Chemical refining of sunflower oil: effect on oil stability, total tocopherol, free fatty acids and colour

TALAL ELSIR MOHAMMED ALHASSAN SULIMAN*,
School of Food Science and Technology, Jiangnan University, Wuxi- 214122, Jiangsu, China,
max244g@hotmail.com

JIANG JIANG,
Doctor, School of Food Science and Technology, Jiangnan University, Wuxi- 214122, Jiangsu, China,
jiangjiang0909@gmail.com

YUANFA LIU,
Professor, School of Food Science and Technology, Jiangnan University, Wuxi- 214122, Jiangsu, China,
foodscilyf@163.com

Abstract

The effect of chemical refining on oil stability index of sunflower oil and other quality attributes free fatty acids, total tocopherols, colour and was investigated. The results revealed that all these quality attributes are decreased during the chemical refining process, except oil stability which was decreased during neutralizing, bleaching and winterizing step, however it was increased in deodorizing step. Deodorization step has a significant effect on all of these quality attributes. Results of this study indicated that, most part of the tocopherols are wasted during deodorizing step. Therefore, oil stability not always depends on the content of tocopherol, however the proper concentration of nutritionists, industrialists, and manufacturers are also needed for the necessary improvements in processing technology to avoid the major loss of tocopherols and to increase the shelf life, as well as the, nutritive value of processed oil.

Keywords: Sunflower oil; Chemical refining; Quality attributes; Oil stability; Tocopherols; Free Fatty Acids.

Introduction

Animal fats and vegetable oils are consumed because of the content of triacylglycerols, but they do not consist only of triacylglycerols, at least when they are obtained from natural materials using industrial processing. They also contain several groups of accompany in substances which may be useful as nutrients, but at the same time they are either objectionable from the point of view of sensory value (they affect the taste, odour, colour, and appearance) or from the point of view of functional properties [Comlik and Pokory, (2000)].

Sunflower oil is characterized by its high content of tocopherols (up to 935ppm) higher than those of other oils such as soybean and peanut to mention a few. It is considered to have the highest stability due to its high content in natural antioxidants [Shahidi, (2005); Bramley et al., (2000)]. Crude sunflower oil obtained by extraction is not edible, because, it contains many undesirable materials, such as free fatty acids, colour pigments, minerals, gums, waxes, phosphates, and odoriferous materials, which must be removed to yield a stable product with a bland or pleasant taste. Thus, in modern society, consumers can not use crude oils directly without proper processing due to the unacceptable colour and odour. This has led to, efficient industrial processing which involves removing these unpleasant impurities with the least possible effect on the desired components (tocopherols, phenols, sterols) with the minimum losses of oil [Verhe´ et al., (2006)]. The elimination of free fatty acids from oils by distillation (steam refining) without using alkali is known as physical refining and consists of degumming, bleaching, winterizing and, finally, deodorizing (steam distillation) stages. Chemical refining includes degumming, neutralizing, bleaching, winterizing and deodorizing stages [Tasan and Demirci, (2005); Dumont and Narine, (2007)]. On the other hand winterization stage is not required for all oils for example soybean oil because it is not contains waxes. Physical refining has several advantages compared to the chemical refining. The process is a more economical (improved yield, lower investment cost, less chemicals used) and an environmentally friendly process (no soap stock to be treated) but has more effect on oil desirable components and oil stability [Kovari et al., (2000)]. While the chemical refining (decreased yield, higher investment cost, high chemicals used and higher waste but has less effect on oil desirable components an oil stability.

Tocopherols (α, β, γ, and δ) are potent natural antioxidants that prevent the oils from rancidity during storage and, thus, increasing the shelf life of edible oils [Aluyor and Jesu, (2008)]. Additionally, tocopherols have an important role in the prevention of many types of diseases (such as Parkinson’s disease, ataxia with vitamin E deficiency, and various cancers, etc.) [Bramley et al., (2000)]. Also, they enhance the body’s immune system
The signal was measured at wavelengths 295 nm [Sanchez et al., (2002)]. A mixture of n-hexane-isopropanol (98.5:1.5 v/v) at a flow rate of 0.15 mL/min was used as a mobile phase. Lichrospher Si-60 column (250×2.0, 5 µm, Hanbon Science and Technology, China), was used for separation. A chromatographic system consisted of a Waters 1525 binary pump (Waters, Milford, USA), 40 µL injection loop, and photodiode Array Detector (Waters, USA) was used to measure tocopherols content (VE). Filtered, cleaned, dried air was allowed to bubble through the hot oil at flow rate of 20 l/hr. The OSIs were collected from each step (de gumming and neutralizing, bleaching, winterizing and deodorization), and stored at 4°C in dark glass containers and purged with nitrogen gas after filling to prevent oxidation.

**Free fatty acids determination**
Free fatty acids were measured using the titration method, of crude and refined oil with a sodium hydroxide solution (phenolphthalein as indicator), suitably diluted with an ethyl alcohol–ethyl ether mix. Results are expressed as % oleic acid [Martinic et al., (2008)].

**Oxidative oil index determination**
The oxidative stability of chemical refined sunflower oil was determined in accordance with the Rancimat method on a Metrohm 743 Rancimat apparatus at temperature range of (50–220) °C. The tests were done with 3 g oil samples. Effluent air containing volatile organic acids from the oil samples were collected in a measuring vessel containing distilled water. The conductivity of the water was measured automatically as oxidation proceeded. Filtered, cleaned, dried air was allowed to bubble through the hot oil at flow rate of 20 l/hr. The OSIs of the oil samples were automatically recorded at 120°C [Farhoosh, (2007)].

**Tocopherols content determination**
A chromatographic system consisted of a Waters 1525 binary pump (Waters, Milford, USA), 40 µL injection loop, and photodiode Array Detector (Waters, USA) was used to measure tocopherols content (VE). Lichroshper Si-60 column (250×2.0, 5 µm, Hanbon Science and Technology, China), was used for separation. A mixture of n-hexane-isopropanol (98.5:1.5 v/v) at a flow rate of 0.15 mL/min was used as a mobile phase. The signal was measured at wavelengths 295 nm [Sanchez et al., (2002)]. Mixed tocopherols (α, β, γ, and δ) was obtained from Roche vitamins Inc – (Parsippany, new jersey 07054- USA). Bleaching earth type (OBT-40) was obtained from Ou Bai Te Shi Ye Company (Wuxi, China). All other chemicals and solvents used were of analytical grade.

**Methods**
Crude oil was degummed by 0.2% citric acid (40%) at 70°C with slow agitation for 30 min. Gums were separated by centrifuging at 10,000 rpm for 10 min. Degummed oil was mixed with (1.4%) sodium hydroxide solutions (8.07%) at 40°C with slow agitation for 30 min, soap stock was separated by decanting and centrifuging at 10,000 rpm for 10 min. The neutralized oil was washed with 15% hot soft water at 85°C. Then, the washed oil was dried by heating at 90°C under 75 mm Hg vacuum for 30 min. In the next step, the oil was bleached at 80°C with vigorous stirring for 30 min using 1% bleaching earth (w/w). Then, cooled to 60°C and filtered. Winterization was carried out at temperature 6 °C for 10 h. After filtering, the winterized oil was deodorized at 240°C for 2 hr under 3 mm Hg vacuum and cooled to 45°C [Tasan and Demirci, (2005)]. Samples were collected from each step (degumming and neutralizing, bleaching, winterizing and deodorization), and stored at 4°C in dark glass containers and purged with nitrogen gas after filling to prevent oxidation.

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Colour determination

Lovibond colours were determined in duplicate, using Lovibond PFX880-Tintometer according to the official AOCS method [Crexi et al., (2009)]. The optical path length of the glass cell was 1” for crude oil and 5.25” for refined oil.

Statistical Analysis

The results of all of the analyzed samples were expressed as mean values with standard deviations. The significant differences between the means of all of the analyzed results were obtained from Duncan’s test at a P-value 0.05 associated with the one-way analysis of variance (ANOVA) using SPSS 16.0 (SPSS Inc., Chicago, USA).

Results and discussion:

Oil Stability Index (OSI)

<table>
<thead>
<tr>
<th>Oil</th>
<th>FFA (%)</th>
<th>OSI (hr)</th>
<th>VE (ppm)</th>
<th>LCY</th>
<th>LCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil</td>
<td>0.50± 0.11&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.76± 0.11&lt;sup&gt;a&lt;/sup&gt;</td>
<td>750.4± 3.55&lt;sup&gt;a&lt;/sup&gt;</td>
<td>70± 0.57&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.2± 0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Neutralized oil</td>
<td>0.10± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.23± 0.07&lt;sup&gt;b&lt;/sup&gt;</td>
<td>670.9± 5.15&lt;sup&gt;b&lt;/sup&gt;</td>
<td>70± 0.57&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.5± 0.10&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Bleached oil</td>
<td>0.13± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.90± 0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>618.2± 4.00&lt;sup&gt;c&lt;/sup&gt;</td>
<td>6.5± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.2± 0.01&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Winterized oil</td>
<td>0.12± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.00± 0.02&lt;sup&gt;c&lt;/sup&gt;</td>
<td>614.6± 4.40&lt;sup&gt;c&lt;/sup&gt;</td>
<td>6.4± 0.05&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.2± 0.01&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Deodorized oil</td>
<td>0.03± 0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.25± 0.02&lt;sup&gt;b&lt;/sup&gt;</td>
<td>530.7± 4.90&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.5± 0.10&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.5± 0.01&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

The oxidative stability is an important quality parameter for fats and oils. It is most commonly determined via the active oxygen method (AOM; AOCS Method Cd 12-57), but, for practical reasons, the simpler (and much faster) rancimat method was used in this study. However, from Table 1, the sunflower oil showed OSIs (2.80, 2.10, 1.88, 1.90, and 2.23 h) respectively during the chemical refining steps. The OSI of crude sunflower oil was higher than that of the treated oil during all refining steps. The above observation may due to its high content of VE, antioxidative phenolic compounds, in addition, maybe also due to its fatty acids composition being more resistant to oxidation [Farhoosh et al., (2009)]. The OSI significantly decreased after neutralizing and degumming step, while it exhibited no considerable change during the bleaching and winterizing steps, while, it increased after deodorizing step. Zacchi and Eggers showed that the OSI of the rapeseed oil decreases significantly after the degumming and neutralization steps and little change occurs during the bleaching and deodorization steps [Zacchi and Eggers, (2008)], which it can be seen in Fig 1. During the degumming and neutralization steps, phenolic compounds are almost completely removed, that has a strong negative influence on the oxidative stability of the oils [Zacchi and Eggers, (2008)]. On the other hand, Fig 2 shows deodorized oil even with fewer content of tocopherol as antioxidants, oxidative stability was higher than the neutralized, bleached, winterized oil. However, that is due to the oxidation products with small molecular weight have been removed, and these results in agreement with the results observed by [Farhoosh et al., (2009)].
Free fatty acids (FFA)

One of the main objectives of edible oil refining is to remove FFA from crude oil. During the chemical refining, such as applied in this study, most of the FFA content is eliminated during the neutralization stage of the process. This results in a residual FFA content of about 0.1%. However, some FFA still has to be removed during the deodorization step to obtain the required final FFA content below 0.03%. Therefore, the deodorization conditions must always be in optimum order to keep the FFA content as low as possible Fig 3.

From Table 1, it can be seen that, the FFA of sunflower crude oil (0.5%) decreased significantly after the neutralization step because of the alkali treatment, after bleaching step its level underwent no very obvious increase and that was returned to removing colour by using bleaching earth activated by acid which leads to increase the acidity of the oil slightly. Also results showed that, after deodorization step, FFA reached to the lowest possible level due to of using high temperature for a long time with an optimum vacuum to remove the undesirable compounds including FFA [De Greyt et al., (2000)].

Total tocopherols (VE)

Table 1 shows the level of total tocopherols (ppm) content in sunflower oil samples taken from the neutralizing and degumming, bleaching, winterizing and deodorizing steps was decreased. The results showed that the total tocopherols content was higher in the crude oil sample (750±3.55 ppm). This level continuously decreased during the neutralizing and degumming step (670.9±5.15 ppm), bleaching (618.2± 4.00 ppm), winterizing (614.6± 4.40 ppm), and deodorizing step (530.7± 4.90 ppm). Table 1 illustrates that the total tocopherols was significantly decreased during neutralizing and degumming, bleaching and deodorizing steps with no significant difference between bleaching and dewaxing steps. In the present study, no β-tocopherol was observed in any sample, while in the reported study no δ-tocopherol was detected which may be due to the different varieties of sunflower oil used and the diverse environmental conditions. The decrease in the total tocopherol level during the caustic neutralization is in agreement with the results obtained by the reported study, according to which
alkali treatment affected the tocopherol content of oils [Tasan and Demirci, 2005]. The decline of tocopherols may be due to the fact that tocopherols are unstable in the presence of longer contact time with air and alkali [Tasan and Demirci, 2005]. In the present study bleaching and winterizing show much lower impact than neutralization and deodorization on the decrease of total tocopherols content. During bleaching and winterizing steps the total tocopherols concentration was slightly reduced due to their possible adsorption on bleaching clay [Naz et al., 2010].

![Figure 4: Effect of sunflower oil chemical refining steps on VE](image)

**LCY and LCR**

Table 1 shows the effect of chemical refining steps of sunflower on the colour LCR and LCY. After neutralizing and degumming step LCR decreased without effect on LCY and that may due to adsorptive deacidification [Wang et al., 2002]. After bleaching step both of LCR and LCY decreased and that was due to the effect of activated bleaching earth on colour pigments. Colour pigments after deodorization step were decreased significantly due to using high temperature for a long time with an optimum vacuum to remove undesirable components including colour pigments as it can be seen clearly in Fig 3. That is due to carotenoids are the principal oil soluble yellow to orange red pigments found in plants and they are highly unsaturated compounds and are easily decomposed at high temperature [Hrastar et al., 2011].

![Figure 5 & 6: Effect of sunflower oil chemical refining on LCY and LCR respectively](image)

**Conclusions**

Although chemical refining steps have disadvantages such as decreasing yield, high investment cost, high chemicals used and higher waste but, on the other hand, they have less effect on desirable compounds such as tocopherols except deodorization step. Deodorization step had a significant effect on all quality attributes of refined sunflower oil. In addition, although there was a linear relationship between oil stability index and
content of total tocopherols, but sometimes oil stability can be higher even in case oil with less amount of total tocopherols which it can be seen in the case of oil stability of deodorized oil compared with bleached and degummed oil. However regarding to the negative effects of deodorizing step on desirable compounds, the parameters of this step should be considered looking for optimum condition to get refined sunflower oil with high quality attributes.

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References:


