Deacidification of High-acid Olive Oil

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Abstract

The objective of the present work was to improve the quality of high-free fatty acid olive (HFFAO) oil. Silica gel (SG) was used as adsorbent by applying filtration and stirring techniques. Chemical treatments with alkali using NaOH and/or Ca(OH)₂ were also conducted to neutralize the acidity of HFFAO oil. The percentages of linoleic acid (C18:2) in the neutralized oils were lower than those in the reference olive oil. Untreated and treated HFFAO oil samples were stored under accelerated conditions for 30 days. The progress of oxidation at 60°C was followed by measuring acid value (AV), the formation of oxidative products (peroxide value (PV) and p-anisidine value (AnV)), total phenolic compounds (TPC), recording radical scavenging activity (RSA) toward 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical and inhibition of β-carotene in a linoleate model system. The results indicated that SG and alkali treatments were effective in reducing the acidity of HFFAO oil. Generally, alkali treatments reduced the AV of HFFAO oil, while treatments with SG induced variable degrees of improvements in HFFAO oil acidity. Alkali treatments resulted in increasing the PV levels to 35 and 28 meq peroxide kg⁻¹ oil for HFFAO treated with soda and lime, respectively. The corresponding improvement in the PV reduction (%) for HFFAO oil using SG was in the range of 10.5% to 47.3%. Treatments with SG or alkali resulted in reduction of AnV, wherein filtration with SG had a remarkable effect on AnV. Levels of TPC were reduced (ca. 70%) with alkali treatments, while treatments with SG resulted in reduction of about 22-48%. Antiradical properties of HFFAO oils were compared using stable DPPH free radicals. After 60 min incubation with DPPH, 78% of DPPH radicals were quenched by control sample, while HFFAO oils treated with SG or alkali were able to quench from 48 to 56%. Different SG and alkali treatments were not effective in inhibiting the oxidation of linoleic acid and the subsequent bleeding of β-carotene in comparison with the control. During oxidation experiments the same trends of results was noted for both control and treated oils.

Practical application: Olive oil is one of the most important edible oils in the world. Crude vegetable oils refined to remove free fatty acids (FFA) as well as other impurities that affect flavor, odor and appearance of oils. Deacidification process significantly influences the economics of oil production. Several methods to remove FFA have been developed to enhance the value of degraded vegetable oils, for example, physical refining based on distillation and chemical refining with sodium hydroxide. In this work, the quality of high-free fatty acid olive (HFFAO) oil was improved using silica gel (SG) as an adsorbent by applying filtration and stirring methods. The results stated that SG with small particle size permitted high adsorbing capacity and close to that induced with chemical treatments which are used commercially in a large scale to improve oil quality.

Keywords: High free fatty acid olive oil; Silica gel; Alkali treatment; Acidity; Oxidation; Phenolic compounds; Radical scavenging activity

Introduction

The world productions of olive oil reach 2,800,000 ton and 98% of this production is to be found in the Mediterranean basin, where this agricultural system has been developed for thousands of years, characterized by its adaptation to the environment and its empiricism. Several factors have modified the olive production and processing systems in the last decades. The crisis of traditional agriculture and the valorisation of olive oil, due to its organoleptic attributes and its beneficial influence on health, are probably the two most important features. As a consequence great advances have been made in olive oil technology.

Degumming, neutralization, bleaching and deodorization are typical refining steps of oil processing. Crude oil must be refined to remove free fatty acids (FFA) and other impurities that impact on flavor, odor and appearance. Thus, the deacidification process significantly influences the economics of vegetable oil production. The purpose of deacidification in the conventional chemical process is to remove non-glyceride impurities consisting of FFA that contribute to bitter and soapy flavor in food [1]. Conventional approaches to refining include degumming, dewaxing, alkali refining, bleaching, and deodorization, and are best used with low-FFA oils. Several methods to remove FFA have been developed to enhance the value of degraded vegetable oils, for example, physical refining based on distillation and chemical refining with soda (sodium hydroxide). Distillation is an effective method to neutralize vegetable oils with high acidity, but this operation is also energy intensive. Moreover, heating oil to high temperature under reduced pressure generates secondary reactions that alter their physicochemical characteristics and organoleptic properties [2]. Pretreatment with alkali prior to membrane filtration resulted in a very high reduction (ca. 90%) of FFA in the processed oils [3,4]. These approaches, however, lead to high refining loss when applied to high-FFA oils. Therefore, several authors have proposed physical refining for high-FFA oils [5-8]. This process removes FFA along with odoriferous compounds by purging saturated steam through the oil at...
a high temperature under high vacuum. Physical refining, however, results in large quantities of distilled fatty acids with concomitant reduction in the quantity of the original oil, especially if the oil being processed is high in FFA content. Alternative approaches have been proposed to reduce neutral oil loss during physical refining. Liquid-liquid extraction with polar solvents (e.g., azetropic isopropanol) was a better process for extracting FFA along with color and peroxide bodies. Treating frying oil with a mixture of gel-derived alumina and activated clay or magnesium silicate had a significant reduction in the amount of fatty acids, aldehydes, ketones and odor- and color-forming compounds [9]. Lin et al. [10] used combinations of four commonly used filter aids (Britesorb, Hubersorb, Frypowder and Magnesol) to recover the used frying oils, where in the levels of FFA were reduced by 82.6-87.6%.

Care must be taken in the selection of filter aids because some of these substances can affect the potential stability of the fats [11]. Clay minerals having these properties are able to adsorb particular amount of trace metals, to reduce the components giving color and chlorophyll, to remove soap and phosphates and to have the effect amount of trace metals, to reduce the components giving color and chlorophyll, to remove soap and phosphates and to have the effect.

Material and Methods

Materials

Lampante high free fatty acid olive (HFFAO) oil was obtained from El-Salheya olive oil company (El-Salhya City, Sharkia Governorate, Egypt). The peroxide value of the oil was 19 meq peroxide kg⁻¹ oil and the acid value was 3 mg KOH g⁻¹ oil, respectively. Silica gel (60-120 mesh) was purchased from BDH Chemicals Ltd (Poole, UK). All solvents and reagents from various suppliers were of the highest purity needed for each application and used without further purification.

Deacidification of HFFAO oil with SG

Filtration: Silica gel was activated by heating at 120°C for 2 h. Glass chromatographic column (50 cm × 10 cm) was filled with activated SG and HFFAO oil samples dissolved in hexane (3 g oil: 1 mL hexane) were filtered through SG. This process was repeated three times using two ratios of SG to HFFAO (1:2 and 1:3, w/w).

Stirring: Silica gel (SG) were added individually to the HFFAO oil (3 g oil: 1 mL hexane) and mechanically stirred on magnetic stirrer for 120 min at 25°C then filtered through Whatman No. 1 filter paper. This process was repeated three times using two ratios of SG to HFFAO (1:2 and 1:3, w/w). The untreated HFFAO oil was also filtered through Whatman No. 1 filter paper.

Neutralization of HFFAO oil using NaOH and Ca(OH)₂

Alkali treatments using NaOH and Ca(OH)₂ were conducted to neutralize and modify the acidity of HFFAO. Neutralization with soda (NaOH) and/or lime Ca(OH)₂ was carried out as follow: one gram of hydroxide sodium or lime was dissolved in 1 mL distilled water then the mixture was added to 150 g olive oil and stirred for 30 min. Hexane (15 mL) was added and the mixture was stirred for 30 min. The mixture was centrifuged at 3500 rpm for 30 min and hexane was evaporated and the oil was used for further analyses.

Oxidation experiments

Samples of HFFAO and untreated HFFAO oils were placed in a series of transparent glass bottles having a volume 20 mL each. The bottles were completely filled with oil and sealed. No headspace was left in the bottles. The oxidation reaction was accelerated in a forced-draft air oven T6 (Heraeus Instruments GmbH; Hanau, Germany) set at 60 ± 2°C for up to 0, 7, 14 and 30 days. Immediately after storage period, oil samples were withdrawn for triplicate analyses.

Analytical procedures

The progress of the oxidative deterioration of the oils during storage was followed by measuring the following parameters.

Fatty acid composition: Fatty acids were transesterified into FAME using N-trimethylsulfoniumhydroxide (TMSH, Macherey-Nagel, Düren, Germany) according to the procedure reported by Arens et al. [19]. In brief, 10 mg of oil sample was dissolved in 500 µL of tert.-Butyl methyl ether then 250 µL of TMSH was added and the mixture was vortexed for 30 seconds before injection. FAME was identified on a Shimadzu GC-14A equipped with flame ionization detector (FID) and C-R4AX chromatopac integrator (Kyoto, Japan). The flow rate of the carrier gas helium was 0.6 mL/min and the split value with a ratio of 1:40. A sample of 1 µL was injected on a 30 m x 0.25 mm x 0.2 µm film thickness Supelco SP®-2380 (Bellefonte, PA, USA) capillary column. The injector and FID temperature was set at 250°C. The initial column...
temperature was 100°C programmed by 5°C/min until 175°C and kept 10 min at 175°C, then 8°C/min until 220°C and kept 10 min at 220°C. A comparison between the retention times of the samples with those of reference compounds mixture, run on the same column under the same conditions, was made to facilitate identification.

**Acid value:** A known weight of oil sample (~ 2g) was dissolved in neutralised alcohol (50 mL) and titrated with KOH (0.1 mol L⁻¹) according to AOAC [20].

**Peroxide value and p-anisidine value:** A known weight of oil sample (ca. 2g) was dissolved in 30 mL chloroform: acetic acid (3:2, v/v) then 1 mL freshly prepared saturated KI solution was added and the mixture vortexed for exactly 1 min. Distilled water (30 mL) and starch solution (0.5 mL, 1%) were added and the liberated iodine was titrated with sodium thiosulfate (0.1 mol L⁻¹) according to AOAC [20]. p-Anisidine value (AnV) was measured according to the official methods of the American Oil Chemists’ Society [21].

**Total phenolics:** Aliquots of oil (2 g) were dissolved in n-hexane (5 mL) and mixed with 10 mL methanol-water (80:20, v/v) in a glass tube for two min in a vortex. After centrifugation at 3000 rpm for 10 min, the hydroalcoholic extracts were separated from the lipid phase by using Pasteur pipet then combined and concentrated in vacuo at 35°C until a syrup consistency was reached. The lipidic residue was redissolved in 10 mL methanol-water (80:20, v/v) and the extraction was repeated twice. Hydroalcoholic extracts were redissolved in acetonitrile (15 mL) and the mixture was washed with n-hexane three times (15 mL each). Purified phenols in acetonitrile were concentrated in vacuo at 30°C then dissolved in methanol for further analysis. Aliquots (0.2 mL) of phenolic extracts were evaporated to dryness under nitrogen. The residue was redissolved in 0.2 mL water and diluted (1:30) Folin-Ciocalteu’s phenol reagent (1 mL) was added. After 3 min, 7.5% sodium carbonate (0.8 mL) was added. After a further 30 min, the absorbance was measured at 765 nm using UV-260 visible recording spectrophotometer (Shimadzu, Kyoto, Japan). RSA toward DPPH radicals was estimated from the differences in absorbance of toluenic DPPH solution with or without sample (control) and the inhibition percent was calculated from the following equation: % inhibition = [(absorbance of control – absorbance of test sample)/ absorbance of control] x 100.

All results presented are mean values of at least three experiments, wherein no statistically significant difference (P > 0.05) was found among the experiments.

**Results**

**Impact of deacidification on the oil recovery and fatty acid composition of HFFAO**

Applying different SG and alkali treatments resulted in weight losing during different treatments. Table 1 present the percentages of weight losing during processing. Stirring techniques with SG leads to higher percentages of weight losing (16-14%) followed by filtration technique (13-12%), while alkali treatments with soda and lime resulted in moderate weight losing (8-7%). The FA compositions of the oils, before and after neutralization, are shown also in Table 1. The majority of free acidity of HFFAO oils was lower than those in the reference olive oil. This reduction was more important with SG neutralization. A reduction in the percentage of palmitic acid (C16:0) was noted in the neutralized oils especially in alkali treated oils, as well as a very clear increase in the percentage of oleic acid (C18:1n-9). Most of the free acidity of HFFAO oil might be attributable to palmitic acid and oleic acid. The results are in agreement with Essid et al. (2006) who used lime (calcium hydroxide) and soda (sodium hydroxide) as the neutralizing agent for refining high acid olive oil.

**Impact of deacidification on the acid value (AV) of HFFAO**

The most versatile fat chemical characteristics for the determination of olive oil quality are: acid value, peroxide value, anisidin value and phenolics content. It has been reported that humidity of the environment has been reported to be a factor affecting hydrolysis of oils [23]. The initial values of HFFAO were, acid value (3 mg KOH g⁻¹ oil), peroxide value (19 meq peroxide kg⁻¹ oil), anisidin value (20), wherein the total phenolics level (0.43 mg/kg as caffeic acid equivalent). These findings indicate that the HFFAO oil was characterized by high level of acidity. Acidic changes taking place in the experiments conducted with SG were investigated. FFA removal profile with SG as well as alkali treatments are plotted in Figure 1. Generally, alkali treatments with soda and/or lime significantly reduced the AV of HFFAO oil. On the other side, treatments with SG induced variable degrees of improvements in HFFAO oil quality. Filtration technique through SG achieved more FFA removal than stirring technique. As seen in the figure, at zero time, maximum FFA removal observed with SG filtration technique (about 57.6%) when the ratio 2:1 was applied. On the contrary, nearly 21.6% FFA removal was achieved with SG stirring technique when the ratio 3:1 was applied for control sample SG.

During storage for 30 days under accelerated oxidation conditions at 60°C the same levels of reducing acid values of stored samples were recorded. The results demonstrated that the treatment of HFFAO oil with alkali (NaOH and/or Ca(OH)_2) greatly lowered the FFA levels. The effect of filtration and stirring using SC was nearly the same during the oxidation experiment.
Impact of deacidification on the peroxide value (PV) and p-anisidine value (AnV)

Peroxides and hydroperoxides, the primary oxidation products, decompose to form aldehydes, ketones, acids, alcohols, hydrocarbons and other compounds. These substances formed during thermal degradation of oils. The products of oil degradation as defined by International Union of Pure and Applied Chemistry [24] are polar materials. The polar fraction is composed of FFA, monoglycerides, oxidized triglycerides and oligomeric triglycerides. All treatments and regeneration adsorbents used in the present work caused an improvement in stored and treated HFFAO oil quality comparable to that of fresh oil.

The initial PV of HFFAO was 19 meq peroxide kg⁻¹ oil. Alkali treatments with soda and/or lime did not improve the quality HFFAO in the terms of PV but resulted in increasing the PV levels to 35 and 28 meq peroxide kg⁻¹ oil for HFFAO treated with soda and lime, respectively (Figure 2). The corresponding improvement in the PV reduction (%) for HFFAO oil using SG was in the range of 10.5% to 47.3%. These results demonstrated that the adsorbing efficiency of SG with small particle size (60–120 mesh) permitted high adsorbing capacity and very good in scavenging the peroxides of HFFAO. Yates et al. [25] added silicates in powdered form and subsequently removed by filtration in order to regenerate the quality of used oils. In this respect, Kalapathy and Proctor [26] prepared sodium silicate films from rice hull ash silica and mentioned that FFA content gradually decreased with treatment time for all films. The PV for the treated oils was progressively increased during storage under accelerated oxidation conditions. However, PV were reduced after 30 days of storage in the samples treated with SG and this finding could be due to the volatilization of some peroxides under accelerated oxidation conditions. The efficiency of various SG: oil ratios (1:2 and 1:3, w/w) on lowering the PV of HFFAO oil was approximately the same at a certain level.

The p-anisidine value (AnV), which measures the unsaturated aldehydes (principally 2-alkenals and 2,4-di-enals) in oils, was determined by reacting p-anisidine with the oil in iso-octane and the resultant color was measured at 350 nm. The initial AnV for HFFAO oil was 20 and it could be noted that treatments with SG or alkali resulted in reduction of AnV (Figure 3). In addition, filtration with SG was more active in reduction of AnV than stirring technique. During autoxidation at 60°C in the dark (Figure 3), treated HFFAO oils were more stable than the control oil. Here again, SG with high polarity led to a higher adsorbing capacity in removing the secondary oxidation products of HFFAO oil. However, at the end of oxidation experiment the AnV levels in treated HFFAO oils (except of oil treated with lime) were higher than control oil. The results demonstrated that all treated HFFAO oils had a potent oxidative stability (OS) higher than control oil. Meanwhile, treatment with SG and alkali caused a decrease in both peroxide and p-anisidine levels during incubation intervals for 30 days.

### Table 1: Fatty acid composition of HFFAO oil and neutralized oils (mass %).

<table>
<thead>
<tr>
<th>Olive oil</th>
<th>% Weight losing</th>
<th>C16:0</th>
<th>C16:1</th>
<th>C17:0</th>
<th>C17:1</th>
<th>C18:0</th>
<th>C18:1</th>
<th>C18:2</th>
<th>C18:3</th>
<th>C20:0</th>
<th>C20:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFFAO</td>
<td>0</td>
<td>21.33</td>
<td>3.33</td>
<td>0.03</td>
<td>0.07</td>
<td>2.66</td>
<td>51.37</td>
<td>17.20</td>
<td>0.55</td>
<td>0.35</td>
<td>0.16</td>
</tr>
<tr>
<td>Filtration 2:1 (oil: SG, w/w)</td>
<td>13</td>
<td>20.11</td>
<td>3.10</td>
<td>0.03</td>
<td>0.07</td>
<td>2.79</td>
<td>55.58</td>
<td>12.94</td>
<td>0.53</td>
<td>0.40</td>
<td>0.16</td>
</tr>
<tr>
<td>Filtration 3:1 (oil: SG, w/w)</td>
<td>12</td>
<td>20.21</td>
<td>3.00</td>
<td>0.02</td>
<td>0.08</td>
<td>2.89</td>
<td>55.48</td>
<td>12.74</td>
<td>0.73</td>
<td>0.41</td>
<td>0.15</td>
</tr>
<tr>
<td>Stirring 2:1 (oil: SG, w/w)</td>
<td>16</td>
<td>20.82</td>
<td>2.94</td>
<td>0.03</td>
<td>0.07</td>
<td>2.69</td>
<td>51.69</td>
<td>15.32</td>
<td>0.52</td>
<td>0.39</td>
<td>0.16</td>
</tr>
<tr>
<td>Stirring 3:1 (oil: SG, w/w)</td>
<td>14</td>
<td>20.62</td>
<td>2.84</td>
<td>0.04</td>
<td>0.06</td>
<td>2.89</td>
<td>51.71</td>
<td>15.30</td>
<td>0.62</td>
<td>0.38</td>
<td>0.17</td>
</tr>
<tr>
<td>Oil neutralized with NaOH</td>
<td>7</td>
<td>13.88</td>
<td>1.64</td>
<td>0.05</td>
<td>0.07</td>
<td>2.58</td>
<td>64.22</td>
<td>16.20</td>
<td>0.52</td>
<td>0.40</td>
<td>0.24</td>
</tr>
<tr>
<td>Oil neutralized with Ca(OH)₂</td>
<td>8</td>
<td>14.19</td>
<td>1.78</td>
<td>0.06</td>
<td>0.08</td>
<td>2.56</td>
<td>63.83</td>
<td>16.43</td>
<td>0.58</td>
<td>0.44</td>
<td>0.19</td>
</tr>
</tbody>
</table>
Impact of deacidification on the total phenolic compounds (TPC)

Figure 4 present the impact of different treatments on the TPC of HFFAO oils during oxidation storage. The initial TPC in HFFAO was 43 mg/kg oil and the levels of TPC were significantly reduced (ca. 70%) with alkali treatments (soda and lime). Treatments with SG also resulted in relative reduction (ca. 22-48%) in the TPC levels. During oxidation at 60°C (Figure 4), all samples showed a gradual decrease, wherein SG treated HFFAO oils were more stable than alkali treated oils. The TPC content of olive oil determined colorimetrically is reduced almost to zero with refining [27]. Nergiz [28] reported that a residual amount of total polyphenols and o-diphenols can be found in refined olive oils.

Impact of deacidification on the radical scavenging activity (RSA) and inhibition of β-carotene co-oxidation in a linoleate model system

Interest has increased in the past few years in the free radical theory of disease causation, particularly in vascular diseases and certain forms of cancer. These developments have led to the investigation on dietary agents, the antioxidant nutrients (mainly vitamins A, C, and E), in a possible prophylactic, even curative, role in the disease process. Closely related to this probable benefit of natural antioxidants is their role in controlling free radicals as they may lead to pathological effects such as vascular diseases and cancer. A free radical is defined as any chemical species that has one or more unpaired electrons. This often results in very reactive compounds. Oxidation is a natural and needed reaction in metabolism. Highly reactive hydroxyl radicals, •OH, results. These can attack DNA, protein and polysaturated fatty acids residues of membrane phospholipids, among others. With the latter, a peroxyl radical is formed. Antioxidants quench this radical. If the supply of antioxidants is inadequate, a chain reaction takes place that may lead to damaged tissue. The evidence in the literature begins to make an overwhelming case for the existence of a relationship between high blood levels of antioxidant nutrients and a lowered incidence of disease [29]. The antioxidant activity of phenolic compounds may inhibit free radicals from initiating the oxidation process and radical chain reaction. For this reason, two different methods were used for the determination of the antioxidant activity of the extracts: inhibition of β-carotene co-oxidation in a linoleate model system and DPPH free radical scavenging.

Apart from the OS of vegetable oils and fats depends on the fatty acid composition, the presence of minor fat-soluble bioactives and the initial amount of hydroperoxides. Antiradical properties of HFFAO oil were compared using stable DPPH free radicals. Figure 5 shows that treatment sample of HFFAO oil has higher RSA than HFFAO oils treated with SG or alkali. After 1 h incubation, 78% of DPPH radicals were quenched by control sample of HFFAO oil, while HFFAO oils treated with SG or alkali were able to quench from 48 to 56% at the same time of incubation. During autooxidation experiment the same trends of RSA was noted for control and treated oil samples. It could be concluded that treatment of HFFAO oils with SG or alkali resulted in reduction in the levels of polar bioactive antioxidants responsible for antiradical action. It could be said that the RSA of oils can be interpreted as the combined action of different endogenous antioxidants. However, when polar fractions, which contain mainly polar lipids and low levels of phenolics, are found in high levels, strong RSA of these components can be expected as well as synergistic activity with primary antioxidants [30,31].

Figures 6 reveal the decrease of absorbance of β-carotene in the presence of different HFFAO oil in the coupled system of β-carotene.
and catalytic reactions lead to the formation of olefin hydrocarbons, di- and triterpenes, and aromatic products as a consequence of tocotrienol degradation.

Sodium hydroxide not only neutralizes FFA, which is the aim, but also attacks neutral oil by saponification, leading to reduced output and the formation of monoacylglycerols and diacylglycerols in neutral oil. From an economic viewpoint, neutralization with soda in a liquid-liquid biphasic medium cannot be applied to oils having acidity >15% because the quantity of neutral oil that is saponified becomes very significant. In addition, soda eliminates some of the principal components responsible for OS, such as tocopherols, and can involve losses of sterols, which constitute 30-60% of the unsaponifiables. Total sterol losses can be as much as 15%.

The aforementioned data indicated that SG was an effective adsorbing substance in removing secondary oxidation substances from HFFAO oil. Silica gel with 60-120 mesh does not exhibit any harmful effects to the handler and possesses adsorbing efficiency in removing secondary oxidation substances. In addition, the price of normal SG is comparable to Magnesol XL and would therefore be useful for regenerating the quality of used oils and high FFA oils. According to the chemical structure of SG, it exhibits dual functions (polar and non-polar characters). In general, one would say that silica gel with 60-120 mesh had the highest adsorbing capacity than that of other adsorbing agents [37]. In this respect, silica offers the greatest potential for refining the edible oil in industry. It is of interest to note that the silicone atoms of SG are joined via oxygen atoms in a giant covalent structure. However, at the surface of the SG, the silicone atoms are attached to –OH groups. So, the surface of the SG is very polar and the –OH groups can form hydrogen bonds with the secondary oxidation products as well as van der Waals dispersion forces and dipole–dipole attractions. In fact, the most important features of SG are the presence of silanol (Si–OH) groups that are polar and ionisable and siloxane (non-polar) characters. In general, one would say that silica gel with 60-120 mesh had the highest adsorbing capacity than that of other adsorbing agents [37]. In this respect, silica offers the greatest potential for refining the edible oil in industry. It is of interest to note that the silicone atoms of SG are joined via oxygen atoms in a giant covalent structure. However, at the surface of the SG, the silicone atoms are attached to –OH groups. So, the surface of the SG is very polar and the –OH groups can form hydrogen bonds with the secondary oxidation products as well as van der Waals dispersion forces and dipole–dipole attractions. In fact, the most important features of SG are the presence of silanol (Si–OH) groups that are polar and ionisable and siloxane (non-polar) characters. The following diagram represents the existence of silanol groups (polar) at the surface while the siloxane groups (non-polar) are located at the interior part of the silica gel molecules.

### Silanol groups (polar) at the surface of SG

\[
\begin{align*}
\text{Si} & - \text{O} - \text{Si} - \text{O} - \text{Si} \\
\text{Si} & - \text{O} - \text{Si} - \text{O} - \text{Si}
\end{align*}
\]

### Siloxane groups (non-polar) inside SG molecules

It is well known that oxidation products are mainly polar and some are non-polar substances. Silica gel molecules have polar and non-polar groups which associate with the secondary oxidation products according to the well known basis ‘likes dissolve likes’. Thus, SG structure allows to great extent improve the quality of oils with high polar levels. It could be concluded that SG with small particle size permitted high adsorbing capacity and close to that induced with chemical treatments which are used commercially in a large scale to improve oil quality.

Figure 6: Changes in the bleaching of β-carotene for untreated HFFAO and treated HFFAO oils as affected by SG and alkali treatments during oven test. Error bars show the variations of three determinations in terms of standard deviation.

Vegetable oils that have been degraded by hydrolysis must be refined before use. Olive-residue oil has a high percentage of FFA, ranging from 5 to 60% by weight. The elimination of FFA is the most important refining operation. Several methods to remove FFA have been developed to enhance the value of degraded vegetable oils, for example, physical refining based on distillation and chemical refining with soda (sodium hydroxide). Distillation is an effective method to neutralize vegetable oils with high acidity, but this operation is typically used to neutralize vegetable oils with high acidity, but this operation is typically used with soda (sodium hydroxide). Distillation is an effective method to neutralize vegetable oils with high acidity, but this operation is typically used with soda (sodium hydroxide). Distillation is an effective method to neutralize vegetable oils with high acidity, but this operation is typically used with soda (sodium hydroxide). Distillation is an effective method to neutralize vegetable oils with high acidity, but this operation is typically used with soda (sodium hydroxide).
References


