Effects of Refining and Bleaching on Oxidative Stability of Sunflowerseed Oil[1]

W.H. MORRISON, III, Richard B. Russell Agricultural
Research Center, Athens, Georgia 30601

ABSTRACT

Sunflowerseed oils extracted from seed grown in the northern and southern US were laboratory refined and bleached with 1 and 3% activated clay. The crude, refined, and bleached oils were heated for four 8-hr days. Samples of oil were taken daily and active oxygen method values determined. In addition, "Ple-zrs," a porous, fat free snack item, were fried in the oils at the end of each day and stored for 5 weeks. Plots of the log of the active oxygen method values versus the number of hr the oil had been heated were straight lines, the slope of which reflected the oxidative stability of the oil on heating. The lack of change in slopes for the southern oils indicated that oxidative stability after heating was not changed markedly by refining or bleaching. Two samples of northern oil, the refined and oil bleached with 1% activated clay, showed an increase in oxidative stability on heating but a lowering of overall stability. The peroxide values of the oils expressed from the stored "Ple-zrs" indicated that the southern oil was slower than the northern oil to oxidize on storage in a fried product.

INTRODUCTION

In recent years, numerous sunflowerseed oil products, as well as products prepared in the oil, have appeared on the shelves of food stores. The increased interest in the oil for the commercial preparation of snack items brings a need for additional information on refining and bleaching without lowering oxidative and flavor stability of the oil.

The effect of bleaching on the oxidative stability of sunflowerseed oil has been investigated (1-3). Ostric-Matijasevic, et al., (1) reported the effects of various bleaching earths on the ultraviolet (UV) spectra and keeping quality of pressed and extracted sunflowerseed oil with an iodine value (IV) range of 132-135. They reported that activated clays reduced stability, removed more color, and brought about greater changes in the UV spectra of the oils than neutral clays did. List, et al., (2) reported that bleached oil with an IV of 140 was consistently less stable after storage than its refined counterpart. The above studies were conducted on oils that were rich in linoleic acid (63-73%) and typical of oils from seed grown in the northern US. Oils from seed grown in the southern US have linoleic acid contents ranging from 30 to 50% (4) and would be expected to be less susceptible to oxidation.

Work (5) in this laboratory demonstrated that stability measurements on unheated oils did not necessarily predict the stability of the oil on heating. The present study was undertaken to determine the influence of refining and bleaching on the oxidative stability of sunflowerseed oil after heating and on storage of a fried product.

TABLE I

Composition and Properties of Crude Northern and Southern Sunflowerseed oils

Evaluations	Northern	Southern
Iodine value (calc.)[a]	129.2	109.4
Peroxide value (meq/kg)	2.1	3.9
Free fatty acids (as % oleic)	1.95	1.48
Active oxygen[b] method (hrs)	10.5	17.9
Fatty acid composition (%)		
16:0	5.9	5.2
18:0	4.7	4.4
18:1	26.4	50.9
18:2	61.5	37.9
20:0	.5	.5
22:0	.7	.7

[a] Iodine values were calculated from fatty acid composition determined by gas liquid chromatography.

[b] Active oxygen method values were determined on oils treated with .076% Tenox 6 antioxidant and 2 ppm Dow Corning Antifoam A.

MATERIALS AND METHODS

Sunflowerseed oils were from seed grown in Minnesota and Texas. The seed were ground in a Wiley Mill to pass a 6-mm screen and the oil was extracted in a large Soxhlet. After removal of solvent with a Precision Scientific Laboratory Concentrator, the oils were refined with 16° Baumé NaOH with .2% excess for 15 min at 36 C and 60 min at 70 C. Soaps were removed by centrifugation. Oils were bleached with Tonsil optimum FF activated clay at concentrations of 1 and 3%. Vacuum bleaching was conducted under optimum conditions (1) of 80 C under 10-15 mm Hg absolute pressure with agitation for 20 min. Bleaching earth was removed by filtration through Whatman 41 filter paper under nitrogen in a Frueger stainless steel pressure filter with Hyflo Super Cel as a filter aid. Prior to heating, .076% Tenox 6 antoxidant and 2 ppm Dow Corning Antifoam were added to the oils.

Initially, 1.5 liters of oil were placed in a 4-qt household deepfat fryer and heated to 180±3 C for four 8-hr days. At the end of each day's heating, 60 ml of oil were frozen for chemical evaluation, and 25 g of "Ple-zrs" (Navaho Corp., Atlanta, GA), a porous, fat free snack item, were fried in the remaining oil and stored in plastic bags in the dark at room temperature for 5 weeks. Aliquots of chips were removed at 1, 3, and 5 weeks, oil was expressed, and peroxide values determined. Ca. 60 ml of make-up oil were added at the beginning of each day's run to maintain the volume of the oil in the fryer at 1.5 liters.

Active oxygen method (AOM) values, peroxide values (PV), and percent free fatty acids were determined by official AOCS methods (6-8). AOM's were run until a PV of 100 was reached, and that time was taken as the end point and recorded in hr. Fatty acid compositions were determined by the method of Metcalfe, et al., (9) by using a Tracor MT220 gas liquid chromatograph equipped with an Infotronics Model CRS 101 digital integrator. A 10 ft by 1/8 in. stainless steel column packed with 10% EGSS-X on 100/120 mesh Gas Chrom P was used for the analyses, and the oven was operated at 190 C. Ultraviolet spectra were measured with a Cary 15 low-UV recording spectrophotometer with cyclohexane as the solvent. Tocopherols were determined by a modification of the method reported by Sturm, et al. (10).

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[1] Presented at AOCS meeting, Cincinnati, September, 1975.

TABLE II

Active Oxygen Method (AOM) Values of Heated Northern and Southern Sunflowerseed Oils[a]

Heating (hr)	AOM values (hrs) Treatment of northern oils Crude	Refined	Bleached[b] 1%	3%	Treatment of southern oils Crude	Refined	Bleached[b] 1%	3%
0	10.5	8.5	8.5	12.8	17.9	21.5	20.5	26.1
8	11.5	10.0	9.6	12.6	17.7	17.5	17.5	20.5
16	10.1	9.5	9.4	10.8	16.0	16.3	15.7	18.7
24	9.5	9.7	9.1	9.4	14.6	15.4	14.6	16.7
32	8.5	9.5	8.7	9.3	13.7	13.5	14.0	15.4
Slope[c] $(m \times 10^{-3})$	-5.2	-0.72	-1.7	-5.6	-4.6	-4.5	-4.0	-5.2

[a] Heated to 180±3 C.

[b] Bleaching earth used was Tonsil optimum FF Activated Clay.

[c] Mean ± standard deviation = -0.0039±0.0017.

RESULTS AND DISCUSSION

The properties and fatty acid composition of the crude oils are shown in Table I. The oils differed principally in their contents of linoleic and oleic acids, which were 61.5 and 26.4%, respectively, for northern oils and 37.9 and 50.9%, respectively, for southern oils. The effects of bleaching had been studied (1,2) on oils containing 63-73% linoleic acid, a range which is typical for northern oils, and stability was measured on fresh unheated oils. Work in this laboratory has shown that stability measurements on unheated oils do not indicate reliably the performance of the oils on heating (5). The AOM values in Table I indicate that the crude northern oil was less stable than the southern oil.

Table II shows the AOM measurements, the slopes from a first order linear regression analysis, and the standard deviation and mean of the heated oils after refining and bleaching. Figure 1, a plot of the log of the AOM values in Table II versus the number of hr the oils had been heated, shows the rates at which the oils lost oxidative stability upon heating at a given temperature (5). The crude samples are to be considered the base line for these evaluations. For crude oils, southern oil has higher initial stability than northern (Table I), but the crude northern (A′) and crude southern (A) have similar slope (Fig. 1) and, therefore, similar rate of loss of oxidative stability. The relative positions of the lines in Figure 1 reflect the overall stability of the oils. Refining increased initial stability for the souther oil (Table II) but had little effect on the rate of loss of stability with heating (B, Fig. 1). With the northern oil, refining lowered stability initially. The refined oil had a slower rate of loss of stability as shown by the reduction of the slope of B′ as compared to A′.

Bleaching the southern oil with 1% activated clay slightly decreased initial stability as compared to the refined oil (Table II); however, upon heating, the 1% bleached oil (C, Fig. 1) showed only a slight change in the rate of loss of oxidative stability as compared to the crude (A) and refined (B) samples. The northern oil bleached with 1% activated clay showed no change in initial stability as compared to the refined samples. Upon heating, however, the oil showed a slight loss of stability (C′, Fig. 1). The northern sunflowerseed oil's performance was as would be expected from earlier work (1-3). Stability was reduced after refining and bleaching. In contrast, initial stability of the southern oil was increased after refining and bleaching.

Bleaching with 3% activated clay had similar unexplained effects on the northern and the southern sunflowerseed oils. In each case, the initial and overall stabilities were increased. The northern oil bleached with 3% activated clay was more stable and had the same rate of loss of stability upon heating as the crude sample (D′, Fig. 1), a rate that was faster than that of the refined and 1% bleached samples. The southern oil (D, Fig. 1) showed a noticeable increase in overall stability, but a slight change in rate of loss of stability.

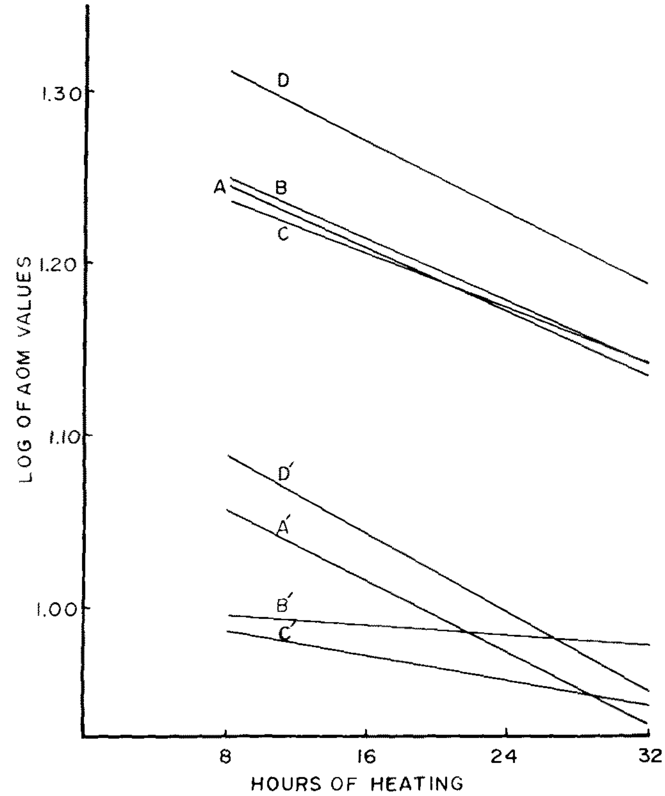

FIG. 1. Changes in active oxygen method (AOM) values with heating (180±3 C). Primed letters indicate northern and unprimed letters indicate southern sunflowerseed oils. A = crude oil; B = refined oils; C = oils bleached with 1% activated clay; D = oils bleached with 3% activated clay.

The data from this study indicate that the northern and southern oils have an intrinsic stability that was not greatly affected by refining or bleaching. The northern oil did change in oxidizability on heating after refining and bleaching with 1% activated clay, but not with 3% clay. Applying the Q test for outlying results to the slopes (rates of loss of oxidative stability) in Figure 1 indicates that only the rates of the northern refined and northern oil bleached with 1% clay were significantly different from the other 6 samples. Apparently oxidative behavior is similar for the northern and southern oils. Overall stability, as indicated by

TABLE III

Effects of Processing on the Tocopherol Content of Northern and Southern Sunflowerseed Oil

Treatment	Tocopherol content[a] (μg/g ±27 μg) Northern	Southern
Crude	716	779
Refined	725	766
1% Bleached[b]	660	745
3% Bleached[b]	308	468

[a] Tocopherol values are the average of triplicate analyses.

[b] Bleaching earth used was Tonsil optimum FF activated clay.

the relative positions of the lines for the northern and southern oils in Figure 1, is related to the content of linoleic acid, with the oils that are low in linoleic acid having the higher stability (11).

List, et al., (2) discussed reports suggesting that the inherent stability of sunflowerseed oil was determined by the ratio of tocopherols (mg %) to linoleic acid (5). Table III shows the tocopherol content of the crude refined and bleached sunflowerseed oil samples prior to the addition of antioxidants. These results indicate that refining removed essentially no tocopherols, and bleaching with 1% activated clay removed only minor amounts. When 3% activated clay was used, the tocopherol content of the northern oil was reduced 57% and the southern, 40% compared to the crude oil.

For both oils, samples bleached with 3% activated clay were more stable than those bleached with 1%. Because bleaching removed substantially more tocopherols with 3% activated clay than with 1%, our data indicate that tocopherol reduction due to processing is not a factor in the oxidative stability of sunflowerseed oil. Similar results have been observed with safflower oil (12).

The results of UV spectrophotometric analysis of the unheated oils (Table IV) are consistent with published values (1). The absorption at 228-232 nm is due to conjugated dienes resulting from the formation of hydroperoxides. Absorption at 228-232 nm was increased by oxidation during refining (13), then decreased due to degradation of the hydroperoxides during bleaching. Bleaching increased the absorption at 270, because triene systems were formed from the additional degradation of hydroperoxides (14).

UV data from the unheated oils indicate that conjugated systems increased with refining and bleaching which would be expected to decrease oxidative stability. This decrease was not indicated from the stability measurements on the southern oil and was questionable for refined and 1% bleached northern oil.

An important consideration in the commercial use of a vegetable oil for the preparation of snack-foods is its stability in fried products on storage. The PVs of the oil expressed from the highly porous stored "Ple-zrs" are shown in Table V. Because peroxides are precursors of off flavor producing materials (15), the greater the increase in PV, the sooner oxidative rancidity would be expected to occur. The PVs reported have not been correlated with off flavor intensity for these oils and chips and are used only as one indication of the degree of oxidation.

Peroxide build up was slower in the southern than in the northern oil. With increased hr of heating, peroxide values generally increased indicating a decrease in oil stability.

TABLE IV

Spectrophotometric Evaluations of Unheated Sunflowerseed Oils

	Absorbance (1 mg/ml)							
	Treatment of northern oils				Treatment of southern oils			
	Crude	Refined	Bleached[a]		Crude	Refined	Bleached[a]	
Wavelength			1%	3%			1%	3%
270 nm	.003	.029	.071	.151	.001	.024	.073	.133
228 nm	.032	.476	.282	.200	.010	.276	.244	.215

[a] Bleaching earth used was Tonsil optimum FF Activated Clay.

TABLE V

Peroxide Values of Oil from Stored "Ple-zrs" Fried in Northern and Southern Sunflowerseed Oils

	Storage of northern oils			Storage of southern oils		
Heating (hr)	1	3 (wks)	5	1	3 (wks)	5
	Refined					
8	2.3	15.9	16.9	2.5	6.5	9.1
16	3.4	14.3	24.0	2.2	6.2	9.7
24	2.6	17.9	26.0	1.8	4.9	16.7
32	4.6	13.5	37.1	2.4	7.4	20.2
	1% Bleaching[a]					
8	5.1	23.1	47.6	3.9	15.0	16.1
16	5.9	30.2	55.3	3.8	13.0	24.2
24	9.3	30.6	64.1	5.8	16.0	26.2
32	9.5	37.4	67.1	2.4	15.9	27.1
	3% Bleaching[a]					
8	2.5	6.8	15.0	2.2	5.5	10.0
16	1.9	9.0	21.9	3.0	7.8	13.8
24	2.8	15.5	27.6	2.5	5.2	15.4
32	2.2	15.0	34.8	2.6	7.3	14.2

[a] Bleaching earth used was Tonsil Optimum FF Activited Clay.

Bleaching with 1% activated clay decreased the storage stability for both northern and southern oils as compared to refined oils, but with 3% clay, storage stability was unaffected. Although bleaching changed both oils, storage characteristics were better in southern than in northern oil, and probably are related to the linoleic acid content of the oils.

Further work is underway to assess the factor governing the inherent stabilities of the oils and their responses to processing conditions.

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