Technical

*Quality of Sunflower Oil Bleached during Deodorization

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ABSTRACT

Experiments with sunflower oil show that it is possible under certain conditions to bleach the oil during deodorization. The color of the oil bleached by deodorization is the same as that obtained with bleaching earth. Deodorization at 200 C yielded an oil with transparency at 455 nm of 78-84%. However, to obtain this degree of transparency, processing steps prior to deodorization must be efficient and not yield an oil with high levels of soaps and trace metals. Bleaching during deodorization. Data are presented that show the combined process yields an oil with better stability, higher tocopherol content and lower conjugated diene content. Oil processed in this manner has acceptable levels of soap, copper and iron. Sunflower oil with different degrees of oxidation levels has been processed to yield a satisfactory finished product.

INTRODUCTION

The process of removing pigments with bleaching earth is a common practice in refining vegetable oils. It is known that this process has advantages and disadvantages. The use of bleaching clay to remove pigments also reduces the soap and trace metal content of an oil which is desirable for improved quality and stability of the oil. However, bleaching also increases the level of conjugated dienes and reduces the concentration of tocopherol (1,2). These changes will produce a finished product with lower stability. Undesirable changes in oil during bleaching has been presented in earlier publications (3-7).

During bleaching, oil is absorbed by the bleaching clay and lost during clay removal. This significant loss plus the time and equipment required for bleaching with clay are reasons to develop an economical alternative process.

Some data have been presented in the literature concerning color changes during deodorization. Baldwin (8) indicated the color of oil becomes lighter during heating. Smidt (9) also showed that oil becomes lighter during deodorization from carotenoid degradation. Anderson (10) suggested that for bleaching during deodorization, it was necessary that the oil contain no oxidation products, soaps or trace metals.

Goldovsky and Nikitinskaja (11) determined the changes of color in sunflower oil during deodorization. They established color reduction would amount to ca. 50% for a high quality oil but only 7-17% for oil obtained from damaged seeds.

Oil bleaching during deodorization has been of interest in our laboratory for some time. Our initial publications were investigations with sunflower oil because we believed that a high-quality oil requires gentle treatment during refining to preserve its valuable components. Oil which is produced from high quality seeds by contemporary production processes may not have the quality of that produced when the bleaching and deodorization processes are combined into a single process.

Although our results indicate that an oil which is

bleached during deodorization is of high quality, previous publications (5,6,12) have indicated situations that must be solved (such as the presence of soap and metal traces) in order for the combined process of bleaching during deodorization to be successful. The quality of oil produced by standard unit processes has been compared to oil produced by the combined bleaching/deodorization process. Crude sunflower oil of various qualities (i.e., oils that had different degrees of oxidation and soap content) were used in these comparisons.

EXPERIMENTAL PROCEDURES

Materials and Methods

Investigations were made with various samples of neutralized sunflower oil. Data on the quality of these oils after neutralization are given in Table I.

For the investigation of oil quality, we used the standard methods elaborated in our previous papers (13,14). Cu and Fe content were determined by atomic absorption spectroscopy. The atomic absorption spectrophotometer used in this study was a Pye Unicam SP 90. The instrument was operated with a lamp current of 4-5 mA for Cu and 15 mA for Fe. The wavelength was 325.8 nm for Cu and 248.3 for Fe.

The standard working curves for Cu and Fe were prepared by dilution of the standard solutions. Samples for these analyses were obtained by coal-burning (20-30 g) in quartz glasses.

In Figure 1, the sequence of operations and working conditions for laboratory investigations of bleaching and deodorization of sunflower oil is given. As shown, the samples of neutralized oil were bleached in 2 ways. In the first case, oil was deodorized in a laboratory deodorizer (bleaching during deodorization) without previous bleaching, whereas in the second case, oil was bleached with 0.2% BRV bleaching earth of domestic production.

TABLE I

Characteristics of Neutralized Samples of Sunflower Oil

	Samples of sunflower oil ^a	
	Α	В
Free fatty acids (% of oleic acid)	0.12	0.11
Peroxide value (meq/kg)	10.5	6.9
Anisidine value	1.8	6.5
Oxidation value (2PV + AV)	22.8	20.3
Na-soap content (ppm)	60	14
Color-transparency (455 nm)-(%)	19.5	46.0
Copper content (ppm)	0.062	0.055
Iron content (ppm)	0.75	0.70

^aSample A was obtained by continuous refining; B was obtained by batch refining.

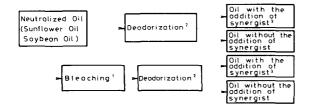


FIG. 1. Operations and working conditions of the laboratory refining of sunflower oil: 1-bleaching: t = 90 C, λ = 10 min, v = 0.2% BRV; 2-deodorization: t = 200 C, λ = 1 hr, V = 2% H₂0/h; 3-addition of 0.01% citric acid.

TABLE II

Soap Content of Sunflower Oil at Various Processing Stages

	Samples ^a (ppm)	
	Ā	В
Neutralized oil	60	14
Bleached oil with clay	37	2
Bleached and deodorized oil	32	0
Bleached during deodorization	52	0

^aSample A was obtained by continuous refining; B was obtained by batch refining.

The results given in this paper represent the mean value of several parallel examinations of bleaching and deodorization processes. The samples were prepared with and without the addition of synergists to the deodorized oil (Fig. 1).

In all of the samples, we have determined the soap content, metal traces, color and AOM-stability in order to obtain a more complete picture of the quality of the particular oil (15-18).

RESULTS AND DISCUSSION

The soap content at various processing steps is given in Table II. Bleaching with 0.2% BRV activated clay reduces the soap content of sample A ca. 40% and of sample B ca. 90%. However, bleaching during deodorization does not reduce the soap content as effectively as bleaching with activated clay. Therefore, bleaching during deodorization can only be applied if the soap content of the refined oil is less than 50 ppm; water-washing of refined oil is necessary to reduce the soap content to less than 50 ppm. Standard refining processes (18) require the soap content to be less

TABLE III

Copper and Iron Content of Sunflower Oil at Various Processing Stages

than 50 ppm. The use of citric acid as a synergist was found to decrease the soap content ca. 60-70%. Citric acid not only chelates trace minerals such as Fe and Cu, but also acts as an acidulant forming free fatty acids and citrate salts.

The Cu and Fe contents at various processing steps are given in Table III. Both trace minerals were found to be within the limits recommended for edible oils (19). At these low levels found in the neutralized oils, both bleaching processes had little effect upon their content.

In addition to removing soap and pigments by bleaching with activated clay, peroxide values (PV) were also decreased. The peroxide value of sample A was lowered from 10.5 meq/kg to 6.3 meq/kg during clay bleaching. Similar effects were observed for sample B in which the PV was lowered from 6.9 to 5.3. Deodorization dismutates all peroxides and all deodorized samples were found to have a PV of zero.

The color of sunflower oil expressed as the percentage transparency at 455 nm is given in Table IV. Bleaching with clay increased the transparency of both samples. Bleaching with clay followed by deodorization made a slightly lighter oil than bleaching during deodorization. However, the color of oil expressed as the percentage transparency at 455 nm is very similar after the deodorization process (78-84.5%).

The color of sunflower oil was measured at 455 nm since maximal absorption occurs at this wavelength. The spectrophotometric absorption curve for sample A from 400 to 700 nm is given in Figure 2. Carotenoids are suspected to be the major pigments which absorb in the area of 455 nm and are heat-destructed. Therefore, whether the oil is bleached with clay or during deodorization, the finished deodorized oil has comparable color characteristics.

The oxidation stability of the various samples was determined by the Active Oxygen Method (AOM). The peroxide values after 8 hr of aeration is given in Figure 3.

The continuous refined oil had a much lower PV after 8 hr of aeration than the batch-refined oil: 70 and 130, respectively. This agrees with the anisidine values given in Table I, which show the batch refined oil had a greater degree of oxidation. Nevertheless, both samples after deodorization had comparable stability. Whether bleaching was done by clay or during deodorization had little effect on the oxidation stability. However, the peroxide values given in Figure 4 show that citric acid was effective in increasing oxidative stability.

List et al. (20) showed that bleaching lowers oxidative stability of sunflower oil. Similar data were obtained in our laboratories when a higher concentration of bleaching clay was used (21). It is believed that clay reduces the tocopherol content and increases the conjugated triene content. Peredi (22) has shown the stability of sunflower oil is

	Samples (ppm) ^a			
	A		В	
	Cu	Fe	Cu	Fe
Neutralized oil	0.062	0.75	0.055	0.70
Bleached with clay	0.055	0.63	0.047	0.63
Clay bleached and deodorized	0.062	0,70	0.055	0.63
Clay bleached, deodorized + citric acid	0.047	0,70	0.055	0.63
Bleached during deodorization	0.050	0.70	0.062	0.70
Deodorization bleached + citric acid	0.050	0.68	0.062	0.63

^aSample A was obtained by continuous refining; sample B was obtained by batch refining.

TABLE IV

Color of Sunflower Oil at Various Processing Stages Expressed As the Percentage Transparency at 455 nm

	Sample ^a		
	A	В	
Neutralized oil	19.5	46.0	
Bleached with clay	63,5	72.0	
Bleached with clay Clay bleached and deodorized	82.2	84.5	
Bleached during deodorization	78.0	81.5	

^aSample A was obtained by continuous refining; sample B was obtained by batch refining.

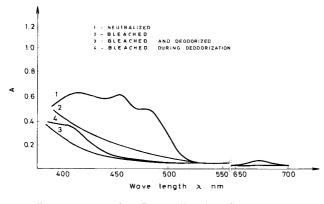


FIG. 2. Spectra of sunflower oil in the refining process.

reduced by 15% by the normal bleaching process. Lezajić (23) also has shown that the normal bleaching process decreases the stability of oil. She found higher absorption at 270 nm resulting from higher conjugated triene content. However, Morrison (24) has shown that by using as much as 3% activated clay, the stability of sunflower oil does not decrease even though 40-57% of the tocopherols are removed and the triene content is increased.

Several advantages of using a combined process of bleaching during deodorization are apparent. It would not be necessary to use activated clay for bleaching so the cost of the clay plus the value of the oil that would not be lost by clay absorption are 2 economical advantages. Also, if high quality crude oil is used with low levels of free fatty acids, the caustic refining process can be eliminated and replaced with the physical refining process. This would also be an economical advantage since refining losses would be lowered and the environmental advantages of not having soap stocks for disposal would be realized. These advantages are clear and should be investigated by the oil industry for future processing of sunflower oil.

Since it has been shown that a high quality sunflower oil can be produced by bleaching during deodorization, we are continuing our experimentation with other vegetable oils whose pigmentation is caused by carotenoids.

REFERENCES

- 1. Hafizov, R.H., N.K. Nadirov and L.A. Tolcina, Pisc. Teh. 71:4,51 (1969)
- Ostrić-Matijasević, B., and K. Mezei, Hem. Ind. 24:257 (1970). Ostrić-Matijasević, B., P. Vranjković, J. Turkulov and O. Timko, Riv. Ital. Sostanze Grasse 48:177 (1971). 3.
- 4.
- Ostrić-Matijasević, B., J. Turkulov, Dj. Karlović and N. Stefa-nović, Bilten: Biljna Ulja Masti 11:3/4, 9 (1974).
- 5. Ostrić-Matijasević, B., J. Turkulov and Dj. Karlović, Hem. Ind. 30:101, 6 (1976).

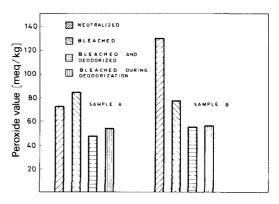


FIG. 3. Stability of samples A and B of sunflower oil.

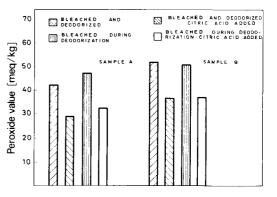


FIG. 4. Stability of samples A and B of sunflower oil after bleaching and deodorization (with and without citric acid).

- Rutkowski, H., and L. Mzyk, Riv. Ital. Sostanze Grasse 46: 6. 614 (1969).
- Guillaumin, R., Formation des Trienes, Moyen de les Eviter, Journee d'information 1967 sur l'huilerie, ITERG, Paris, 1967.
- Baldwin, R., JAOCS 25:33 (1948).
- Smidt, A.A., Teoreticeskie osnovi rastiteljnih masel, Piscevaja promizdat, Moskva 1962
- Andersen, A.J., Refining of Oils and Fats for Edible Purposes, Pergamon Press, London 1962. Goldovskij, A.M., and V.N. Nikitinskaja, Maslo Zhir. Prom. 10.
- 11. 6. 39 (1973).
- Petty, E.E., Processing of Vegetable Oils, Symposium on Soybean Treatment, Budva, 1975. 12
- Ostrić-Matijasević, B., J. Turkulov and Dj. Karlović, Quality and Stability of Sunflower Oil Evaluated by Benzidine Value, International Congress of Food Science and Technology, Madrid, 1974.
- Mezei, K., B. Ostrić-Matijasević, J. Turkulov and I. Mezei, Bilten: Biljna Ulja Masti 14:3/4, 21 (1977).
- JUS E.K. 8.026, 43/1962.
- Bergner, K.G., K.F. Gander, K. Hummel, H. Pardun, H. Pezold and H. Wissebach, Handbuch der Lebensmittelchemie, Band IV, Springer Verlag, Berlin, 1969. Holm, U., and K. Ekbom-Olsson, *p*-Anisidin As a Reagent of
- Secondary Oxidation Products in Oils and Fats, The 11th World Congress of the International Society for Fat Research, Göteborg, 1972.
- 18 Official and Tentative Methods of the American Oil Chemists' Society, 3rh edition, Champaign, IL, AOCS Tentative Method Cd 12-57
- CAC RS 20-1969 Recommended International Standard for 19. Edible Soybean Oil.
- G.R. List, C.D. Evans and H.A. Moser, JAOCS 49:287 (1972). Ostrić-Matijasević, B., J. Turkulov, P. Djurković, Influence of 20.
- 21. Bleaching on the Quality and Stability of Sunflower Oil, ISF World Congress, Chicago, 1970.
- Peredi, J., Olaj, szappan, kozmet. 65:3 (1971). Lezajić, J., Bilten: Biljna Ulja Masti 14:3/4, 17 (1977). 23.
- 24. Morrison, W.H., JAOCS 52:522 (1975).

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