Technical

Hydrogenated Sunflowerseed Oil: Oxidative Stability and Polymer Formation on Heating

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ABSTRACT

The effects of hydrogenation on the stability of pilot plant refined and deodorized northern and southern sunflowerseed oil were studied. Light hydrogenation reduced the iodine value of the northern oil from 134 to 120 and the southern oil from 106 to 102. Hydrogenation increased the overall stability of both oils but did not alter the rate of loss of oxidative stability as represented by a plot of the log of the active oxygen method values versus the number of hours the oil had been heated. Non-gas liquid chromatography eluting material which includes oxidation products, polymers, and unsaponifiables reached a maximum of 4.1%.

INTRODUCTION

Studies have demonstrated the acceptability of sunflowerseed oil for deep-fat frying (1-5). There are, however, only limited studies on the stability of hydrogenated sunflower oil and its acceptability as a cooking oil (1,3,5). These studies indicate that hydrogenated sunflower oil is quite acceptable and has good flavor and oxidative stability.

The oleic and linoleic acid contents of sunflower oil vary depending on the daily temperature between flowering and physiological maturity (6,7). Typically linoleic acid content of oil ranges from 55 to 70% for seed grown in the northern U.S. and from 30 to 50% for seed grown in the southern U.S. (8). This wide range of polyunsaturation makes this oil suitable either for deep-fat frying or as a salad oil; its oleic and linoleic acid contents might be tailored for a particular use by producing the crop in the appropriate area.

Most of the oilseed-type sunflowers are grown in Minnesota and the Dakotas and have high linoleic acid contents which could be lowered by light hydrogenation to increase stability. The increased stability would improve acceptability of the oil to industry for commercial frying operations.

We undertook this study to evaluate the stability of lightly hydrogenated northern and southern sunflower oils

TABLE I

Fatty Acid Composition (wt %) of Hydrogenated and Unhydrogenated Northern and Southern Sunflowerseed Oils

	Northern		Southern	
Fatty acid	Unhydrogenated	Hydrogenated	Unhydrogenated	Hydrogenated
16:0	5.8	6.0	5.1	4.9
18:0	3.9	4.5	3.9	4.3
18:1	26.0	32.1	55.5	56.9
18:2	64.4	53.3	33.4	30.8
20:0	.5	.2	.5	.3
22:0	.7	.6	.7	.5
Iodine value	133.9	119.9	105.6	102.3
% Trans Fatty acids	0	6.4	0	3.3

TABLE II

Free Fatty Acid (FFA) Content and Viscosity of Heated Hydrogenated and Unhydrogenated Sunflowerseed Oils

	Northern				Southern			
	Unhydrogenated		Hydrogenated		Unhydrogenated		Hydrogenated	
Hours of heating	%FFA[a]	Vis.[b]	% FFA	Vis.	% FFA	Vis.	% FFA	Vis.
0	.18	13.9	.16	14.4	.15	13.4	.20	15.4
8	.18	14.3	.18	14.8	.17	15.5	.18	15.7
16	.22	14.6	.24	15.1	.22	15.9	.23	16.0
24	.25	15.0	.29	15.3	.25	16.2	.27	16.3
32	.33	15.3	.40	15.7	.33	16.8	.37	16.7

[a] As oleic acid.

[b] Centistokes at 70 C.

TABLE III

Effects of Heating on Oleic and Linoleic Acids (wt %) in Hydrogenated and Unhydrogenated Sunflowerseed Oils

Hours of heating	Northern				Southern			
	Unhydrogenated		Hydrogenated		Unhydrogenated		Hydrogenated	
	% FFA[a]	Vis.[b]	% FFA	Vis.	% FFA	Vis.	% FFA	Vis.
0	26.0	64.4	31.1	53.3	55.5	33.4	56.9	30.8
8	25.8	64.7	31.8	52.1	56.4	32.5	58.0	31.3
16	25.3	60.7	32.2	51.9	57.1	32.0	57.5	29.9
24	26.1	62.5	31.9	51.5	57.4	31.9	57.7	30.3
32	24.9	59.3	32.2	51.5	56.3	30.7	57.7	30.1

TABLE IV

Effect of Heating on AOM Values (Hr) of Hydrogenated and Unhydrogenated Sunflowerseed Oils

Hours of heating	Northern		Southern	
	Unhydrogenated	Hydrogenated	Unhydrogenated	Hydrogenated
0	18.1	24.3	29.0	33.5
8	9.3	13.8	16.7	21.1
16	7.8	11.5	13.2	16.1
24	7.2	9.3	10.6	12.4
32	6.6	7.9	8.8	11.5
Slope (m x 10^{-3})	-6.0	-10.2	-11.6	-11.5

TABLE V

Noneluting Material (%) of Heated Sunflowerseed Oils and % Oil Absorbed by Fried Potatoes

Hours of heating	Northern		Southern	
	Unhydrogenated	Hydrogenated	Unhydrogenated	Hydrogenated
0	.63	.35	.15	1.25
8	1.76	.80	1.38	.52
16	2.11	1.90	1.35	2.28
24	2.53	3.54	1.32	.27
32	3.94	3.29	4.12	1.32
Average oil content of potatoes (% as is)	13.4	13.1	13.1	14.7

and to determine the amounts non-gas liquid chromatography-eluting materials that are produced during frying.

MATERIALS AND METHODS

Oils extracted from seed grown in Minnesota and Texas were pilot plant refined and deodorized. Approximately 4 liters of each oil was lightly hydrogenated with .05% Nysel nickel catalyst (Harshaw Chemical Co., Cleveland, OH) at 125 C and 20 psig H_2 with the progress of the reaction followed by refractive index. After hydrogenation the oils were filtered and stored at 0 C under nitrogen. To both the hydrogenated and unhydrogenated oils were added .076% Tenox 6 antioxidant, .01% citric acid, and 2 ppm Dow Corning Antifoam A. Daily for 4 days, eight 1-pound batches of potatoes were fried at 180 C, and oils were sampled as described (5). The first sample of potatoes fried in the fresh oil and the last sample fried each day were frozen for later chemical evaluation. The freeze-dried fried potatoes were ground, and the oils were extracted in a Soxhlet with petroleum ether.

Active oxygen method (AOM) values (9) and percents of free (10) and of trans fatty acids (11) were determined by official AOCS methods. Viscosity was determined at 70 C (12). Fatty acid composition was determined by the method of Metcalfe et al. (13) with triheptadecanoate added as an internal standard prior to saponification, and noneluting materials were determined by the method of Waltking et al. (14). All analyses were run in duplicate. For the analysis a Tracor MT 220 gas liquid chromatograph was used under published conditions (15). Linear regression analyses were carried out on the AOM values versus the number of hours of heating to obtain the rates of loss of oxidative stability.

RESULTS AND DISCUSSION

The fatty acid compositions of the two oils before and after hydrogenation are shown in Table I. Hydrogenation decreased the linoleic acid content from 64.4 to 53.3% for the northern oil and from 33.4 to 30.8% for the southern oil and increased oleic acid from 26.0 to 32.1% for the northern oil and from 55.5 to 56.9% for the southern oil. Hydrogenation reduced the calculated iodine value from 133.9 to 119.9 and 105.6 to 102.3 for the northern and southern oils, respectively. Isomerization on hydrogenation was slight in both oils, yielding 6.4% trans fatty acids in the northern and 3.3% in the southern.

Heating produced the expected changes in free fatty acids and viscosity as shown in Table II with both indices increasing with heating time. The build-up of free fatty acids apparently did not differ between the hydrogenated and unhydrogenated oils. Hydrogenation initially increased viscosity more for southern than for northern oil but did not affect final viscosities.

Table III shows the changes in oleic and linoleic acid contents of heated oils. The linoleic acid content decreased only slightly for unhydrogenated oils, did not decrease for southern, and decreased slightly for the northern hydrogenated oils. Those reductions in unsaturated acids result from oxidation or polymerization which occurs during heating.

Table IV shows the AOM values and the rates of loss of oxidative stability for each oil over the 32 hr period of heating. Our earlier study (5) indicated that initial AOM values do not necessarily predict an oil's stability during heating and that a plot of the log of the AOM values versus the number of hours of heating better reflects the oil's oxidative stability during heating. Figure 1 is a plot of the log of the AOM values (Table IV) versus the hours of heating. The relative position of each line reflects the overall stability, and the slope indicates the rate of loss of oxidative stability on heating.

Hydrogenation increased the initial AOM values and the overall stability for both the northern and southern oils. The southern oil, with its lower percentage of polyunsaturated fatty acids, had the higher initial AOM value and overall stability than the unhydrogenated northern oil.

Published work (15) indicates that the inherent oxidative stabilities of northern and southern sunflower oils are similar and not affected by refining and bleaching. Present data indicate that this inherent stability was not affected by hydrogenation as illustrated by the uniform rates of loss of oxidative stability in Table IV. The low value for the unhydrogenated northern oil suggests that the rate of loss of stability increased with the level of polyunsaturated fatty acids. We are investigating that possibility. Preliminary studies indicated that with a given antioxidant the oxidative stability is fairly constant. A change in antioxidant, however, was associated with a change in the rate of loss of oxidative stability of heating (Morrison, unpublished work).

The analysis of polymers and oxidized material that are produced on heating an oil and the nutritional aspects of these materials are a matter of continuing research and have been reviewed by Perkins (16).

The oil content of the fried potatoes and polymer contents of the cooking oils are shown in Table V. The amount of oil absorbed was fairly uniform except for the hydrogenated southern oil which was 14.7%, nearly 1.5% higher than for the other oils. During heating polymers gradually accumulated. Because of the erratic results of polymer content for the hydrogenated southern oil, no firm conclusions could be made concerning the effectiveness of hydrogenation in reducing polymer formation.

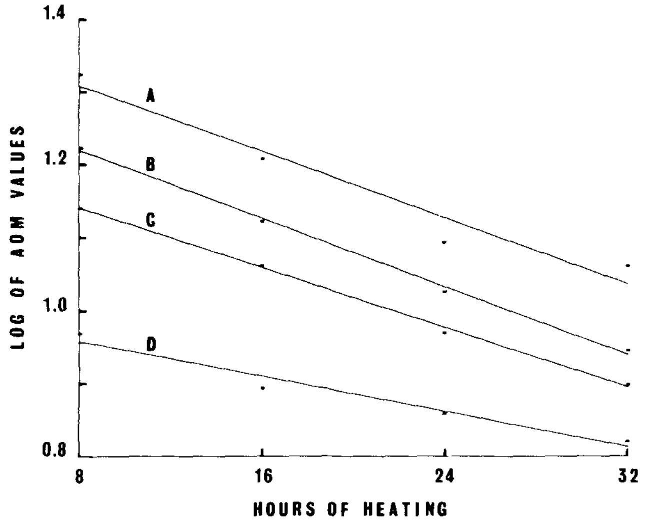

FIG. 1. Changes in active oxygen method (AOM) values of sunflower oils with heating. A = hydrogenated southern oil; B = unhydrogenated southern oil; C = hydrogenated northern oil; D = unhydrogenated northern oil.

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