

Influence of High Temperature and Duration of Heating on the Sunflower Seed Oil Properties for Food Use and Bio-diesel Production

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Abstract: Two important problems for the food industry are oil oxidation and oil waste after frying. Sunflower seed oil is one of the vegetable oils most commonly used in the food industry. Two variables were applied to the low oleic sunflower seed oil in this work i.e. heating temperature (180-210-240°C) and time of heating (15-30-60-120 minutes), to study from the edible point of view the variations of its physico-chemical properties. After 120 minutes heating at 240°C the following was found: refractive index (1.476), free acidity (0.35%), K232 (2.87), K270 (3.71), antiradical activity (45.90% inhibition), total phenols (523 mg kg⁻¹), peroxide value (17.00 meq kg⁻¹), *p*-anisidine value (256.8) and Totox (271.7), all of which showed a constant deterioration. In relation to the use as a feedstock for bio-diesel production, after 120 minutes heating at 240°C the following was found: acid value 0.70 mg KOH g⁻¹ oil, iodine value 117.83 g I₂ 100 g⁻¹ oil, oil stability index 0.67 h, kinematic viscosity (at 40°C) 77.85 mm² s⁻¹, higher heating value 39.86 MJ kg⁻¹, density 933.34 kg/m³ and cetane number 67.04. The parameters studied in this work were influenced, in different ways, by the applied variables. Heating temperature between 180 and 210°C and 120 min heating duration were found to be the most appropriate conditions for sunflower seed oil both from the deep frying point of view and from a subsequent use as feedstock for bio-diesel production. In light of the vegetable oils' International standards for an edible use and for a bio-diesel production, findings of this work can be used to set heating temperature and heating duration to preserve as long possible the physico-chemical properties of a low oleic sunflower seed oil for both its edible use as a fat during cooking and for its re-use after frying.

Key words: fatty acid methyl esters, international standard, mono-alkyl esters, renewable energy, vegetable oil quality standard

1 Introduction

Sunflower seed oil (SSO) is the fourth vegetable oil by quantity produced in the world. In the 2014-2015 crop year, 14.91 million metric tons was produced, i.e. 3 times more than peanut oil and almost 6 times more than olive oil¹.

Frying is a rapid cooking method and fried food is appreciated for its flavour and consistence. Restaurant and food industries produce fried vegetable oil which can be considered as a free feedstock for bio-diesel production instead of a waste. The re-use of fried vegetable oil is also a good way to reduce environmental pollution both because the oil is not discarded and also because no energy is necessary to produce the bio-diesel feedstock but only to rectify it. SSO is one of the most widely used in frying because of its low price, in fact this is one of the most important parameters

when a vegetable oil is chosen for fast food cooking. In addition, nowadays there is a media campaign against the use of palm oil and a large part of Italian biscuits industries has changed palm oil with SSO. Deep frying implies the total immersion of a food in a fat at high temperature which is set in relation to the fat composition and the quantity and dimension of food. Frying temperature is generally higher than 185°C even if in the fast-foods, frying apparatus are not always equipped with a precise thermometer but with knob to regulate 4-5 different heating positions. In light of our experience, usually frying temperature ranges between 195-200°C before to insert food in the fat and between 185-190°C when the food is just immersed in the hot fat. In addition, 180-200°C is also the temperature to which oven is set for the common home food cooking. During high temperature treatment modifications and deteriorations in the

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Accepted June 8, 2017 (received for review May 5, 2017)

Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online

<http://www.jstage.jst.go.jp/browse/jos/> <http://mc.manuscriptcentral.com/jjocs>

physicochemical properties of a vegetable oil take place both for its edible use and for bio-diesel production. One of the most pernicious is oil oxidation which influences negatively both edible use and bio-diesel production and which is responsible for the variation of many parameters such as free acidity (FA), peroxide value (PV), *p*-anisidine value (*p*-AnV), total phenols, kinematic viscosity (KV), density (D), cetane number (CN). If the sunflower seed oil is to be used as a feedstock for bio-diesel production it must meet certain requirements such as: low acidity²⁾ and a low content of water and saturated triglycerides³⁾. Low acidity and low saturated fatty acids are also important in the case of the raw edible use of SSO. Therefore it is important to know how long a sunflower seed oil can be heated before deterioration. Excessive oil oxidation produces reactive oxygen species which can damage DNA and reduce repair capacity⁴⁾. For this reason, this work studies the influence of temperature and heating duration together with the variation in the physicochemical properties of the sunflower seed oil for edible use and for bio-diesel production and how many hours SSO can be used at a specific temperature for an edible use, and if it can be still used for a bio-fuel production.

2 EXPERIMENTAL

2.1 Vegetable oil regulations for edible use and quality standards for bio-diesel production and classification

The edible physico-chemical properties of sunflower seed oil are stated by the Codex Stan for named vegetable oils⁵⁾.

The DIN 51605:2010 is the German standard for 'rape-seed fuel for Diesel engines' requirements and contains the values required for a crude rapeseed vegetable oil to be used as a source for bio-diesel production; methods for oil testing are also listed⁶⁾.

The EN 14214:2014 lists the parameters that must be met to achieve the European quality standards for a bio-diesel, analytical methods are also listed⁷⁾.

The ASTM D6751 is the bio-diesel standard edited by the American Society for Testing and Materials specifying the parameters for B100 fuel. This standard identifies the parameters that pure bio-diesel (B100) must meet before being used as a pure fuel or being blended with petro-diesel⁸⁾.

2.2 Experimental design

Five 1L polyethylene bottles from the same lot, containing a labelled SSO were purchased from a supermarket.

The SSO from all the bottles was placed in a glass container and the SSO was stirred at room temperature for 10 minutes.

Twelve 100 g aliquots were placed in pyrex containers

and were heated at 180°C: three for 15 min, three for 30 min, three for 60 min and three for 120 min. The same heating times were repeated for a further 24 aliquots: twelve at 210°C and twelve at 240°C.

At the end of heating, heated sunflower seed oil (H-SSO) was cooled to room temperature and stored in amber glass bottles (100 mL) until analyses which were conducted within 2 hours from cooling.

2.3 Chemicals

All reagents for analysis type, for spectrophotometry type and for gas-chromatographic type were from Carlo Erba (Milan, Italy). All standards were from Sigma-Aldrich (St. Louis, MO, USA).

2.4 Analyses

2.4.1 Refractive index

Refractive index (RI) was determined at 20°C by an Abbe refractometer, after zero setting with bi-deionised water, the AOAC, 921.08 method was applied⁹⁾.

2.4.2 Free Acidity

FA (g oleic acid 100 g⁻¹) was determined by titration of the oil with a NaOH 0.1 N solution¹⁰⁾.

2.4.3 Spectrophotometric indexes

K232, K266, K270, K274 and ΔK were obtained after oil dilution in cyclohexane (1% w/v solution). The absorbance was measured in a glass quartz cuvette (1 cm) at 232 nm, 266 nm, 270 nm and 274 nm by a Perkin Elmer instrument, model Lambda 2¹⁰⁾.

2.4.4 Antiradical Activity

The antiradical activity (AA) was determined as suggested by Kalantzakis *et al.*¹¹⁾ and modified by Giuffrè *et al.*¹²⁾. In brief, a freshly prepared DPPH· solution was dissolved with ethyl acetate and sunflower oil. The absorbance of this solution was read at 515 nm with an Agilent spectrophotometer, model 8453, Santa Clara, CA, USA). Data were expressed as percentage of inhibition.

2.4.5 Total phenols

The total phenols (mg kg⁻¹) were determined by the Folin-Ciocalteu colourimetric procedure with the method proposed by Singleton *et al.*¹³⁾ and adapted by Giuffrè *et al.*¹⁴⁾.

2.4.6 *p*-Anisidine Value

A SSO or H-SSO/iso-octane solution was placed to react in acetic acid with *p*-anisidine, afterwards the absorbance was spectrophotometrically determined in a Perkin Elmer instrument, model Lambda 2¹⁵⁾.

2.4.7 Totox index

This was calculated with the following formula: *p*-AnV + 2PV.

2.4.8 FAMES

The fatty acids were transformed into their methyl esters (FAME) with KOH in methanol at room temperature by the procedure proposed by Consleg, annex XB method

A¹⁰). Gas chromatographic conditions were previously described¹⁶).

2.4.9 Acid Value

For the acid value (AV) determination The oil was dissolved in an ethanol/ether solution (1:1) and an acid-base titration was conducted by KOH (0.1 N), results were expressed as mg KOH g⁻¹ using the AOAC 969.17 method¹⁷).

2.4.10 Peroxide Value

The oil was dissolved in a chloroform/acetic acid solution (2:3) and titration was carried out by sodium thiosulfate in water (0.01 N), results were expressed as meq O₂ kg⁻¹¹⁰).

2.4.11 Iodine Value

The iodine value (IV) determination is based on the titration of the liberated iodine through the potassium iodide from the excess solution of unreacted monochloride, with a solution of 0.1N thiosulphate, result was expressed as g I₂ 100 g⁻¹¹⁰).

2.4.12 Oil Stability Index

A Rancimat model 679 (Metrohm, Switzerland) was used to determine the oil stability index (OSI). A 3 g aliquot of oil was weighed and heated at 110°C. A 10L h⁻¹ air flow was directed into the oil and the oxidative compounds were carried out into 60 mL of bi-deionised water. Data were expressed as hours of oxidation resistance.

2.4.13 Kinematic Viscosity

This was determined as suggested by the method NGD¹⁵), using an Ubbelohde viscometer at 30-40-50°C (mm²s⁻¹).

2.4.14 Higher Heating Value

The method modified by Giuffrè *et al.*¹⁸) was used. In brief, 1 g of oil was placed into a 1 g pellet of pressed cellulose before being burned and the higher heating value (HHV) was determined. Thereafter a 1 g pellet of pressed cellulose was burned and the HHV was determined again. The HHV of SSO and H-SSO was calculated by the difference between the HHV of the value determined with and without oil. Data were expressed as MJ kg⁻¹.

2.4.15 Estimated Higher Heating Value

HHV was found to be related to the KV. The higher the KV, the higher the HHV (regression coefficient for a vegetable oil, r = 0.9435). Estimated higher heating value (EHHV) was calculated by the formula 0.0317 KV + 38.053¹⁹) and the KV was measured at 40°C. Data were expressed as MJ kg⁻¹.

2.4.16 Density

D was determined with the method suggested by AOAC 920.212⁹), with a glass pycnometer (kg/m³).

2.4.17 Cetane Number

FAMES and CN are co-related and CN can be predicted as the product of the experimental CN of a FAME and the sum of its molar fraction as suggested by other Authors^{12, 20-25}).

2.5 Statistical analysis

Means of analyses in triplicate and standard deviation were calculated by the Microsoft Excel software (2010

version). Analysis of variance (one-way ANOVA) was performed by SPSS software version 17.0 for Windows (SPSS Inc., Chicago, IL, U.S.A.), using the Tukey test and the significance level was set at $p < 0.05$. The effect of temperature and heating duration were analysed by a two-way ANOVA by SPSS software version 17.0 for Windows (SPSS Inc., Chicago, IL, U.S.A.).

3 RESULTS AND DISCUSSION

3.1 Refractive Index

The refractive phenomenon that a ray of light undergoes, when passes from one medium to another, is quantitatively determined by a number which is called the refractive index, relative to the two means, in this case, air and SSO. The higher the RI, the more pronounced is the phenomenon of refraction. Temperature very highly significantly influenced the RI ($p < 0.001$), more than heating time ($p < 0.01$), and more than the combination of the two applied variables ($p < 0.05$), (Table 2). During heating the RI increased constantly from 1.472 of SSO to the significantly highest values found at 240°C (1.475-1.476). These data are in agreement with Manral *et al.*²⁶) who found a constant RI increase in sunflower seed oil used to fry fish.

3.2 Free Acidity

Heating determines the hydrolysis of triglycerides and produces free fatty acids. FA is one of the most important parameter to judge the edible quality of a vegetable oil. FA is lowered in a vegetable edible oil by rectification after oil extraction, for this reason SSO showed an initial very low FA. In the studied SSO and H-SSOs the combination of heating time and heating temperature were found to significantly influence FA (Table 2). In the worst conditions (240°C) FA of H-SSO was more than double than SSO, from 0.15% to 0.35% after two hours of heating and showed a constant increase during heating. After 120 min of SSO heating, the FA was 0.28% and 0.31% respectively at 180°C and 210°C (Table 1). Temperature did not significantly influence free acidity whereas heating time had a very significant influence ($p < 0.01$), (Table 2). FA was found to be correlated with p -AnV (0.7802), with TOTOX (0.7629) and with K270 (0.7162). FA of a vegetable oil used as a feedstock for bio-diesel production is a very important parameter because if FA is less than 1% the alkali catalytic method is used for trans-esterification, whereas if FA is higher than 1% the acid catalytic process is adopted²⁷). The experimental conditions studied in this work produced a H-SSO which requires the alkali catalytic method for bio-diesel conversion.

3.3 Spectrophotometric indexes

This analysis measures the absorption at typical wave-

Table 1 Physicochemical parameters of sunflower seed oil for edible use.

Temp. (°C)	Time (min)	RI	FA (%)	K232	K266	K270	K274	Δ K	AA (% inhibition)	Total phenols (mg kg ⁻¹)	PV (mEq O ₂ kg ⁻¹)	p-AnV	TOTOX
180°C	0	1.472 g	0.15 e	2.20 g	1.21 g	1.27 i	1.02 g	0.16 g	73.03 a	845 a	2.47 gh	2.17 h	7.09 e
	15	1.473 ef	0.21 d	3.05 def	1.94 f	1.94 h	1.57 f	0.18 fg	68.12 b	581 e	1.73 h	42.62 g	57.70 d
	30	1.472 fg	0.21 d	2.99 def	2.59 d	2.49 f	2.04 e	0.17 g	62.79 c	570 e	2.78 fgh	70.92 f	89.07 c
	60	1.473 efg	0.21 d	2.92 ef	2.89 c	3.08 cd	2.80 bc	0.23 def	48.41 e	483 f	3.75 ef	123.48 d	147.48 b
210°C	120	1.473 de	0.28 bc	2.90 ef	3.06 b	3.57 b	3.34 a	0.37 b	26.22 g	428 g	9.06 c	233.51 b	267.52 a
	15	1.473 de	0.14 e	3.72 a	1.98 f	1.98 h	1.65 f	0.17 g	74.91 a	835 a	2.47 gh	65.56 f	69.02 d
	30	1.472 efg	0.21 d	3.63 ab	2.39 e	2.37 fg	2.01 e	0.17 g	73.01 a	789 b	3.62 fg	87.27 e	92.83 c
	60	1.473 efg	0.25 cd	3.28 bcde	2.85 c	2.95 d	2.61 c	0.22 ef	56.29 d	719 c	4.36 e	151.48 c	158.98 b
240°C	120	1.474 d	0.31 ab	3.20 cdef	2.82 c	3.11 c	2.84 b	0.27 cd	36.72 f	662 d	7.45 d	256.79 a	274.91 a
	15	1.475 c	0.21 d	3.57 abc	2.28 e	2.28 g	1.89 e	0.19 fg	71.17 ab	739 c	7.54 b	65.27 f	70.21 d
	30	1.475 bc	0.21 d	3.34 bcd	2.78 c	2.77 e	2.24 d	0.26 de	67.44 b	716 c	9.07 c	87.23 e	94.46 c
	60	1.476 ab	0.28 bc	3.11 def	3.56 a	3.53 b	2.88 b	0.31 c	57.79 d	569 e	12.00 b	150.69 c	159.41 b
	120	1.476 a	0.35 a	2.87 f	3.63 a	3.71 a	2.86 b	0.47 a	45.90 e	523 f	17.00 a	256.80 a	271.70 a
Sign.		***	***	***	***	***	***	***	***	***	***	***	***

Means in the same column followed by a different letter are significantly different according to Tukey's test (***, $p < 0.001$).

Table 2 Sunflower seed oil as a food with significant differences.

Property	Temperature	Time	Temperature × Time
Refractive index	***	*	**
Free acidity (g oleic acid 100 g ⁻¹)	n.s.	**	***
K 232	**	*	*
K 266	**	***	***
K 270	**	***	***
K 274	n.s.	***	***
ΔK	*	**	***
AA (% inhibition)	*	***	***
Total phenols (mg kg ⁻¹)	***	***	**
Peroxide value (mEq O ₂ kg ⁻¹ oil)	***	**	***
p-Anisidine Value	***	***	n.s.
TOTOX index	**	***	n.s.

Two-way ANOVA experiment: temperature. time. temperature x time.

***, $p < 0.001$; **, $p < 0.01$; *, $p < 0.05$; n.s., not significant, $p < 0.05$.

Each result is calculated as the mean of three different replicates for each treatment.

lengths of conjugated dienes and trienes. The isolated double bonds and the non-conjugated double bond systems do not show the characteristic bands in the spectral region between 210 nm and 300 nm, whereas the conjugated dienes have a maximum absorbance at 232 nm, and conjugated trienes have a maximum absorbance at 270 nm. The rectification of the oil after extraction and the oxidative process cause an increase in absorbance at 232 nm and 270 nm. In the studied oils the lowest K232 value was found in the SSO, thereafter this index quickly increased after 15 min heating and decreased with heating time (Table 1). This could be due to the subsequent oxidative reaction to which the primary oxidation products are subjected. On

the contrary, the K270 increased constantly with time and temperature. The worst K270 index was found at 240°C after 120 min of heating. The Consolidated Text on the characteristics of olive oil¹⁰⁾ indicates 2.50 and 2.60 as the maximum absorbance values at 232 nm for an extra virgin and a virgin olive oil respectively; only SSO was below these limits whereas H-SSO exceeded these limits within 15 min of heating at 180°C. K270 always exceeded 1.10 of absorbance stated for a refined olive oil, the minimum value (1.27) was found in SSO. Both K232 and K270 indexes confirm findings of Casal *et al.*²⁸⁾ which found an initial increase and a subsequent decrease in K232 and constant increase in K270 during frying (9 hours) of a vegetable oil

based mostly on SSO.

3.4 Antiradical Activity

This test determines the antioxidant power by reacting the SSO and H-SSO with a DPPH solution and analysing the UV decrease of the peak of the radical at 515 nm. The antioxidant compounds transfer an atom of the hydrogen radical, causing a decolourisation of the solution from purple to yellow. In the studied samples, the percentage of inhibition decreased during heating but remained near the initial value for the first 30 mins. At 180°C and at 210°C the AA value decreased twice in 120 min heating at 240°C H-SSO i.e. 30% compared to SSO in the 120 min of heating (Table 1). The AA decrease was significantly influenced by temperature ($p < 0.05$) and very highly significantly influenced by heating time treatment ($p < 0.001$), (Table 2). AA had a low correlation with phenols (0.5589) and a good correlation with K270 (-0.6119), with PV (-0.7055) and with OSI (0.7442).

3.5 Total phenols

Phenols are among the most important antioxidants in a vegetable edible oil²⁹. As all the minor components of an oil they are related to many factors such as: the vegetable specie, the geographical area of production, the agronomical practices, the harvest date, the extraction system. In this study, the total phenolic content showed a constant decrease during heating and the worst result was found at 180°C. The best performance of the SSO after heating was at 210°C which had the lowest loss in phenols during heating: from 845 mg kg⁻¹ to 662 mg kg⁻¹ (Table 1). If data are considered from a relative point of view, one can see that the applied heating temperatures showed the following total phenolic decrease: 49.35% (180°C), 21.66% (210°C) and 38.10% (240°C). Both temperature and the heating time influenced negatively this parameter ($p < 0.001$), (Table 2).

3.6 Peroxide Value

Hydroperoxydes are unstable molecules and do not accumulate during frying but they decompose and form volatile compounds³⁰.

The Codex Standard indicates a maximum of 10 mEq O₂ kg⁻¹ oil for a refined edible vegetable oil. During heating the PV increased constantly from 2.47 meq O₂ kg⁻¹ oil in SSO to 9.06 mEq O₂ kg⁻¹ oil found in H-SSO after 120 min at 180°C (Table 1). H-SSO oil exceeded the Codex Standard limit only at 240°C and after 60 min and 120 min treatment: 12.00 and 17.00 mEq O₂ kg⁻¹ respectively (Tables 1 and 8). After 120 min heating, PV increased 3.7, 3.0 and 6.9 times when the SSO was at 180, 210 and 240°C (Table 1). Both temperature and heating time influenced very highly significantly the PV variation ($p < 0.001$), (Table 2). The PV trend is specific for each oil or fat.

There is an initial phase of PV increase and a successive phase of decrease in relation to the oil/fat physico-chemical composition, mainly antioxidant content and FAME composition influence this rate. Bensmira *et al.*³¹ heated a SSO for 30 min and found an increasing PV varying from 4, 9, 9.5 and 10.5 mEq O₂ kg⁻¹ when the SSO was treated at 25, 150, 180 and 200°C respectively; the same Authors found a lower PV when the SSO was incorporated with Lavender and Thyme.

3.7 *p*-Anisidine Value

The *p*-AnV is the level of aldehydes (2-alkenals) present in fatty substances, it is based on reactivity of the carbonyl group of the aldehydes with the amino group of the *p*-anisidine, which leads to the formation of a Schiff base. The *p*-AnV measured in an edible vegetable oil is considered to be acceptable when it is lower than 10³². Only SSO before heating was within this maximum limit (Tables 1 and 8). The heating process caused a fast increase of this parameter and the *p*-AnV was 42.62, 65.56 and 65.27 within 15 min of heating at 180, 210 and 240°C respectively (Table 1). The heating process produced a very highly significantly negative effect on the SSO and the *p*-AnV increased 108 times after 120 min at 180°C and 120 times after the same period at 240°C (Table 1). Both temperature and time of heating very highly significantly influenced the *p*-AnV (Table 2).

3.8 TOTOX index

TOTOX index describes the primary and secondary products of the oil oxidation³³ and informs about the past and actual oxidative state³⁴. At 180 and 210°C the TOTOX index increased mainly as a result of *p*-AnV because the high temperatures used in this experiment caused the spontaneous decomposition of hydroperoxides into volatile compounds and a reduced PV increase (Table 1). At 240°C the *p*-AnVs and the TOTOX index were similar to those found at 210°C whereas PV increased rapidly. At 240°C the TOTOX index was found to be more related to PV rather than *p*-AnV, whereas at 180°C and 210°C the TOTOX index was more related to the *p*-AnV. Time of heating showed the highest influence on this parameter ($p < 0.001$), the temperature highly significantly influenced TOTOX ($p < 0.01$) (Table 2). TOTOX index of SSO and H-SSO was found.

3.9 Fatty Acid Methyl Esters

FAME composition affect the edible properties of a vegetable oil. Oleic acid, essential fatty acids and UFA are among the most important parameters from the dietary point of view^{35, 36}. The complete FAME composition and the *cis*, *trans* functional groups are evaluated in deep-fat frying oils³⁷. Many types of SSO exist, as a result of their FAME composition. Two main SSO types can be distinguished on the basis of the high (70%)³⁸ or low (30-35%)

oleic acid content, and many other types having an oleic acid content between these two values of the total FAME content. The SSO studied in this work was a low oleic type. The two applied variables caused a variation in the FAME composition. In detail, the relative content of oleic acid (mono-unsaturated) increased during heating whereas the relative linoleic acid (di-unsaturated) content decreased under the same experimental conditions (Table 3). If the FAMEs are grouped in relation to their double bonds one can see that the sum of SFAs increased as a percentage with heating time and the sum of UFAs decreased (Table 4). The UFA decrease was due to the PUFA decrease because MUFAs increased. PUFAs are linoleic and linolenic acids, two essential fatty acids and their total content decreased after 120 min of heating from 56.24 to 53.29% at 180°C, to 52.49% at 210°C and to 50.91% at 240°C ($p <$

0.001). As a consequence, the PUFAs/MUFAs ratio increased during heating ($p < 0.001$), (Table 4). The 18:2/16:0 ratio can be used as an indicator of oil degradation; this ratio showed a tendency to decline during heating, according to Marinova *et al.*³⁹⁾, this trend was more evident at 240°C (Table 4). The two-way ANOVA analysis showed that the variation in composition found in the FAMEs was due to the heating time, whereas the temperature was not significant in the large part of cases (Table 5).

A very low content of α -linolenic acid was found in the SSO, which is the precursor of docosahexanoic acid, a long chained PUFA having a protective activity against dementia, Alzheimer's disease and the chronic daily headache³⁵⁾. However, a high linolenic acid content is not advisable in a vegetable oil for frying use because the three double bonds

Table 3 Single fatty acid methyl esters of sunflower seed oil (% m/m) .

Temp. (°C)	Time (min)	C14:0	C16:0	C16:1	C17:0	C17:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1	C24:0
180°C	0	0.07 bc	6.86 d	0.09 b	0.03 d	0.03 a	3.20 e	32.47 ef	56.18 a	0.06 a	0.17 c	0.15 f	0.48 c	0.05 f	0.16 ef
	15	0.07 bc	6.60 def	0.09 ab	0.05 bc	0.03 a	3.34 cde	32.60 ef	55.78 b	0.05 ab	0.20 abc	0.17 ef	0.58 abc	0.22 b	0.19 def
	30	0.08 abc	6.97 bc	0.09 ab	0.05 bcd	0.02 a	3.47 abcd	32.37 f	55.77 b	0.06 ab	0.18 bc	0.16 ef	0.51 bc	0.12 cd	0.14 f
	60	0.07 bc	6.85 cde	0.09 ab	0.04 cd	0.03 a	3.39 bcde	33.40 d	54.84 d	0.05 ab	0.20 abc	0.18 ef	0.60 abc	0.05 ef	0.19 def
210°C	120	0.07 bc	7.27 ab	0.09 ab	0.07 a	0.03 a	3.58 abc	34.03 c	53.25 e	0.04 bc	0.22 ab	0.19 ef	0.61 abc	0.15 c	0.38 ab
	15	0.07 bc	6.76 bcde	0.09 ab	0.05 bc	0.02 a	3.35 cde	32.57 ef	55.78 b	0.06 ab	0.21 abc	0.18 ef	0.56 abc	0.10 de	0.19 def
	30	0.07 bc	6.69 bcde	0.09 ab	0.05 bcd	0.02 a	3.36 de	32.76 ef	55.71 b	0.06 ab	0.20 abc	0.18 ef	0.58 bc	0.05 ef	0.16 def
	60	0.08 ab	6.79 bcde	0.09 ab	0.00 e	0.00 b	3.48 abcd	33.50 d	54.60 d	0.05 ab	0.23 a	0.23 cd	0.63 ab	0.02 f	0.28 c
240°C	120	0.09 a	7.47 a	0.10 ab	0.00 e	0.00 b	3.65 ab	34.66 b	52.44 f	0.04 bc	0.22 ab	0.27 c	0.63 ab	0.04 f	0.38 abc
	15	0.07 bc	6.51 ef	0.08 ab	0.05 bc	0.03 a	3.35 cde	32.58 ef	55.77 b	0.05ab	0.19 abc	0.20 de	0.56 abc	0.28 a	0.24 cde
	30	0.07 bc	6.80 bcde	0.09 ab	0.07 a	0.03 a	3.25 de	32.83 e	55.27 c	0.04 bc	0.19 abc	0.24 cd	0.53 abc	0.29 a	0.29 bcd
	60	0.06 c	6.44 b	0.08 b	0.03 d	0.02 a	3.46 cde	33.70 cd	54.49 d	0.03 cd	0.22 ab	0.35 b	0.65 a	0.14 c	0.31 bc
	120	0.08 ab	7.33 a	0.10 a	0.06 ab	0.03 a	3.72 ab	35.69 a	50.89 g	0.02 d	0.23 a	0.58 a	0.66 a	0.15 c	0.44 a
Sign.		**	***	*	***	***	***	***	***	***	***	***	**	***	***

Means in the same column followed by a different letter are significantly different according to Tukey's test (*, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$).

Table 4 Fatty acid methyl ester elaboration data of sunflower seed oil.

Temp. (°C)	Time (min)	SFA (%)	UFA (%)	MUFA (%)	PUFA (%)	UFA / SFA	C18:1/ C16:0	C18:1/ C18:2	C18:2/ C18:3	C18:2/ C16:0	MUFA/ PUFA	SFA/ PUFA	PUFA/ MUFA
180°C	0	10.99 e	89.01 a	32.77 f	56.24 a	8.10 a	4.73 bcd	0.58 f	891.31 d	8.19 abc	0.58 i	0.20 i	1.72 a
	15	11.04 de	88.96 ab	33.12 ef	55.84 b	8.06 ab	4.94 bc	0.58 ef	1048.51 cd	8.45 ab	0.59 hi	0.20 ghi	1.69 b
	30	11.41 bc	88.59 cd	32.76 f	55.83 b	7.77 cd	4.64 d	0.58 f	987.27 cd	8.00 c	0.59 hi	0.20 defg	1.70 ab
	60	11.34 bcd	88.66 bcd	33.77 d	54.89 d	7.82 bcd	4.88 bcd	0.61 d	1091.20 cd	8.00 c	0.62 ef	0.21 de	1.63 cd
210°C	120	12.21 a	87.79 e	34.50 c	53.29 f	7.19 e	4.68 cd	0.64 c	1236.40 c	7.33 d	0.65 c	0.23 c	1.54 f
	15	11.20 bcd	88.80 abcd	32.96 f	55.84 b	7.93 abcd	4.82 bcd	0.58 ef	987.98 cd	8.25 abc	0.59 hi	0.20 eg	1.69 ab
	30	11.11 cde	88.89 abc	33.12 ef	55.77 b	8.00 abc	4.90 bcd	0.59 ef	988.23 cd	8.33 abc	0.59 h	0.20 ghi	1.68 b
	60	11.51 b	88.49 d	33.84 d	54.65 de	7.69 d	4.93 bc	0.61 d	1030.42 cd	8.04 c	0.62 de	0.21 d	1.61 de
240°C	120	12.45 a	87.55 e	35.06 b	52.49 g	7.03 e	4.64 d	0.66 b	1222.57 c	7.02 d	0.67 b	0.24 b	1.50 g
	15	10.99 e	89.01 a	33.18 ef	55.83 b	8.10 a	5.00 ab	0.58 ef	1052.17 cd	8.56 a	0.59 gh	0.20 hi	1.68 b
	30	11.21 bcde	88.79 abcd	33.48 de	55.32 c	7.92 abcd	4.83 bcd	0.59 e	1288.10 c	8.13 bc	0.61 fg	0.20 efgh	1.65 c
	60	11.19 bcde	88.81 abcd	34.30 c	54.52 e	7.94 abcd	5.23 a	0.62 d	1815.22 b	8.46 ab	0.63 d	0.21 def	1.59 e
	120	12.54 a	87.46 e	36.55 a	50.91 h	6.98 e	4.87 bcd	0.70 a	2543.50 a	6.94 d	0.72 a	0.25 a	1.39 h
Sign.		***	***	***	***	***	***	***	***	***	***	***	***

Means in the same column followed by a different letter are significantly different according to Tukey's test (***, $p < 0.001$).

Table 5 Fatty acid methyl esters of sunflower seed oil with significant differences.

Fatty Acid Methyl Esters	Temperature	Time	Temperature × Time
Myristic (14:0)	n.s.	n.s.	* *
Palmitic (16:0)	n.s.	* *	* *
Palmitoleic (16:1)	n.s.	n.s.	n.s.
Heptadecanoic (17:0)	n.s.	n.s.	* * *
Heptadecenoic (17:1)	n.s.	n.s.	* * *
Stearic (18:0)	*	*	n.s.
Oleic (18:1)	n.s.	* * *	* * *
Linoleic (18:2)	n.s.	* * *	* * *
Linolenic (18:3)	*	*	* *
Arachidic (20:0)	n.s.	*	n.s.
Eicosenoic (20:1)	n.s.	n.s.	* * *
Behenic (22:0)	n.s.	* *	n.s.
Docosenoic (22:1)	* *	*	* * *
Lignoceric (24:0)	*	* * *	*
SFA	n.s.	* * *	* *
UFA	n.s.	* * *	* * *
MUFA	n.s.	* *	* * *
PUFA	n.s.	* *	* * *
PUFA/MUFA	n.s.	* * *	* * *
UFA/SFA	n.s.	* * *	* * *
MUFA/PUFA	n.s.	* * *	* * *
SFA/PUFA	n.s.	* * *	* * *
Oleic/Linoleic	n.s.	* * *	* * *
Oleic/Palmitic	n.s.	* * *	* * *
Linoleic/Palmitic	n.s.	* * *	* * *
Linoleic/Linolenic	n.s.	n.s.	* * *

Two-way ANOVA experiment: temperature. time. temperature x time.
 ***, $p < 0.001$; **, $p < 0.01$; *, $p < 0.05$; n.s., not significant, $p > 0.05$. Each result is calculated as the mean of three different replicates for each treatment.

are highly susceptible to oxidation.

If the studied oil is considered to be a source for bio-diesel production, the linolenic acid methyl ester was always well within the 12% maximum stated by the EN 14214 Biodiesel Quality Standard⁷⁾ (Table 3). The decrease in linoleic acid and the increase in oleic acid was related to the increase in KV, the lower the linoleic acid, the higher the KV⁴⁰⁾. FAMES of SSO and H-SSO always were in the range of the edible and bio-diesel International standards (Table 8).

3.10 Acid Value

A low AV is required when a vegetable oil is used as a

source for bio-diesel production for which the homogenous basic transesterification is commonly used. Transesterification shows a very fast kinetic reaction but increases the saponification reaction and the loss in bio-diesel yield production^{3,41)}.

In our study, the AV of SSO was 0.31 mg KOH g⁻¹ oil and increased constantly during heating. It was almost double (0.56 mg KOH g oil⁻¹) after 120 min heating at 180°C and it was double after 120 min heating at 210°C. The increase was more than double (0.70 mg KOH g oil⁻¹) for H-SSO after 120 min at 240°C (Table 6).

The Codex Standard indicates 0.6 mg KOH g⁻¹ of refined edible vegetable oil as the maximum limit⁵⁾. The studied

Table 6 Physicochemical parameters of sunflower seed oil for bio-diesel production.

Temp. (°C)	Time (min)	AV (mg KOH g ⁻¹)	IV (g I ₂ 100 g ⁻¹)	OSI (h)	KV (30°C) (mm ² s ⁻¹)	KV (40°C) (mm ² s ⁻¹)	KV (50°C) (mm ² s ⁻¹)	HHV (MJ kg ⁻¹)	EHHV (MJ kg ⁻¹)	D (kg/m ³)	CN
180°C	0	0.31 f	132.82 a	3.77 a	50.27 h	37.72 h	29.71 i	37.07 h	38.31 a	918.44 e	53.78 b
	15	0.42 e	130.04 ab	2.37 c	50.75 h	38.01 h	29.90 i	37.34 g	38.31 ab	918.96 e	53.27 b
	30	0.42 e	126.19 cde	1.93 ef	52.25 g	37.66 h	29.10 i	38.06 ef	38.30 cd	918.51 e	59.39 ab
	60	0.42 e	124.06 def	1.80 f	56.92 f	44.33 e	34.59 f	38.22 de	38.30 bcd	919.72 e	56.34 ab
210°C	120	0.56 bc	122.30 f	0.13 h	67.24 c	52.44 c	41.16 c	38.59 c	38.28 e	921.88 d	59.65 ab
	15	0.33 f	126.79 bcde	2.20 cd	51.05 h	39.68 g	31.45 h	37.11 gh	38.30 abcd	927.51 b	56.19 ab
	30	0.42 e	126.06 cdef	2.10 de	52.97 g	41.91 f	31.05 h	37.94 f	38.31 abc	928.17 b	56.30 ab
	60	0.62 cd	126.44 bcde	1.93 ef	57.63 f	43.93 e	33.61 g	38.43 cd	38.30 d	928.67 b	56.39 ab
240°C	120	0.62 ab	123.31 ef	0.13 h	72.74 b	54.09 b	42.51 b	39.27 b	38.28 e	932.88 a	62.64 ab
	15	0.42 d	128.49 bc	3.67 b	63.19 d	46.80 d	36.49 e	38.02 ef	38.31 a	924.34 c	56.31 ab
	30	0.42 d	127.99 bc	2.77 b	60.08 e	46.95 d	37.71 d	38.49 c	38.30 abcd	924.97 c	56.42 ab
	60	0.56 bc	127.56 bcd	2.27 cd	62.76 d	47.27 d	37.03 de	39.45 b	38.30 abcd	927.54 b	62.61 ab
	120	0.70 a	117.83 g	0.67 g	106.71 a	77.85 a	63.38 a	39.86 a	38.27 e	933.94 a	67.04 a
	Sign.	***	***	***	***	***	***	***	***	***	*

Means in the same column followed by a different letter are significantly different according to Tukey's test (*, $p < 0.05$; ***, $p < 0.001$).

Table 7 Sunflower seed oil for bio-diesel production with significant differences.

Property	Temperature	Time	Temperature × Time
Acid value (mg KOH g ⁻¹)	n.s.	* *	* * *
Oil Stability Index (h)	* *	*	* * *
Iodine Value (g I ₂ 100 g ⁻¹)	n.s.	*	* * *
Kinematic Viscosity 30°C (mm ² s ⁻¹)	n.s.	*	* * *
Kinematic Viscosity 40°C (mm ² s ⁻¹)	n.s.	*	* * *
Kinematic Viscosity 50°C (mm ² s ⁻¹)	*	*	* * *
Higher Heating Value (MJ kg ⁻¹)	* *	* * *	* * *
Estimated Higher Heating Value (MJ kg ⁻¹)	n.s.	* * *	* * *
Density (kg/m ³)	* * *	*	* * *
Cetane Number	n.s.	*	n.s.

Two-way ANOVA experiment: temperature, time temperature x time.

***, $p < 0.001$; **, $p < 0.01$; *, $p < 0.05$; n.s., not significant, $p > 0.05$.

Each result is calculated as the mean of three different replicates for each treatment.

oils exceed this value only after 120 min heating at 240°C and after 60 min heating at 210°C (Tables 6 and 8). A low acidity is related to an easier digestibility of the H-SSO. If the H-SSO is considered as a source for bio-diesel production, heating never caused the AV to exceed the 2.0 mg KOH g⁻¹ set as the maximum limit stated by the DIN 51605 for a rapeseed oil to be used for bio-diesel production⁶). In bio-diesel production a high AV causes a loss in quantity of bio-diesel produced and an increased cost of production. The combination of temperature and heating time showed the highest influence on AV ($p < 0.001$), (Table 7). AV was correlated with KV40 (0.6699), with UFA (-0.6041), with C18:2 (-0.7768) and with PUFA (-0.7777).

3.11 Iodine Value

IV gives information about the amount of unsaturations of a fat. IV is almost the same in fat/oil and in their corresponding methyl esters⁴²). A high bio-diesel unsaturation degree can affect the polymerization of glycerides and the oxidation stability and form deposits in the injectors of the diesel engines⁴³). Both in deep frying and in bio-diesel production, a low IV (i.e. a low From the edible point of view, the Codex Standard for vegetable oils states a range of 78-90 g I₂ 100 g⁻¹ of oil for high oleic type SSO⁵); a range of 94-122 g I₂ 100g⁻¹ of oil for mid oleic type SSO and a range of 118-141 g I₂ 100 g⁻¹ of oil for low oleic type SSO. The heating treatment applied to SSO in this work produced a continuous decrease in IV from the initial 132.82. The lowest IV (117.83) was found when the H-SSO was subject-

ed to the worst stress (240°C - 120 min), this value was below the minimum request for an edible SSO (Tables 6 and 8). The IV decrease could be due to the formation of volatile compounds and to the formation of polymers from double bonded fatty acids. The decrease in IV of the SSO and of the H-SSOs was in agreement with the linoleic acid (%) and PUFA (%) decrease and with the SFA (%) increase (Table 4). From the bio-diesel production point of view, the DIN 51605 states a maximum of 125 g I₂ 100g⁻¹ of oil⁽⁶⁾ and the heating treatment did not worsen this parameter (Table 8). The two-way ANOVA analysis showed that temperature did not influence the IV; heating time showed a significant effect ($p < 0.05$) and the combination of temperature and time had a very highly significant effect ($p < 0.001$), (Table 7). Similar data for IV decrement were found in fried SSO⁽²⁶⁾.

3.12 Oil Stability Index

Rancimat instrument accelerates the natural processes of oil ageing by exposing the sample to a high temperature in the presence of a high air flow and determines the time required to start the oxidation induction time. The SSO showed a low OSI already before heating (3.77 h) and the heating treatment caused a continuous decrease in less than 1 h of resistance for H-SSO after 120 min of heating (Tables 6 and 8). Temperature highly significantly influenced OSI ($p < 0.01$), heating time showed a significant effect ($p < 0.05$), and the combination of the two variables had a very highly significant effect ($p < 0.001$), (Table 7). The DIN 51605 states a minimum of 6 h for a rapeseed oil to be used for bio-diesel production⁽⁶⁾, for this reason if H-SSO is to be used for bio-fuel production, the OSI has to be improved. Marinova *et al.*⁽³⁹⁾ compared the OSI of SSO with other vegetable edible oils such as: corn, grape, pomace olive, soybean and found SSO to have the lowest resistance to oxidative induced degradation. Findings of this analysis confirm that SSO, particularly the low oleic type, do not have to be heated for long time.

3.13 Kinematic Viscosity

The KV of a fried vegetable oil was found to influence the oil content in fried food: the higher the viscosity, the more oil absorbed by the fried food⁽⁴⁴⁾, therefore it is advisable to fry below 210°C, in fact, the KV increase measured at 40°C from SSO (37.72 mm²/s) to H-SSO in 120 min at 210°C (54.09 mm² s⁻¹) was 30.26%, whereas the KV increase at 240°C after 120 min (77.85 mm² s⁻¹) was 51.42%.

KV of a bio-fuel is related to the KV of the vegetable oil from which bio-fuel has been produced. A high KV causes the formation of larger droplet size, the formation of polymers⁽⁴⁵⁾ and the possible formation of deposits in the engine⁽²⁵⁾. The DIN 51605 states a maximum of 36 mm² s⁻¹ when the KV is determined at 40°C⁽⁶⁾. SSO showed a KV of 37.72 and this value increased with time, consequently

SSO and H-SSO were always above the maximum stated by the actual regulation (Table 8). The two-way ANOVA analysis showed that temperature did not significantly influence KV ($p > 0.05$), whereas heating time had a significant effect ($p < 0.05$); the combined temperature and time showed a very highly significant effect ($p < 0.001$), (Table 7). The longer the time of heating of SSO, the worse the KV of the H-SSO as a source for bio-diesel production.

3.14 Higher Heating Value and Estimated Higher Heating Value

Lower heating value (LHV) is the quantity of heat produced during the combustion of a vegetable oil which assumes the latent heat of vapourisation of water in the reaction products is not recovered. HHV is the quantity of heat produced by the combustion of one gram of vegetable oil once the combusted products have returned to their initial temperature (before combustion), which considers the latent heat of vapourisation of water in the combustion products. The HHV of methyl ester is lower than that of diesel because of its higher O₂ content^(43, 46). As SSO is extracted by an apolar solvent, it does not contain water and HHV can be considered very similar to LHV. The German standard DIN 51605 indicates 36 MJ/kg as a minimum LHV for a rapeseed oil⁽⁶⁾. The studied SSO and H-SSOs showed an HHV and EHHV always above this minimum value (Tables 6 and 8) and the heating treatment did not reduce the potential of SSO for bio-fuel production. HHV increased with the increase of temperature ($p < 0.01$) and increased with the time of heating ($p < 0.001$), (Table 7).

3.15 Density

The density of a vegetable oil influences the density of a bio-fuel. RD is negatively related to the molecular weight of fatty acids and it is positively related to the degree of unsaturations⁽⁴⁷⁾. The German DIN 51605 states a minimum RD of 910 and a maximum of 925 kg/m³ for a rapeseed oil⁽⁶⁾. The SSO and the H-SSO were within this range at the lowest temperature applied; thereafter the RD exceeded the maximum limit at 210°C and at 240°C after 60 and 120 min of heating (Tables 6 and 8). D increased constantly with heating duration, the same happened with the increase in temperature. The temperature ($p < 0.001$) influenced more significantly the D, than the time of heating ($p < 0.05$), (Table 7). Anjum *et al.*⁽⁴⁸⁾ in SSO extracted from roasted seeds exposed to a different roasting duration, found an increasing trend in D, in fact, the longer the roasting, the higher the SSO D.

3.16 Cetane Number

The CN is positively related to chain length and negatively related to number of double bonds of fatty acids⁽⁴⁹⁾. It is negatively related to the NO_x emissions⁽⁵⁰⁾, with particulate emissions⁽⁵¹⁾ and with ignition delay⁽⁵²⁾. A high CN facili-

tates the cold start of an engine and reduces the white smoke production⁵³). During heating the CN increased from 53.78 of SSO to 59.65 of H-SSO (180°C - 120 min), to 62.64 of H-SSO (210°C - 120 min) and to 67.04 of H-SSO (240°C - 120 min), (Table 6). No H-SSO was always above the minimum 51 CN stated by the European standard for bio-diesel (EN 14214:2014) and above the minimum 47 CN stated by the American specification for bio-diesel (ASTM D 6751), (Tables 6 and 8). CN was significantly influenced by heating time ($p < 0.05$) and not significantly influenced by temperature ($p > 0.05$), (Table 7).

4 CONCLUSIONS

The high temperature and the heating time influence negatively and progressively all the physicochemical and the nutritional properties of sunflower seed oil, however, the peroxide value after 120 minutes at 240°C, remained below the maximum stated by the Codex Alimentarius for an edible vegetable oil. After 120 min heating at 240°C the sunflower seed oil maintains the acid value, the iodine value, the higher heating value required by the German specifications DIN51605 for rapeseed oil as a source for bio-diesel production, and also maintains the cetane number required by the European EN 14214 and by the American ASTM 6751 bio-diesel quality standards. Findings of this work showed that the most appropriate heating temperature for low oleic sunflower seed oil is ranging between 180 and 210°C and that this oil can be heated for 120 min long because in these conditions it shows a degradation compatible both with its use as a food and for its subsequent use as a feedstock for bio-diesel production.

AKNOWLEDGEMENTS

This research was supported by PON03PE_00090_1 fund: 'Process and product innovations in baked products and confectionary food chain'.

Conflict of interest

The authors declare no conflict of interest.

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