grown in Beja region (latitude 36°43′32″; longitude 9°10′54″; elevation 248 m), located in the north-west 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 in the order of 180°C and 10 minutes. 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 a better cooking. Seeds were baked and broiled for about 10 minutes. Occasionally, seeds were stirred 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 in the European Parliament and European Council EEC regulation 2568/91 (1991) [7] adapted for sunflower oil. Fatty acids were converted to fatty acid methyl esters (FAMEs) before being analysed 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 analysed 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°C and 250°C, respectively. The initial oven temperature was held at 120°C for 1 min and then raised to 240°C at a rate of 4.0°C/min for 4 min. The FAMEs 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 methylester C17:0 was added as an internal standard before methylation 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 with a differential refractometer detector. 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 a reference. The data mean was calculated from three biological repeats obtained from three independent experiments.

2.5. PEROXIDE VALUE, ACID VALUE AND THERMAL OXIDATION

Official methods American Oil Chemist's 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 the automatic determination of the oxidation stability of oils and fats. The stabilisation level was measured by the oxidative-induction time using 3.5 ± 0.01 g samples of oils. The temperature was set at 100°C, with the purified air flow passing through at a rate of 10 l/h. During the oxidation process, volatile acids were formed in the deionised water and were measured conductmetrically [10]. Samples of oils were placed in the apparatus and analysed 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. OIL YIELD

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 cell structure

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, the extraction of oil can be considered as a process aimed at degrading proteins that results in the oil release. However, the quality of the oil obtained depends on the extraction operating conditions [12]. 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 the extraction time and temperature can also be significant for the oil yield. However, several researchers have studied the aqueous extraction of oil from sunflower [3]. They have studied the feasibility of an aqueous process to extract sunflower seed oil using a co-rotating twin-screw extruder. The best oil yield extraction obtained was approximately 55%.

3.2. FATTY ACID COMPOSITION

Table I 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 45.15 g/100 g; 37.08 g/100 g; 8.34 g/100 g and 5.39 g/100 g respectively for the raw sunflower seed. According to the work of [13], 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 was modified by breeding and mutagenesis parameters for minimum and maximum oleic acid percentage [14]. The roasted sunflower seed fatty acid contents were found to be 43.56 g/100 g; 36.97 g/100 g; 8.25 g/100 g and 5.27 g/100 g respectively for oleic, linoleic, palmitic, and stearic acids. Linoleic acid is the fatty acid most susceptible to degradation in sunflower oils [15]. The high amount of linoleic acid 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 new fatty acids appear: arachidic (0.26%) and behenic acid (0.19%). These fatty acids were detected in sunflower seeds in low amount by Amalia *et al*. [12]. They were 0.23% and 1.35% respectively for arachidic and behenic acid. De Mello Silva Oliveira *et al*. [16] confirmed that the amount of arachidic and behenic acid were respectively 0.33% and 0.52%.

Table I - Fatty acid composition of sunflower seed oil (g/100 g)

Fatty acid content (%)	Symbol	Raw	Roasted
Myristic acid	C14:0		
Palmitic acid	C16:0	8.34	8.25
Palmitoleic acid	C16:1	0.43	-
Stearic acid	C18:0	5.39	5.27
Oleic acid	C18:1	45.15	43.56
Linoleic acid	C18:2	37.08	36.97
Linolenic acid	C18:3	0.48	-
Arachidic acid	C20:0	-	0.26
Behenic acid	C22:0	-	0.19
Lignoceric acid	C24:0	-	-
SFA		13.73	13.97
MUFA		45.58	43.56
PUFA		37.56	36.97
PUFA/SFA		2.73	2.64

SFA: Saturated Fatty Acid; MUFA: Mono-Unsaturated Fatty Acid; PUFA: Poly-Unsaturated Fatty Acid.

Sunflower seed oil is very nutritional because of its content on oleic acid. The oleic acid content is varied: 46.64% for our study, 85.8% [12] and 24.86% [17]. Marmesat *et al*. [15] and Perez *et al*. [18] showed that fatty acid composition is highly variable. 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%. Thereby, we can consider that our oil is High Linoleic Sunflower Oil (HLSO). Sunflower seed oil was fully liquid at room temperature as it is very rich in monounsaturated (oleic) and polyunsaturated (linoleic) fatty acid. Sunflower seed oil has better functional properties such as good spreadability at refrigeration temperatures because of its high content of PUFA [19].

3.3. TRIGLYCERIDE COMPOSITION

The composition of triglycerides (TGs) expressed as the equivalent carbon number (ECN) found in sunflower seed oil samples reported in Table II. The main triglycerides (TG) found in the sunflower seed oil samples analysed 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, were remarkably high, with a concentration of 25.90%; 24.50% and 21.30%; 26.90% respectively for raw and roasted samples. The OOL + LnOO content of raw sunflower seed oil are greater than that in the roasted sample. However, the OOO + PoPP content are lower in the raw sunflower seed oil one. The next three TG frac-

Table II - Triacylglycerol composition of sunflower seed oil

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; A: arachidic acids.

tions are POP, OOLn + PLL and SOL with contents of 11.91%, 10.80%, 10.34% and 18.17%, 7%, 9.62 respectively for raw and roasted samples.

3.4. PEROXIDE VALUE, ACID VALUE AND THERMAL OXIDATION

Peroxide value (PV) 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 III. Peroxide value increases considerably from 5.79 meq.O_2/kg to 213.68 meq.O_2/kg, respectively for raw and roasted samples oil. This is due to the high linoleic acid content, which is the fatty acid most susceptible to degradation in sunflower oils. Thermal oxidation assays sunflower seed oil were carried out and samples were evaluated by measuring the new compounds formed [15]. Results showed that the levels of all the new compounds analysed, greatly depended on the oil unsaturation degree; unsaturated oils with low content of linoleic acid and high content of palmitic acid behaved exceptionally well. The linoleic acid is most susceptible to polymerisation. The saturated fatty acids show a great importance in delaying oil polymerisation [15].

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 TGs hydrolysis occurred during the heat treatment. However, it can be considered 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 American Fats and Oils Associations shall be pure with a free fatty acid of maximum of 3% or acid value below 6mg of KOH/g of oil [21]. Saydut *et al*. [22] showed that the feedstock sunflower oils possessed high free fatty acid. Hydrolysis reactions of triglyceride (TGs) with enzymatic and chemical pathways produce the free fatty acid (FFA). FFA is one of the important quality parameters. The formation of a free fatty acids chain due to hydrolysis may lead to sensorial characterisation [23]. The stability of sunflower seed oil expressed as the oxidation induction time were about 16.23 and 2.67 h respectively for raw and roasted seed. 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), ranging from the function as 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 like phenolic compounds. Besbes *et al*. [24] and Guinda *et al*. [26] indicated that the species containing linoleic acid were oxidised more rapidly than those containing oleic acid. TAG polymers are the most characteristic compounds formed at high temperatures, their formation rate is dependent on the content of polyunsaturated fatty acids [27].

Table III - Peroxide value and oxidative stability 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

4. CONCLUSION

The results and discussion of the study showed that the operating condition of torrefaction had an important influence on the oil extraction yield and on the quality of oil extracted. Higher oil extraction yield was reached with an increased temperature (torrefaction). The oil extraction yield of 52% was obtained under operating conditions of 180°C and 10 minutes. How-

ever, the torrefaction process produced oil of bad quality. Changes of fatty acid composition, triglyceride composition peroxide value, acid value and oxidative stability were observed. During the torrefaction process oxidised species were produced under the effect of a high temperature. Thus, we can understand some diseases that appeared to the customer of this kind of product (glibettes), like the activation of inflammatory pathways in the small intestine.

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