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EFFECT OF DIFFERENT ALKALI CONCENTRATIONS DURING THE REFINING PROCESS ON THE FATTY ACID COMPOSITION OF SUNFLOWER AND SOYBEAN OILS

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Abstract

The effect of NaOH and KOH at concentrations of 12, 14 and 16 Bé° during the refining of sunflower and soybean oils on the fatty acid composition was studied using GLC technique. The quantity of linolenic, linoleic, oleic, palmitic and stearic acid as well as the USFA (unsaturated fatty acids): SFA (saturated fatty acids) ratio were measured.

Only slight changes in the quantity of individual fatty acids were found particularly at higher alkali concentrations. The changes in the USFA : SFA ratio compared with crude or semirefined oil were not significant.

Keywords: soybean oil, sunflower oil, refining, fatty acids, alkali treatment.

Introduction

The physical and nutritional properties of edible oils are strongly connected with the chemical composition, particularly with the concentration of individual fatty acids and their ratios. So it is understandable that the fatty acid composition of edible oils is widely investigated and controlled. Concerning the fatty acid composition it is generally stated that five fatty acids (palmitic, stearic, oleic, linoleic and linolenic acid) are the main components of triglycerides. Their total quantity amounts to about $90 - 95$ % of the fatty acid content [1, 2, 3, 4, 5, 6, 7]. These general data are valid for the Egyptian and Hungarian sunflower and soybean oils, too [2, 7, 8, 9, 10].

During the processing of edible oils some chemical and thermal treatments are used, which may affect the quantity of individual fatty acids.

This work was an attempt to study the effect of alkali refining on the fatty acid composition of sunflower and soybean oils after bleaching.

Materials and Methods

Sampling

The samples used in this work were local crude soybean oil and semi-refined sunflower oil which was imported from the USA by Misr Oils and Soap Company in Sandoub, Mansoura, Egypt.

Process of Refining

Degumming: The degumming was carried out according to the method suggested by WIEDERMANN [17].

Dewaxing: The method used in this work was desribed by HARALDSSON [18].

Alkali refining: Alkali refining for dewaxed oil was performed according to the method of WIEDERMANN [17] as follows: The dewaxed oils were heated to 33 °C then treated with alkali solutions of different concentrations. The refining losses were determined for the different samples.

Sodium hydroxide and potassium hydroxide were used with both oils (i.e. sunflower and soybean oils) at concentrations of 12, 14, 16, 18 and 20 Bé°, also sodium carbonate and sodium bicarbonate were used, with both oils at concentrations of 12, 14, 16 and 20 Bé°. The alkalies were added in equivalent amounts to the free fatty acid present in dewaxed warm sunflower or soybean oil. Both oils and alkali were heated at 75 °C. Then, all the samples were centrifuged to separate the soapstock from the neutral oil. The neutral oil was dissolved in ether, transferred to a separatory funnel for washing with saturated sodium chloride solution to remove the formed soap. The etheral oil was dried over anhydrous sodium sulphate, filtered and the ether was evaporated at 40 °C.

The refining loss was estimated for each treatment followed by the determination of physical and chemical properties.

Bleaching: Bleaching was carried out for the neutral oil according to the method of WIEDERMANN [17].

Gas-liquid Chromatographic Analysis

The samples under investigation were methylated by diazomethane prepared from methylamine according to the method described by VOGEL [11].

The fatty acid methyl esters obtained from different samples were analyzed using a Pye Unicam GCV gas chromatographic system according to the method described by FARAG et al [12], under the following conditions:

- Column PEGA 10% (Polyethylene glycol adipate 10%)
- Chart speed 0.5 cm/min
- Initial temperature 60 °C, final temperature 190 °C, heating rate 8 °C/min
- Detector temperature 220 °C
- Injection temperature 220 °C
- Flow rates of gases: nitrogen 30 ml/min, hydrogen 33 ml/min and air 330 ml/min.

The retention times of fatty acid methyl esters were calculated. Peak identification was carried out by comparison of the retention time for each peak with the standard chromatogram.

The percentage of each acid was obtained by using triangulation method and the relative proportions of the individual compounds were estimated as the ratio of the partial areas to the total area.

Results and Discussion

The fatty acid composition of sunflower oil (refined and treated with NaOH and KOH) is shown in *Table 1* As it is seen the quantities of most typical fatty acids are in good agreement with literature data [1, 2, 3, 5, 13]. The ratio of USFA to SFA was high (nover 7 : 1).

No significant differences were observed between the fatty acid composition of the bleached oil for three bleached samples and those obtained for semi-refined sunflower oil.

The results in *Table 1* indicate that the percentages of saturated fatty acids were slightly higher than the values of the untreated semi-refined oil, whereas the amounts of unsaturated fatty acids were slightly lower than those of semi-refined oil, except for treatment with 12 Bé° NaOH which was very close to that of untreated semi-refined sunflower oil (*Table 1*).

No remarkable differences were found in the relative percentages of fatty acids between refined or the semi-refined sunflower (*Table 1*) oil.

Generally, it may be concluded that the fatty acid content was slightly lower than that of the semi-refined sample, except for the sample treated

Table 1
Fatty acid composition of semi-refined sunflower oil and bleached samples which were previously refined using 12, 14 and 16 Bé° of NaOH and KOH

Peak No.	Fatty acids	Semi refined oil	Bleached samples					
			NaOH concentration			KOH concentration		
			12 Bé°	14 Bé°	16 Bé°	12 Bé°	14 Bé°	16 Bé°
1	$C_{16:0}$	7.14%	7.46%	7.83%	7.58%	7.10%	7.19%	7.24%
2	$C_{18:0}$	4.55%	4.26%	4.76%	4.50%	4.56%	4.20%	4.23%
3	$C_{18:1}$	24.78%	24.66%	24.25%	24.73%	24.84%	24.87%	24.67%
4	$C_{18:2}$	63.53%	63.62%	63.15%	63.19%	63.50%	63.74%	63.86%
	Sat. FA*	11.69%	11.72%	12.59%	12.08%	12.66%	11.39%	11.47%
	Unsat. FA**	88.31%	88.28%	87.41%	87.92%	88.34%	88.61%	88.53%
	Ratio of*** Unsat./Sat.	7.55	7.53	6.94	7.28	7.58	7.78	7.72

* Sat. FA = Saturated fatty acids.
** Unsat. FA = Unsaturated fatty acids.
*** Unsaturated/Saturated fatty acids ratio

with 12 Bé° KOH which was very close to that of the semi-refined oil (i.e. 11.66%). On the other hand, total unsaturated fatty acids were slightly higher than that of semi-refined oil, except for the sample treated with 12 Bé° KOH which was similar to that obtained for the semi-refined (i.e. 88.34% and 88.31% , respectively). Thus the unsaturated/saturated ratio for the sample treated with 12 Bé° KOH was close to that of semi-refined oil while in the case of 14 and 16 Bé° KOH the values were slightly higher than those obtained for semi-refined sunflower oil.

It can be concluded that NaOH at concentrations higher that 12 Bé° may cause breakdown of the unsaturated fatty acids. On the other hand, the use of KOH with concentrations higher than 12 Bé°, may cause breakdown of the saturated fatty acids [7], when both of alkalis were used as an alkali agent in the refining process before bleaching of sunflower oil.

The fatty acid composition of treated soybean oils are summarized in *Table 2* The total saturated fatty acids in crude oil amount to 15.00% and the total unsaturated fatty acids to 85.00%, therefore the unsaturated/saturated fatty acid ratio was 5.67. The results agree with those obtained by JUNG et al. [14]. WARNER et al. [13] and ZEIN EL-DEIN [9] found an average value of 5.45 for this ratio.

Table 2
Fatty acid composition of crude soybean oil and bleached samples which were previously refined using 12, 14 and 16 Bé° of NaOH and KOH

Peak No.	Fatty acids	Semi refined oil	Bleached samples					
			NaOH concentration			KOH concentration		
			12 Bé°	14 Bé°	16 Bé°	12 Bé°	14 Bé°	16 Bé°
1	$C_{16:0}$	10.84%	10.81%	10.95%	10.32%	10.99%	10.96%	10.25%
2	$C_{18:0}$	4.16%	4.11%	4.63%	4.05%	4.61%	4.15%	4.14%
3	$C_{18:1}$	24.30%	24.57%	24.24%	24.83%	24.17%	24.76%	24.41%
4	$C_{18:2}$	51.81%	51.83%	51.61%	51.86%	51.56%	51.68%	51.40%
5	$C_{18:3}$	8.89%	8.68%	8.57%	8.94%	8.67%	8.45%	8.80%
	Sat. FA*	15.00%	14.92%	15.58%	14.37%	15.60%	15.11%	14.39%
	Unsat. FA**	85.00%	85.08%	84.42%	85.63%	84.40%	84.89%	85.61%
	Ratio of*** Unsat./Sat.	5.67	5.70	5.42	5.86	5.41	5.62	5.95

* Sat. FA = Saturated fatty acids.
** Unsat. FA = Unsaturated fatty acids.
*** Unsaturated/Saturated fatty acids ratio

The bleached soybean oil which was treated with 12 Bé° alkali had the same percentage of saturated and unsaturated fatty acids. These results agree with those mentioned by ZEIN EL-DEIN [9].

14 Bé° NaOH slightly increased total saturated fatty acid content (15.58%) while the total unsaturated fatty acid content decreased (84.42%).

In case of treatment with 16 Bé° NaOH, the percentage of saturated fatty acids increased, while the same values decreased on treatment with 14 Bé° NaOH as shown in *Table 2*.

Similar behaviour was noticed in case of NaOH with the same oil (*Table 2*), i.e. a slight increase in the saturated fatty acid content with slight decrease in the unsaturated fatty acid content in the case of 12 Bé° KOH. In contrast, with 16 Bé° KOH a slight increase in the total unsaturated fatty acid content and a slight decrease in the total saturated fatty acid content were obtained.

Finally, no significant changes in the relative percentage of fatty acids were found in the case of using 14 Bé° KOH.

In general, no significant differences were observed in the composition of fatty acids in sunflower or soybean oil after alkali refining. This findings was similar to that reported by MOUNTS [15], CAMPBELL [16] and ZEIN EL-DEIN [9].

Therefore, the door is still open to decide which alkali and its concentration is suitable for the refining process.

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