

INVESTIGATING CHANGES AND EFFECT OF PEROXIDE VALUES IN COOKING OILS SUBJECT TO LIGHT AND HEAT

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The quality of the oils is dependent on their chemical compositions, like the percentage of the degree of unsaturation. The peroxide value (PV), which depends on temperature, time and light, measures the extent of primary oxidation of oils (rancidification). Rancidity of oils can produce potentially toxic compounds associated with long-term health effects such as neurological disorders, heart and cancer. Oils with a high degree of unsaturation are highly susceptible to oxidation as compared to saturated oils. Moreover vegetable oils become rancid much faster than animal oils. Oils also become susceptible to microbial rancidity, in which microorganisms such as bacteria and yeast use their enzymes to break down chemical structures in the oil, leading to the production of unwanted odors and flavors. To investigate oxidative initial rancidity of oils the PV value is determined. Twenty different oils were selected and subjected to two different frying temperatures: 130°C and 170°C. This change from 130°C to 170°C using same frying time (20 minutes) was noticed to cause changes in PV of pure oil, though in many cases (except Seasons corn oil, Season canola, Kausar banaspati, Dalda Groundnut) the PV value was constant after 130 °C. These results show that it is important to add antioxidants such as vitamin E or C as preservatives in vegetable oils to delay or down slow the development of rancidity.

Introduction

Cooking oil of plant and animal origin or synthetic fat is used in frying, baking, and other types of cooking. It is also used in food preparation and flavoring not involving heat, such as salad dressings and bread dips, also termed edible oil. Cooking oils are liquid, although some oils that contain a high amount of saturated fat, such as coconut oil, palm oil and palm kernel oil, are solid at room temperature. Cooking oils are derived from animal fat, as butter, lard and other types, or plant oils from the olive, maize, sunflower and many other species. Different types of cooking oil include: olive oil, soybean oil, palm oil, canola oil (rapeseed oil), corn oil, pumpkin seed oil, sunflower oil, safflower oil, peanut oil, grape seed oil, sesame oil, rice bran oil and other vegetable oils, as well as animal-based oils like butter and lard. Oil can be flavored with aromatic foodstuffs such as herbs, chilies or garlic.

Different oils such as palm oil are known to support the growth of fungi and bacteria especially when it contains moisture. Under unfavorable conditions lipolytic enzymes of oils are active and produce free fatty acid (FFA) content of less than 2%. Different microorganisms such as *Aspergillus niger* and *Mucor sp.* survive in oil by producing the lipase (Adams and Moss, 1999). The ability of fungi to produce spores makes them survive in anaerobic conditions of the oil because their spores are resistant to heat. The fungi *Aspergillus flavus* is important because of its ability to produce aflatoxin, which sometimes induce toxic syndromes especially cancer (Okechalu *et al.*, 2011). The presence of bacteria such as *Enterobacter* has also been found and pathogenic *Bacillus sp.* microorganisms which can cause food poisoning, bacteremia and endocarditis (Okechalu *et al.*, 2011). Lipids in edible oils are susceptible to photo-oxidation and auto-oxidation during processing and storage (Choe and Min, 2006), which is a major problem for the oil industry. Oxidation may cause undesirable flavors and taste, decomposing the nutritional quality, and leading to production of toxic compounds. Oxidation of oils may be influenced by different factors such as the degree of unsaturation, heat, light, oil processing, antioxidants and transition metals. Another important issue is the reusing of fried oils. This practice is not only restricted to roadside food stalls, and reputable food outlets in large cities also use this technique to lower their costs. The repeated heating of cooking oil result in oil that is more prone to lipid peroxidation (Jaarin *et al.*, 2011). Furthermore repeated frying of oils darken the oil at different rates, and the oil is discarded only when the oil becomes foamy or smelly (Azman *et al.*, 2012).

Auto-oxidation, where peroxide is the main product that gives rise to objectionable flavor in food products, proceeds through the free radical chain reaction, where it attacks on the double bond at room temperatures. Photo-oxidation is a much faster reaction that involves attack at double bond (Lawson *et al.*, 1997). Rancidity of food items can be the result of auto and photo-oxidation, which are natural oxidation and chemical degradation processes of edible oils, where fatty acid esters of oils are converted into FFA giving a smell observed in many vegetable oils (Anwar *et al.*, 2003). Indicators of poor oil quality include elevated FFA, low smoke point, change of color, low iodine value, peroxide value, total polar material, high foaming properties and increased viscosity (Kheang *et al.*, 2006). The double bonds found in fats and oils play an essential role in autoxidation.

Oils with a higher degree of unsaturation are highly susceptible to autoxidation. The best test for autoxidation (oxidative rancidity) is determination of the peroxide value (PV). Peroxides are intermediated in the autoxidation reaction. In contrast it is not always useful in quality control, especially in the absence of sensory evaluation and other tests. As soon as the food, feed or product is manufactured it begins to go through a variety of chemical and physical changes. Oxidation of lipids is one more common and often undesirable chemical change that may influence flavor aroma nutritional quality and in some cases even the fineness of the product. The tertiary oxidation products; dimers and polymers are formed as a result of polymerization of secondary oxidation products. These products cause darkening of the oil color, formation of foam on the oil surface and an increase in viscosity of the oil.

Autoxidation is a free radical reaction involving oxygen that leads to deterioration of fats and oils which form off-odors and off-flavors. PV value is useful to assess the extent to which spoilage has taken place. Autoxidation can be inhibited or retarded by some methods such as vacuum packing, modified atmosphere packing and refrigeration/freezing. Addition of natural antioxidants and precursors of plant origin into the frying oils is the best way of enhancing oxidative and flavor stability.

Materials and Methods

The edible vegetable oils utilized in this work were collected from the local market in Lahore. The physical characteristics of edible oils used are shown in the Table 1.

Table 1. Different oils purchased from the local market of Lahore.

Trade name	Producer	Product type*
Sufi canola cooking oil	Hamza Vegetable Oil Refinery and Ghee Mills (PVT) Ltd.	Natural oil 100% canola oil
Dalda olive oil	Dalda foods (PVT) Ltd.	Natural oil 100% olive oil
Planta cooking oil	Dalda foods (PVT) Ltd.	Blend of soybean, canola and sunflower oil
Manpasand cooking oil	Dalda foods (PVT)Ltd.	Blend of Canola, Soybean and Cottonseed Oil.
Mezan sunflower cooking oil	Paracha textile mills limited (Ghee unit), Karachi, Pakistan	Natural oil 100% sunflower
Kashmir Banaspati	United industries limited (UIL) Faisalabad	Soya Bean, Cotton Seed and Canola blend with palm Oil
Dalda groundnut cooking oil	Dlada foods (PVT)Ltd.	100% peanut oil
Nayaab cooking oil	Habib oil mill (PVT) Ltd. Karachi, Pakistan	Canola oil
Handi cooking oil	Habib oil mill (PVT) Ltd. Karachi, Pakistan	Canola oil
Seasons canola cooking oil	Seasons Foods (PVT) Ltd.	Canola oil
Seasons corn oil	Seasons Foods (PVT) Ltd.	100% corn oil
Punjab banaspati	Seasons Foods (PVT) Ltd.	
Kausar banaspati	Kausar Ghee Mills (PVT)Ltd.	
Tullo sunflower cooking oil	Wazir Ali Industries Ltd.	100% pure sunflower
Shan cooking oil	Mahboob Industries (PVT) Ltd	Canola oil

Salamatak oil	National company for vegetable Oil and ghee industries (S.Y.C)	Purely refined vegetable palm oil and soya bean oil.
Afia corn oil	National company for vegetable oil and ghee industries	Purely refined corn oil
Sultan Al-sham oil	National company for vegetable oil and ghee industries	Extra virgin olive oil
Mazola corn oil	Basateen Foods, Saudi Arabia.	Pure oil 100% corn oil
Olive premium cooking oil	Punjab Oil Mills Limited (POM)	Olive Oil

*All oils are produced in 2014 and expired in 2015

Sampling and storage: All samples were collected from local market of Lahore. Samples consist of commercially available (local and imported) cooking oil. All practical work was carried out in the department of Zoology of Lahore College for Women University, Lahore. 200 mL oil sample was used to determine the PV number of oils. Two frying temperatures were used, 130°C to 170°C. Frying was performed for 20 minute for each process. The frying vessel was a stainless steel coffee pan with a capacity of 500 mL.

Determination of peroxide value (PV): Titration of oil samples was performed with solution (0.01M) sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$). 5 g of the sample and 12 mL chloroform is added to 25 mL beaker using a graduated cylinder. Then it was shaken gently and transferred to a 250 mL conical flask. 18ml of acetic acid (98%) and saturated potassium iodide KI solution (0.5-1.0) mL was added. The mixture was shaken for at least one minute and then distill water (30 mL) was added. The mixture was titrated with sodium thiosulphate (0.01M) until the yellow color of the reactant has approximately been disappeared. Five drops of starch solution (1%) was added, which gave a light blue color. The mixture was titrated again until the light blue color discharged (Pomeranz, 1994).

Statistical analysis: All tests were performed in triplicates. Statistical analyses were carried out with SPSS 17.0 software (SPSS Inc., Chicago, Illinois, USA). The results are presented as the mean \pm SEM. Differences were considered significant at $p < 0.05$.

Results and Discussion

In the present study, physical and chemical parameters were used as an indicator for assessment of quality of thermally oxidized oil samples. The most common change in the oil or fat during use is the darkening. Food compounds (as carbohydrates, phosphates, sulfur compounds, and trace metals) react with the oil or their breakdown products, which contributes to the formation of color. The temperature dependent changes in PV of thermally oxidized oil samples are presented in Fig. 1.

Vegetable oils are a popular cooking medium in many parts of the world. Despite problems related with the intake of excessive calories and health concerns regarding the ingestion of trans-fatty acids, the flavor and texture of fried food continue to be greatly appreciated. In this study changes in PV of different brands of cooking oil and banaspati ghee at different frying temperatures were analyzed. The results show an increase in POV with increase in temperature (see Fig. 1). It is found that the heating of the oil causes the increase of the index of peroxide at the beginning of cooking to a maximum value and then there is a decrease. Oils that are more unsaturated are oxidized more quickly than less unsaturated oils (see (Parker *et al.*, 2003)). The results showed that the trend of the PV is fluctuated for all samples. In the beginning, the peroxides value of original cooking oils increased. This is due to the formation of hydroperoxides of unsaturated fatty acids that were obtained as a result of lipid oxidation. The vegetable oils examined in the present study, showed variations in PV of 20 samples only 3 had a PV below 3 meq/kg. These variations can arise from different factors such as the degree of unsaturation of the fatty acids present in the particular oil, storage, exposure to light, and the content of metals or other compounds that may catalyze the oxidation processes (Choe and Min, 2006). It was observed that the trends of the peroxide values were unstable because the hydroperoxides of unsaturated fatty acids formed by lipid oxidation are very unstable and break down into a wide variety of volatile flavor compounds as well as nonvolatile products. Therefore, at the beginning the increasing of PV showed that the concentration of hydroperoxides is higher, while the PV decreased when the secondary products are observed. The fluctuated of the peroxide values were due to the rapid decomposition of the peroxides that are formed during primary oxidation to secondary oxidation products. Production of secondary oxidation products from primary oxidation product, hydroperoxide, varies with different oils. Immediately after hydroperoxide formation secondary

oxidation products are formed in olive and rapeseed oils, but in sunflower and safflower oils, production of secondary oxidation occurs when concentration of hydroperoxides reaches a certain level (Guillen and Cabo, 2002).

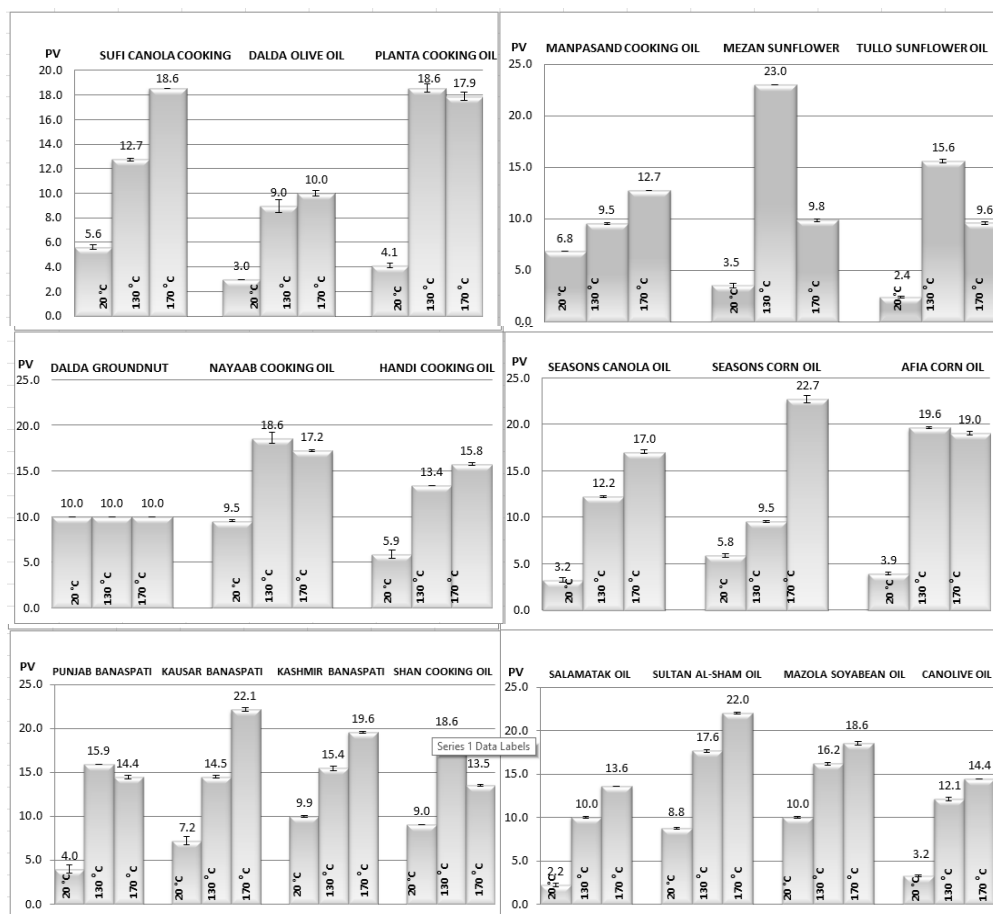


Fig. 1. Change in PV of different oils at different temperatures.

Table 2. Percentage increase or decrease of PV at 130 °C* and 170 °C**.

Oil Sample	Increase or decrease of PV (%) at 130 °C*	Increase or decrease of PV (%) at 170 °C**
Sufi Canola Cooking	127.7	231.5
Dalda Olive Oil	201.8	236.0
Planta Oil	350.8	334.3
Manpasand Oil	40.3	87.7
Mezan Sunflower	553.5	179.4
Tullo Sunflower	556.8	303.1
Dalda Groundnut	0.0	0.0
Nayaab Oil	95.1	80.5
Handi Oil	127.4	167.8
Seasons Canola Oil	276.8	425.0
Seasons Corn Oil	63.0	287.5
Afia Corn Oil	400.0	384.5
Punjab Banaspati	301.0	264.9
Kausar Banaspati	101.2	207.2
Kashmir Banaspati	55.2	96.8

Shan Oil	106.7	50.3
Salamatak Oil	354.5	518.2
Sultan Al-Sham Oil	101.2	150.8
Mazola Soyabean Oil	61.7	85.6
Canolive Premium Oil	274.5	345.4

*(PV(130°C)- PV(20°C))*100/PV(20°C); ** (PV(170°C)- PV(20°C))*100/PV(20°C).

Oxidative stability of oils is defined as the resistance to oxidation during processing and storage (Guillen and Cabo, 2002), which can be expressed as the period of time necessary to attain the critical point of oxidation, depending on sensorial change or a sudden acceleration of the oxidative process (Silva *et al.*, 2001). Low-molecular-weight off-flavor compounds are produced during oxidation, and off-flavor compounds make oil less acceptable to consumers or for industrial use as a food ingredient. Furthermore the oxidation of oil also destroys essential fatty acids and produces toxic compounds and oxidized polymers. Oxidation of oil is very important in terms nutritional quality, and toxicity of edible oils. Our study shows the PV and the percentage increase and/or decrease of the PV value in different brands of oils. Different brands of canola oil including Shan, Nayaab, Handi, Sufi, seasons canola all showed different peroxide value though the values are close to each other (see Fig. 1). The difference in the values is due to many factors. The peroxide value is affected by packaging also. Transparent plastic bottles are more exposed to sunlight which causes photo-oxidation. Tin packed cooking oils are safe from photo-oxidation. Another factor is due difference in conditions and climate of area where the process of refinement takes place. More over storage time also has an effect on the quality of oil.

The results of our study showed higher % increase in the PV values over 20°C of two brands of sunflower cooking oil namely Tullo sunflower cooking oil and Mezan sunflower cooking oil (Table 1). Both oils show an increasing POV at 130°C, which decreases at 170°C. Another study gives the same results of PV for four different brands of sunflower oil (Al-Fatlawi and Abbas, 2010) with a slight difference in value but the same trend. This difference could be due to some other factors like exposure to light and air and oil refining method. Because oxidation of oxygen occurs in the presence of light, the packaging is very important. Transparent plastic bottles may increase oil oxidation. Incorporation of different preservatives (UV-absorbers) such as Tinuvin 234 (2-(2-hydroxy-3,5-di(1,1-dimethylbenzyl)phenyl) benzotriazole) or Tinuvin 326 (2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzo-triazole), in transparent plastic bottles improved oxidative and sensory stability of soybean oil under light exposure (Pascall *et al.*, 1995; Azeredo *et al.*, 2003). Oxidation of oils often takes place when oil, oxygen, and catalysts are in contact. Both concentration and type of oxygen affect the oxidation of oils. Oxygen in oil is dependent on its partial pressure in the headspace of the oil (Andersson and Lingnert, 1998). When the partial pressure of oxygen in the headspace is then higher amount of oxygen is dissolved in the oil, which leads to increase oxidation of the oil (Min and Wen, 2006). Edible oils naturally contain antioxidants such as tocopherols, -trienols, phenolic compounds, carotenoids and sterols. These are intentionally added to oils for improvement of its oxidative stability. Metal chelators such as citric acid, phosphoric acid, ascorbic acid, and EDTA decrease oil oxidation (Halliwell *et al.*, 1995). Citric acid improves the sensory quality of soybean oil containing 1 ppm iron during storage at 55 °C (Min and Wen, 2006). Citric acid is also very often added to oil in the field to reduce its oxidation during storage before processing (Min and Wen, 2006). Vitamin E also acts as an antioxidant and is most common added in vegetable oils.

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