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The Effect of Bleaching Process on the Physical and Chemical Characteristics of Canola and Sunflower Seed Oils

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ABSTRACT: Bleaching process is an essential stage in the refining of vegetable oils and fats. In this process the colour and the primary and secondary oxidation products are removed by the treatment with the acid activated bleaching earth .The aim of this project is to understand the effect of bleaching on the physical characteristics and chemical constituents of neutralized canola and sunflower seed oils. Canola and sunflower seed oils were bleached at 100^o C for 30 minutes. The results indicated that there were significant reductions in peroxides and red and yellow colours of the oils. The induction period representing the oil resistance to oxidation was improved however the acidity was increased that might be due to the nature of the acid activated earth that has caused slight hydrolysis. Slight changes in fatty acid composition was observed that was due to the oxidation of poly unsaturated fatty acids namely linoleic acid in both oils. Some reduction in the total non saponifiable matter was observed. This might be due to the oxidation of tocopherols and changes of the sterols structures due to their conversion to steroidal hydrocarbons.

Keywords: *Bleaching, Canola oil, Sunflower Seed Oil.*

Introduction

Oils and fats are refined in order to remove the undesirable impurities with the minimum damage to the desirable components present either as triglycerides or compounds that might be solubilised in the substrate. Bleaching is an essential parts of refining operation where the colour and oxidation products are removed by the aid of bleaching earth (Baileys, 2002). Although one of the main object of bleaching earth is the removal of natural pigments present as chlorophylls and carotenoids but some other colouring matter formed as the result of heat treatment of the seeds and oil due to fatty acid oxidation are also removed (Naji *et al*., 2010).

The natural bleaching earth or fullers earth is mainly consisted of hydrated aluminium silicate with some other compounds. The earth is activated with Sulphuric or Hydrochloric acids and the acid activated earth depending on the degree of activation and composition is used for different types of oils and fats (Mirnezami, 2010).

Although the earth is employed to remove the colour and oxidation matter but sometimes at elevated temperatures might exert and cause changes in the chemical constituents of the oil namely the sterols, the major fraction present in the non-saponification matter and other related fractions .When the oils are bleached at high

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temperature some of the sterols are converted to hydrocarbons as they lose water and steroidal hydrocarbon are formed.

The effects of refining operations namely bleaching with fullers' earth and acid activated earth were investigated by Ghavami *et al*. (2003). It was concluded that free fatty acids, peroxides, phospholipids, induction period ,colour, metals, non-saponifiable matters and tocopherols were reduced in the refining operations and indicated that acid activated earth; fulmont AA, had a major role in the removal of pigments and primary and secondary oxidation products. Therefore the aim of this project is to evaluate the effect of bleaching process on the physical and chemical characteristics of canola and sun flower seed oils.

Materials and Methods

Both canola and sunflower seed oils prior and after bleaching operation were donated by Behshahr edible oil Industry, Tehran. The non saponifiable matter of the oils were isolated and determined according to AOAC standard method; 933.08 by alcoholic potassium hydroxide saponification of the oil followed by the extraction of the non saponifiable matter with ether. Colour measurements were carried out by Lovibond Tintometer model F according to AOCS standard method CC 13e-92. Acid value was obtained by dissolving the oil in ethanol and ether and titrating the solution with standard NaOH using phenolphthalein as indicator according to AOCS standard method 940.28.

Peroxide value was determined by dissolving the oil in acetic acid and chloroform and titrating the solution with sodium thiosolphate using starch indicator according to AOCS standard method Cd8-53.

Induction period measuring the secondary oxidation products was determined by Rancimat model 743 apparatus at 110^{o} C with an air flow rate of 20 l/h according to the Iranian standard method 3734.

Fatty Acid composition of the oils were determined by the formation of their methyl esters according to AOAC standard method 969.33 and injection of the methyl esters onto a GC equipped with a flame ionisation detector and a 30 m DEGS capillary column according to AOCS standard method 91-Cele.

In order to identity the sterols and tocopherols, the non saponifiable matter was spotted on a 0.5mm thickness silica gel G type 60 plate and developed in a TLC tank using hexane: ether (4:1) as developing solvents and finally spraying the plate with 0.01% Rhodamin 6G in ethanol. The NSM was fractionated into numbers of chemical classes of compounds consisting of different components. The sterols were isolated and identified according to AOAC standard method 970.51 by injection of the isolated sterol fraction into a GC equipped with SE54 capillary column and flame ionisation detector. Finally the tocopherols were identified by HPLC apparatus according to AOCS standard method Ce 8-89

Statistical analyses were carried out using SPSS software and Duncan test. Analysis of variance (ANOVA) was applied to detect significant differences.

Results and Discussion

Table 1 presents the fatty acid composition of both neutralized and bleached canola and sunflowers seed oils.

Table 1. Fatty acid composition of neutralized and bleached canola (NCO, BCO) and sunflower seed (NSFSO, BSFSO) oils

Fatty acid	NSFSO	BSFSO	NCO	BCO
C16:0	5.81	5.96	4.89	5.25
C18:0	3.35	3.65	1.90	2.06
C18:1	23.81	25.53	56.42	58.00
C18:2	65.73	63.12	26.16	24.27
C18:3	0.38	0.65	8.60	8.55
Other	0.92	1.09	2.03	1.87

Oleic acid followed by linoleic acid are the predominant fatty acids in canola. There is an increase in the concentration of saturated and mono unsaturated fatty acid in canola while the polyunsaturated fatty acids have been reduced as the result of bleaching process. This might be due to the higher stability of saturated and mono unsaturated fatty acids as compared to the polyunsaturated fatty acids and since bleaching is carried out under reduced pressure (< 5 mmHg) and the fatty acids composition is based on the percent of fatty acids in the oil, the losses of polyunsaturated fatty acids has caused an increase in the composition of saturated fatty acids. Similar observations are made in sunflower seed oil where linoleic acid is the predominant fatty acid. The two substrates examined might be employed for different practices in the oil industries.

Fig 1 shows the removal of red and yellow colours from canola and sunflower seed oils. The use of acid activated earth such as tonsil and fulmont AA are quite effective not only in the removal of pigments but also the removal of substances produced as the result of fatty acid oxidation.

This finding is in consistent with the works carried out by other researchers (Ghavami *et al.*, 2003) who studied the effect of refining operations on soya bean oil.

The fatty acid values of both oils have increased as the result of bleaching. This might be due to the nature of bleaching earth that is activated by the acid and the duration and temperature of the treatment. The acid value will be decreased to nil in due course when the oils are subjected to deodorisation process.

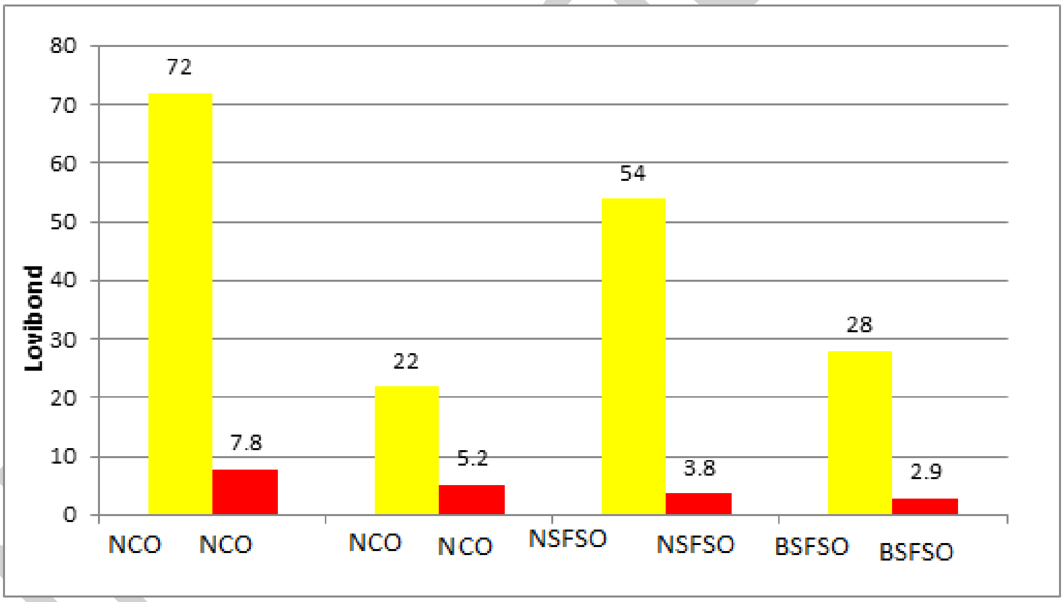

Fig. 1. The effect of bleaching on red and yellow colours of canola and sunflower seed oils.

Table 2. The effect of bleaching process on the chemical characteristics of canola and sun flower seed oils.

Properties	NSFSO	BSFSO	NCO	BCO
Acid value (mg/g)	0.51	0.63	0.75	0.93
%FFA(oleic)	0.25	0.31	0.37	0.46
Peroxide value (meq/kg)	10.26	6.11	11.81	8.37
Nonsaponifiable matter (%)	2.43	2.82	3.35	4.50
Sterols (ppm)	3043	2231	7208	5962
Tocopherols (ppm)	608.34	352.6	575.81	352.6

The peroxide values indicating the primary oxidation products have been decreased by approximately 30% and 40% for canola and sunflower seed oils respectively. This might be due the nature of the earth employed and the fact that peroxides are unstable at high temperatures and are decomposed above 70C^{o} to form aldehyde and ketones and some other secondary oxidation products. Since the temperature employed for bleaching process is 100^{o} C and the procedure is carried out under vacuum (5mmHg), therefore apart from the decomposition of peroxides some compounds might have been driven out of the system by the strong vacuum.

The induction period of both oils have been increased to some extent. This is due to the removal of some prooxidants as the result of bleaching. The non-saponificable matter of the oils consisting of sterols, 4methysterols, triterpene alcohols, tocopherols and hydrocarbons have been reduced as the result of bleaching treatments. The results are in consistent with the work carried by Ghavami *et al*. (2003) and Gutfinger and letan (1974).

The sterol fraction of the non saponificable matter constitutes the major fraction of the oils examined. The quantity of the sterols is reduced as the result of bleaching. This might due to the changes that might have occurred as the result of the treatments of the oils at elevated temperature with the bleaching earth. The treatment might have caused the loose of water from the sterols and resulted in the formation of steroidal hydrocarbon (Johansson & Hoffman, 1979).

The predominant sterol present in canola and sunflower seed oils was β-sitosterol as this is the case for all the vegetable oils. The results also indicated that the tocopherols were reduced as the result of bleaching process and γ and α tocopherols were the predominate tocopherols in canola and sun flower seed oils respectively.

Conclusion

It might be concluded that bleaching of canola and sunflower seed oils using acid activated earth effectively removes the colour and oxidation products to a desired degree. Some wanted compounds namely tocopherols are removed but the quantity remained after bleaching process and even after deodorisation stage is sufficient to stabilize the oils. The sterols are reduced and some are converted to the steroidal hydrocarbons as the result of bleaching operation carried out at elevated temperature and the treatment with acid activated earth.

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