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EFFECT OF REFINING ON THE PHYSICAL AND CHEMICAL PROPERTIES OF SUNFLOWER AND SOYBEAN OILS

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Abstract

The effect of different refining processes on the physical (colour, specific gravity, refractive index) and chemical (acidity, saponification number, ester number, iodine value, peroxide value, unsaponifiable matter) properties of sunflower and soybean oils was studied.

Degumming and dewaxing procedures caused negligible differences in the properties mentioned above.

Treatment with NaOH or KOH of 12, 14 and 16 Bé° concentration resulted in a reasonable refining loss and residual acidity. Using Na_2CO_3 and $NaHCO_3$ or KOH and NaOH of higher concentration (over 16 Bé°) caused high refining losses and unacceptable residual acidity.

Keywords: soybean oil, sunflower oil, refining, physical properties, chemical properties.

Introduction

Vegetable oils including sunflower and soybean oils play an important role in Egyptian and also Hungarian nutrition (particularly sunflower oil).

The effect of the refining process on the properties of edible sunflower and soybean oils was studied by numerous researchers [1], [2], [3], [4], [5], [6]. Changes in colour, acidity, unsaponifiable matter were first detected. Although some general rules concerning optimal processing are known, the elaboration of an optimal technology applicable to a given edible oil needs further specialized investigations. The aim of the research described in this paper was to obtain such special data.

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 [6].

Dewaxing: The method used in this work was described by HARALDSSON [13].

Alkali refining: Alkali refining of dewaxed oil was performed according to the method of WIEDERMANN [6] as follows: The dewaxed oils were heated toz 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) in concentrations of 12, 14, 16, 18 and 20 Bé°, also sodium carbonate and sodium bicarbonate were used, with both oils in concentrations of 12, 14, 16 and 20 Bé°. Such alkalies were added in amounts equivalent to the free fatty acid present in dewaxed warm sunflower or soybean oil. Both oils and the alkali were heated to 75°C, then 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: The bleaching of the neutral oil was carried out according to the method of WIEDERMANN [6].

Analytical Procedures

Colour determination: The colour of the various samples was measured using the Wesson method (Lovibond Tintometer, Model E, Salisbury, England), using a 2.5 inch cell according to A.O.C.S. official methods [7].

Specific gravity: The specific gravity was determined using a pycnometer as suggested by A.O.C.S. official methods [7] at 25°C.

Refractive index (RI): The refractive index of the crude, semi-refined degummed, dewaxed, refined and bleached sunflower and soybean oils was determined according to the A.O.C.S. official method [7], using an Abbe Refractometer at 20°C.

Acid value (AV) and free fatty acids (FFA): The acid value and free fatty acid content (calculated as oleic acid percentage) were determined according to the AOCS official methods [7].

Saponification value (Sap.V.) and Ester number (EN): The saponification value was determined according to the official methods of analysis of A.O.C.S. [7].

The ester number is the difference between the saponification value and the acid value.

Iodine value (IV): The determination of iodine value was carried out according to Wij's method in AOCS official methods [7].

Peroxide value (PV): The peroxide values of the samples were determined according to the AOCS official methods [7].

Results and Discussion

The physical and chemical properties of semi-refined sunflower and crude soybean oil are shown in *Table 1.* The data are generally in agreement with literature data.

In *Table 2* are summarized the same properties after degumming and dewaxing. Comparing these data with those in *Table 1*, it could be stated that degumming and dewaxing caused only insignificant changes.

Table 1
Some physical and chemical properties of semi-refined sunflower and crude soybean oils

Properties	Sunflower oil	Soybean oil
Colour*	$Y = 30$, $R = 2.1$	$Y = 30$, $R = 2.5$
Specific gravity at 25°C	0.925	0.926
Refractive index at 25°C	1.4722	1.4660
Acid number	3.60	0.88
Acid value (as oleic acid %)**	1.8%	0.44%
Saponification number	192.6	190.5
Ester number	189.0	189.62
Iodine value	132.31	124.56
Peroxide value	13.5	12.81
Unsaponifiable matter	0.53%	1.76%

* The colour was determined using a Lovibond tintometer as red units, with the yellow readings.
** Acid value (as oleic acid %) = Free fatty acid % (as oleic acids %).

Table 2
Some physical and chemical properties of dewaxed sunflower and crude soybean oils

Properties	Sunflower oil	Soybean oil
Colour*	$Y = 30$, $R = 1.7$	$Y = 30$, $R = 1.3$
Specific gravity at 25°C	0.924	0.925
Refractive index at 25°C	1.4725	1.4659
Acid number	3.88	0.98
Acid value (as oleic acid %)**	1.95%	0.49%
Saponification number	192.16	191.00
Ester number	188.28	190.02
Iodine value	131.00	124.75
Peroxide value	12.48	11.84
Unsaponifiable matter	0.51%	1.72%

Alkali Refining of the Oils

The success and applicability of any alkali refining process is related directly with the minimum refining loss, i.e. a maximum yield of refined oil free from acidity must be obtained.

Sodium hydroxide as a refining agent

It is apparent that caustic soda (NaOH) solutions of 12, 14 and 16 Bé° concentration have almost the same effect on the neutralization of sunflower and soybean oils and resulted low residual acidity and losses after refining as shown in *Table 3*.

Table 3

Residual acidities and refining losses in sunflower and soybean oils after their alkali refining with sodium hydroxide

Concentration of NaOH in Bé°	Sunflower oil		Soybean oil	
	Refining loss %	Residual acidity %	Refining loss %	Residual acidity %
12 Bé°	7.11	0.12	5.73	0.10
14 Bé°	7.15	0.10	5.50	0.11
16 Bé°	7.13	0.11	5.29	0.12
18 Bé°	8.57	0.20	6.80	0.18
20 Bé°	10.81	0.19	7.10	0.19

It is clear that concentrations of 18 and 20 Bé° were not suitable for sunflower and soybean oils because of the higher residual acidity and refining loss than with other treatments (*Table 3*).

Potassium hydroxide as a refining agent

The refining losses and residual acidities are summarized in *Table 4*.

Table 4

Residual acidities and refining losses in sunflower and soybean oils after their alkali refining with potassium hydroxide

Concentration of KOH in Bé°	Sunflower oil		Soybean oil	
	Refining loss %	Residual acidity %	Refining loss %	Residual acidity %
12 BÉ°	8.65	0.13	5.52	0.09
14 Bé°	8.35	0.14	5.69	0.08
16 Bé°	8.98	0.12	5.41	0.10
18 Bé°	9.45	0.16	7.10	0.12
20 Bé°	9.79	0.17	7.80	0.14

The data obtained indicate that the optimum concentration in the case of sunflower oil was not exactly detected, but the suitable concentration may be between 12 to 16 Bé°.

It was also clear from the same table that the concentrations of 18 or 20 Bé° should not be chosen due to the high residual acidity and refining loss for both sunflower and soybean oils.

Comparing data in *Tables 3* and *4*, it could be noticed that NaOH solutions were relatively more suitable in respect of the refining loss after neutralization than KOH.

The above finding directed our attention to the use of other alkalies to overcome the difficulties in the choice of the suitable concentration of the alkali and, on the other hand to the minimization of the values of refining loss and residual acidity. For the above mentioned reasons sodium carbonate and bicarbonate were tested as refining agents.

Sodium carbonate and bicarbonate as refining agents

The data in *Table 5a* indicate that the refining loss and residual acidity for all treatments were higher than those obtained when using the same concentrations of NaOH or KOH with sunflower or soybean oils (*Tables 3* and *4*), but the residual acidity was higher for 12 Bé° concentration of Na_2CO_3 than that obtained at the same concentration of NaOH or KOH (*Tables 3* and *4*). These results agree with those mentioned by BAILEY [10].

It is worth stating that Na_2CO_3 or $NaHCO_3$ did not minimize the refining losses and/or residual acidities. This may be due to the reaction which may take place between weak alkali and weak acid.

It can be concluded from the results presented in *Tables 3, 4* and *5* that NaOH and KOH were superior to other agents in the refining process, especially at concentrations of 12, 14 and 16 Bé°.

Physical and Chemical Properties of the Oils after Alkali Refining

The physical and chemical properties of the refined oils obtained after treatment with solutions of alkali 12, 14 and 16 Bé° concentrations were determined to evaluate and compare the results with those previously found for semi-refined and crude oils.

Table 5
Residual acidities and refining losses in sunflower and soybean oils after their alkali refining with

a) Sodium carbonate (Na_2CO_3)

Concentration of Ha_2CO_3 in Bé°	Sunflower oil		Soybean oil	
	Refining loss %	Residual acidity %	Refining loss %	Residual acidity %
12 Bé°	9.96	0.88	4.50	0.22
14 Bé°	9.16	0.82	7.61	0.36
16 Bé°	8.90	0.79	7.44	0.43
20 Bé°	7.39	0.84	8.70	0.19

b) Sodium bicarbonate ($NaHCO_3$)

Concentration of $NaHCO_3$ in Bé°	Sunflower oil		Soybean oil	
	Refining loss %	Residual acidity %	Refining loss %	Residual acidity %
12 Bé°	8.95	0.99	5.10	0.25
14 Bé°	8.87	0.93	8.13	0.52
16 Bé°	8.48	0.99	7.07	0.49
20 Bé°	6.90	0.98	9.80	0.44

Refined samples of sunflower oil:

In *Table 6* are summarized the physical and chemical properties of sunflower oil after refining. It is clear that alkali refining with NaOH or KOH resulted less intense colours compared with semi-refined or dewaxed oils as shown in *Tables 1* and *2*.

The specific gravities are lower than the values for semi-refined and dewaxed oils. These reductions in the specific gravity may be due to the removal of some polar compounds from the oil by alkali refining. These results are in agreement with those mentioned by MOUNTS [2].

A slight increase in refractive index induced by alkali refining may be to due the exclusion of some saturated fatty acids and/or compounds which could affect this property. The results agree with those stated by MOUNTS [2].

The saponification values obtained (around 192.60) were similar to the values of the semi-refined oils (i.e. 192.6, *Table 1*). On the other hand.

the ester number was slightly higher than that obtained for semi-refined or dewaxed oil (*Tables 1* and *2*).

In the case of NaOH, the iodine values of the refined sunflower oil remain nearly the same as the value obtained for semi-refined and dewaxed sunflower oils (*Tables 1* and *2*). It is worth mentioning that the iodine values show similar tendency to the results of refractive index for the same sample.

The peroxide values were close to those obtained for semi-refined and dewaxed sunflower oils (*Tables 1* and *2*).

The unsaponifiable matters of sunflower oil decreased by about 15% compared with dewaxed oil (*Table 6*) and by about 14% compared with semi-refined sunflower oil (*Table 1*). These results agree with those published by KHALIL [8].

Table 6

Physical and chemical properties of sunflower oil refined with 12, 14 and 16 Bé° solutions of NaOH and KOH

Properties	The concentration of alkali in Bé°					
	NaOH			KOH		
	12 Bé°	14 Bé°	16 Bé°	12 Bé°	14 Bé°	16 Bé°
Colour	R, 0.4	R, 0.3	R, 0.4	R, 0.8	R, 0.7	R, 0.5
Specific gravity at 25°C	0.922	0.923	0.922	0.922	0.923	0.921
Refractive index at 25°C	1.4725	1.4727	1.4727	1.4727	1.4728	1.4728
Acid number	0.24	0.20	0.22	0.26	0.28	0.24
Acid value (as oleic acid %)	0.12%	0.10%	0.11%	0.13%	0.14%	0.12%
Saponification value	192.76	192.66	192.83	192.25	192.38	192.96
Ester number	192.52	192.46	192.61	192.99	192.10	192.72
Iodine value	131.16	131.34	133.54	133.48	133.15	133.15
Peroxide value	11.25	12.67	12.63	13.20	11.97	11.38
Unsaponifiable matter	0.48	0.47	0.48	0.46	0.47	0.47

Refined samples of soybean oil:

The results are shown in *Table 7*. The colour intensities were lower after treatment with both alkalies than the values obtained for crude soybean oil.

The specific gravity and refractive index were similar to those obtained for crude and/or dewaxed soybean oils (*Tables 1* and *2*). The results

Table 7
Physical and chemical properties of soybean oil refined with 12, 14 and 16 Bé° NaOH and KOH solutions

Properties	The concentration of alkali in Bé°					
	NaOH			KOH		
	12 Bé°	14 Bé°	16 Bé°	12 Bé°	14 Bé°	16 Bé°
Colour	R, 1.2	R, 1.1	R, 1.2	R, 0.9	R, 0.8	R, 0.5
Specific gravity at 25°C	0.926	0.925	0.926	0.925	0.924	0.925
Refractive index at 25°C	1.4662	1.4659	1.4659	1.4658	1.4659	1.4658
Acid number	0.20	0.22	0.24	0.18	0.16	0.20
Acid value (as oleic acid %)	0.10%	0.11%	0.12%	0.09%	0.08%	0.10%
Saponification value	190.85	191.01	190.99	190.91	190.87	191.01
Ester number	190.65	190.79	190.75	190.73	190.71	191.81
Iodine value	124.91	125.03	124.99	124.89	124.98	124.96
Peroxide value	10.00	10.16	10.50	10.88	9.57	9.66
Unsaponifiable matter	1.67	1.68	1.66	1.67	1.69	1.66

are in agreement with those mentioned by ZEIN EL-DEIN [4]. Obviously the acid values decrease after alkali refining.

The results obtained for saponification, ester and iodine values were close to the values obtained for crude and dewaxed soybean oils (*Tables 1* and *2*).

The unsaponifiable matter (*Table 7*), decreased by 5% in all treated samples compared with crude or dewaxed soybean oils (*Tables 1* and *2*). These results agree with those found by GUTIFINGER and LETAN [9]. The peroxide value slightly decreased. These results indicate that the refining process does not affect the stability of the oils studied.

Physical and chemical properties of bleached oils:

Sunflower and soybean oil samples refined using NaOH and KOH at concentrations of 12, 14 and 16 Bé° were also subjected to bleaching. The results obtained are tabulated in *Tables 8* and *9*.

Bleached samples of sunflower oil:

Bleaching of refined sunflower oil resulted colourless products (*Table 8*), in agreement with the results mentioned by AOCS [7] and MOUNTS [2]. It

Table 8

Physical and chemical properties of bleached sunflower oil previously refined using 12, 14 and 16 Bé° solutions of NaOH and KOH

Properties	Bleached sunflower oil samples previously refined with NaOH			KOH		
	12 Bé°	14 Bé°	16 Bé°	12 Bé°	14 Bé°	16 Bé°
Colour	Zero	Zero	Zero	Zero	Zero	Zero
Specific gravity at 25°C	0.921	0.922	0.921	0.921	0.921	0.921
Refractive index at 25°C	1.4726	1.4725	1.4727	1.4727	1.4726	1.4727
Acid number	0.24	0.20	0.22	0.26	0.28	0.24
Acid value (as oleic acid %)	0.12%	0.10%	0.11%	0.13%	0.14%	0.12%
Saponification value	192.86	192.81	192.66	192.52	192.54	192.69
Ester number	192.62	192.61	192.44	192.26	192.26	192.45
Iodine value	131.16	131.27	133.40	133.46	133.23	133.15
Peroxide value	2.20	2.40	1.90	2.10	2.00	2.10
Unsaponifiable matter	0.44	0.43	0.42	0.43	0.41	0.42

Table 9

Physical and chemical properties of bleached soybean oil samples previously refined using 12, 14 and 16 Bé° NaOH and KOH solutions

Properties	Bleached sunflower oil samples previously refined with NaOH			KOH		
	12 Bé°	14 Bé°	16 Bé°	12 Bé°	14 Bé°	16 Bé°
Colour	Zero	Zero	Zero	Zero	Zero	Zero
Specific gravity at 25°C	0.925	0.926	0.925	0.926	0.925	0.924
Refractive index at 25°C	1.4661	1.4660	1.4660	1.4658	1.4661	1.4659
Acid number	0.20	0.22	0.24	0.18	0.16	0.20
Acid value (as oleic acid %)	0.10%	0.11%	0.12%	0.09%	0.08%	0.10%
Saponification value	190.76	190.81	190.79	190.83	190.69	190.68
Ester number	190.56	190.59	190.55	190.65	190.53	190.48
Iodine value	124.92	124.96	124.83	124.93	124.89	124.90
Peroxide value	1.80	1.70	1.90	1.70	1.90	1.80
Unsaponifiable matter	1.43	1.41	1.42	1.42	1.43	1.41

may be noticed that the method used for the extraction of oils was highly efficient and the oils were readily bleached.

It may be noticed that some other constant values of refined and bleached sunflower oil samples were similar to those obtained for semi-refined (*Table 1*), dewaxed (*Table 2*) and refined oil (*Table 6*), except the peroxide value and unsaponifiable matter which were lower for bleached oils than for semi-refined, dewaxed and refined oils (*Tables 1, 2* and *6*). These results agree with literature data [10, 11].

Bleached samples of soybean oil:

The results summarized in *Table 9* indicate that soybean samples were in general colourless after bleaching. The specific gravity, refractive index, acidity, saponification, ester and iodine value were similar to data obtained for crude, dewaxed and refined samples (*Tables 1, 2* and *7*) and in general the differences were insignificant.

A remarkable decrease in the peroxide value was observed after bleaching which may be due to the adsorption reaction of peroxide products with the bleaching agent during the process.

From the data in *Table 9*, it can be concluded that the average value of the unsaponifiable matter is 1.42%. Compared with the value in crude oil (1.76%) a loss of 19.32% can be found in the unsaponifiable matter. It is worth mentioning that the reduction of unsaponifiable content after bleaching due to the exclusion of a significant proportion of unsaponifiable matter agrees with the data published by HALLABO [12].

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