Flavor Evaluation of Copper-Nickel Hydrogenated Soybean Oil and Blends with Unhydrogenated Oil[1]

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ABSTRACT

Soybean oils hydrogenated to zero linolenate in the pilot plant with a mixed copper-nickel catalyst and a straight copper chromite catalyst were evaluated and compared for flavor and odor. Hydrogenated oils were winterized and deodorized and stabilized with butylated hydroxytoluene, butylated hydroxyanisole, citric acid, and methyl silicone. Taste panel flavor scores of stored oils and room odor scores of oil at frying temperature were similar for oils hydrogenated either with straight copper chromite or with mixed copper chromite-nickel catalysts. Blends containing 1, 2, and 3% linolenate made from unhydrogenated soybean salad oil and soybean oil hydrogenated to 0% linolenate with mixed copper chromite-nickel catalyst were similarly evaluated. Panel responses indicated a blend of 29% unhydrogenated soybean salad oil and 71% hydrogenated soybean oil scored slightly lower than the hydrogenated soybean oil.

INTRODUCTION

A cooking or table oil must satisfy the consumer in terms of flavor, nutritional value and low cost. To meet these demands, the oil processor must market a stable oil as inexpensively as practical. Fat and oil consumption is expected to increase in 1974. Currently, soybean oil (SBO) accounts for 63% of all fats and oils produced, 77% of the total edible vegetable oil (1). Processing improvements have been responsible for the more universal acceptance of SBO, particularly the reduction of linolenate by partial hydrogenation with a suitable catalyst without appreciably reducing linoleate (2-4). Use of either copper chromite or copper-on-silica catalysts for the partial hydrogenation of SBO has been reported (5-12).

It costs less to hydrogenate SBO with a nickel catalyst than with a copper chromite catalyst using present technology. However, it is not economical to hydrogenate an oil to less than 2% linolenate using a nickel catalyst, and unless the linolenate is completely removed, oils prepared by hydrogenating SBO with copper chromite are not stable (2,13). Instability of such oils may be due to a large amount of conjugated diene formed during the first stages of hydrogenation (11,12). For this reason, the complete removal of linolenate from SBO has been emphasized (13-14) by using copper catalyst, and particularly if the oil is intended to be used for cooking.

Within the past year new legislation was enacted in France limiting linolenate in vegetable oils for cooking and dressings to a maximum of 2%. This regulation naturally prohibits for these uses Ni-hydrogenated soybean oil (HSBO) with 3% linolenate commercially available in the US. Reportedly, Ni-HSBO (3% linolenate) has an undesirable room odor (14,15) when heated to cooking temperatures. Zero linolenate copper-hydrogenated oils and blends up to 2% linolenate, such as those described here, should satisfy the maximum French linolenate limit, as well as the customer.

Blends of unhydrogenated salad grade SBO with zero linolenate HSBO might produce an acceptable stable

TABLE I

Typical Fatty Acid Composition and Pertinent Data for Hydrogenated Oils, Unhydrogenated Oils, and Blended Oils

Characteristics	CuCr-HSBO[a]	CuCr-Ni-HSBO[a]	Unhydrogenated oils	Oils blended to contain linolenate (%)		
				1	2	3
Fatty acid composition[b]						
C16:0	10.0	10.0	11.1	10.2	10.3	10.3
C18:0	4.6	4.0	4.6	4.1	4.1	4.1
C18:1	42.6	47.0	26.0	43.2	42.5	37.9
C18:2	42.2 (38.5)	39.0 (34.8)	51.2	41.0 (36.7)	41.3 (39.0)	44.7 (41.7)
Conjugated diene	0.6	0.5	0.4	0.7	0.6	0.6
C18:3	0.6 (0.0)	0.0 (0.0)	7.0	1.5 (0.5)	1.8 (2.0)	3.0 (2.8)
trans	14.8	19.7	1.3	17.9	14.3	12.0
Iodine value (calculated)[c]	110	108	129	109	113	117
Selectivity ratio, K_{Le}/K_{Lo}	16	13	--	--	--	--
Peroxide value (PV)						
Initial (meq/kg oil)	0.2	0.2	0.3	0.4	0.1	0.2
8-Hr AOM[d] (meq/kg oil)	2	2				
Hours to 100 PV	48	56				
Metal content in oil						
Cu (μg/g oil)	0.02	0	0.04			
Unhydrogenated SBO in blend (%)	--	--	--	14.5	29	43

[a] HSBO = hydrogenated soybean oil; abbreviations refer to oils containing 0% linolenate hydrogenated with commercial copper chromite catalyst (CuCr-HSBO) and mixed catalyst.

[b] Composition determined by gas liquid chromatography (GLC) except by alkali isomerization (AI) in ( ); conjugated diene by ultraviolet spectrophotometry; *trans* by infrared spectrophotometry.

[c] Iodine value (IV) calculated from GLC values for oleate and linoleate plus value for linolenate by AI.

[d] ACM = active oxygen method.

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TABLE II

Flavor and Oxidative Stability of Hydrogenated Oils

Conditions	CuCr-HSBO[a]	CuCr-Ni-HSBO
Initial (no storage)		
Flavor score[b]	8.2	8.2
Description (FIV)[c]		
Bland	0.4	0.5
Buttery	0.9	0.9
Stored 4 days at 60 C		
Flavor score	6.6	6.4
Description (FIV)		
Bland	1.0	0.8
Beany	0.3	0.3
Rancid	0.6	0.4
Hydrogenated	0.3	
Stored 8 days at 60 C		
Flavor score	5.8	6.2
Description (FIV)		
Buttery	0.8	0.8
Grassy	0.5	
Rancid	0.4	0.6
Hydrogenated		0.4
Light exposure for 4 hr		
Flavor score	6.1	6.1
Description (FIV)		
Buttery	0.9	1.1
Grassy	0.6	0.5
Rancid		0.4
Painty	0.6	
Hydrogenated	0.4	
Initial (no storage)		
Room odor score	6.4	6.5
Description (OIV)		
Heated/hot oil	0.7	1.0
Rancid	0.3	0.3

[a] HSBO = hydrogenated soybean oil; 0% linolenate.

[b] Flavor and odor scores were averaged on a 1 (low) to 10 (high) rating (24).

[c] Flavor intensity value (FIV) and odor intensity value (OIV) rated on a scale of 1 to 3, where 1 was a weak response, 2 was medium, and 3 was strong (16).

product at less cost than an all hydrogenated oil. Savings should result in part from lower processing costs due to hydrogenation, bleaching or water washing, and winterization of less oil and, in part, from less costly unhydrogenated SBO in the blend. In our research, we identified the most stable zero linolenate HSBO that could be blended with unhydrogenated salad SBO. We also found the maximum amount of unhydrogenated salad SBO that could be used in such a blend consistent with good flavor and room odor scores.

ANALYTICAL METHODS

Compositions of the unhydrogenated SBO and partially HSBO were determined by gas liquid chromatography (GLC) and alkali isomerization (AI). Methods to determine composition, conjugated diene and *trans* isomer were described in detail previously (12). Selectivity ratio K_{Le}/K_{Lo} was calculated according to method described by Butterfield, et al., (16). Because only soybean oils of similar unsaturation were hydrogenated for this study, and according to AOCS Method Cc 7-25 (17), refractive index was a suitable method to indicate the degree of unsaturation in similar oils; a refractometer was used in the plant to determine when the linolenate was essentially zero. Peroxide value of the oils was obtained by AOCS Tentative Method Cd 8-53 (18) and active oxygen method (AOM) by AOCS Method Cd 12-57 (19). Copper in the hydrogenated oils was measured by atomic adsorption according to the procedure of List, et al., (20).

EXPERIMENTAL PROCEDURES

Soybean Oils

Two lots of commercially refined and bleached SBO were hydrogenated separately with 2 different catalysts. Two different lots of commercially deodorized unhydrogenated salad SBO with citric acid added were used separately to blend with hydrogenated oils.

Catalysts

HSBO (CuCr-HSBO and CuCr-Ni-HSBO) were produced using a commercial CuCr catalyst and a CuCr-Ni catalyst, respectively. CuCr-Ni catalyst was made by mixing 2 parts Ni catalyst with 1000 parts CuCr catalyst as described previously (12).

Oil Blends

Deodorized unhydrogenated salad soybean oils were combined with CuCr-Ni hydrogenated, water-washed, deodorized, and stabilized soybean oils (CuCr-Ni-HSBO) to give blend oils with 1, 2, and 3% linolenate. The blended oils were thoroughly mixed by bubbling with nitrogen and then were stored at 0 C until tested.

Hydrogenation

In a 15-gal convertor equipped with a gas dispersion agitator, 105 lb of each lot of refined and bleached SBO were partially hydrogenated. SBO was hydrogenated with either the CuCr catalyst or CuCr-Ni catalyst under similar conditions, i.e., 0.5% catalyst, reaction temperature of 175 C, and hydrogen pressure of 50 psig.

SBO and catalyst were first charged to the convertor. The convertor alternately was purged with nitrogen and evacuated 3 times before its contents were stirred vigorously while heating under 26-in. vacuum to the reaction temperature, at which time hydrogen was admitted to the convertor to reach and maintain the reaction pressure. Representative samples (20 ml) were withdrawn from the convertor periodically and filtered. These samples were analyzed immediately by refractive index at 40 C and later by GLC, ultraviolet (UV), and infrared (IV). When the linolenate content in hydrogenated oil was reduced to zero as indicated by refractive index, the convertor was evacuated. The oil was cooled to 80 C under vacuum and filtered.

Post-Hydrogenation Processing

The filtered CuCr-HSBO and CuCr-Ni-HSBO were water washed continuously as described previously (21) to reduce copper in oil to 0.02 ppm or less and were dried under vacuum.

Hydrogenated washed oils were winterized at 5 C. The stearine was separated by vacuum filtration from the winter oil. Winter oils were deodorized in a 15-gal deodorizer at 220 C, $<$1 mm Hg for 4 hr with 11 lb of stripping steam. After deodorization, the oils were cooled to 70 C and stabilized with 5 ppm methyl silicone (Antifoam A compound, Dow Corning Corp, Midland, MI), 0.005% citric acid, and 0.076% Tenox 6 (Eastman Chemical Products, Inc., Kingsport, TN) containing butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate, and citric acid. The stabilizers in warm ethanol were drawn into the deodorizer and followed by 2 ethanol washes to ensure that each deodorized oil contained exactly the same amount of stabilizer. The deodorized oils again were heated to 130 C, held for 15 min, and then cooled to 65 C. Vacuum was broken with nitrogen and the deodorized products were bottled under nitrogen and stored at 0 C until use. A nitrogen cover over the oils was maintained between each intermediate step of the post-hydrogenation process.

Flavor and Odor

Taste panel evaluations for flavor and odor were conducted on all finished oils and blends, each in duplicate, initially without storage, after storage 4 and 8 days at 60 C, and after 4- and 8-hr exposure to fluorescent light. Room odor evaluations were conducted in duplicate on oils and blends heated to 375 F. Testing was divided into 2 parts: a) comparison of CuCr-Ni-HSBO, 0% linolenate to CuCr-HSBO, 0% linolenate, and b) comparison of CuCr-Ni-HSBO, 0% linolenate, to each oil blend. Comparisons were conducted and calculated to show statistical differences. Direct comparison of unhydrogenated SBO, hydrogenated SBO, and the 3 blends was not made because it had been established (2-4,13,14,22) that hydrogenation of SBO to zero linolenate improves flavor and odor.

The 16-member taste panel was trained to discriminate and identify oil flavors and odors prevalent as edible oils deteriorate during storage. Detailed description of the testing methods has been reported previously (2,13,23,24). Flavor intensity value (FIV) and odor intensity value (OIV) (15) were rated on a scale of 1-3, where 1 was weak intensity, 2 was medium, and 3 was strong. FIV or OIV was the total of the intensity weighted flavor and odor descriptions of the panel divided by the number of tasters. Although in these tests only weak intensity values were observed, the type of description, i.e., rancid, painty, grassy, even when recorded as weak, contributed collectively to the taster's numeric score.

RESULTS AND DISCUSSION

Fatty acid compositions and pertinent analytical data of representative oils studied are given in Table I. All oils possessed high oxidative stability, i.e., initial peroxide values (PV) were low (0.2 meq/kg oil), 8-hr active oxygen method (AOM) values were low (2 meq/kg oil), and oils did not reach 100 PV for at least 48 hr under AOM conditions. All hydrogenated and post-processed oils contained <0.02 ppm copper. Winter oil yields were similar to previously reported values (11). Selectivity ratios were equal to or larger than values reported previously (12). The amount of unhydrogenated SBO in the blends ranged from 14.5% to 43%.

Table II is a compilation of flavor and oxidative stability averaged data for 2 lots of commercially refined and bleached soybean oils hydrogenated separately with CuCr or CuCr-Ni catalyst. Table III contains a compilation of flavor and oxidative stability averaged data for duplicate batches of 3 oil blends and the CuCr-Ni-HSBO.

Comparison of Hydrogenated Oils

All hydrogenated oils had good flavor scores initially. Even after storage for 4 and 8 days at 60 C, after 4-hr exposure to fluorescent light, and during room odor tests, all samples of CuCr-HSBO and CuCr-Ni-HSBO scored equally well and were not statistically different. Because these 2 hydrogenated oils had similar scores and descriptions, and because CuCr-Ni catalyst was judged previously (12) to be more active, CuCr-Ni-HSBO was chosen to be the oil to blend with unhydrogenated SBO. Because scores and descriptions for oils exposed 8 hr to fluorescent light were no different from those for oils exposed 4 hr, only the latter are reported here.

Evaluation of Blends of Hydrogenated and Unhydrogenated Oils

If a good quality unhydrogenated SBO were added to HSBO (0% linolenate), oxidative stability of the blend should decrease even though flavor and room odor scores for unhydrogenated SBO have been reported to be low (2,14). But the question of how much unhydrogenated SBO can be added to 0% linlenate HSBO without substantially lowering the critical flavor or odor scores and without causing significant grassy, beany, or rancid descriptions remained. Surprisingly, there was no consistent significant difference between CuCr-Ni-HSBO and the 1% and 2% linolenate blends (Table III). Initial flavor scores of 7.7 for the 2% linolenate blend, although judged statistically lower than 0% HSBO, were equal to those of a good oil. Likewise, flavor scores of 5.5 for oils stored 8 days at 60 C, as well as flavor scores of 5.6 for 4-hr exposure to fluorescent light, both considered severe tests, were not too low. Long term storage at 78 F for 26 weeks for HSBO covered with air produced a flavor score of 5.6 (25). The 3% linolenate blend prepared with 43% unhydrogenated SBO tested significantly different from CuCr-Ni-HSBO initially, after 8 days of storage at 60 C and after 4-hr light exposure. Although these scores in themselves may be representative of a stable oil, the flavor descriptions and FIV are such that the inclusion of 43% unydrogenated oil in the blend may be too large to produce a stable oil consistently.

TABLE III

Flavor and Oxidative Stability of Hydrogenated Soybean Oil and Oil Blends

		Oils blended to contain linolenate (%)		
Conditions	CuCr-Ni-HSBO[a]	1	2	3
Initial (no storage)				
Flavor score[b]	8.1	8.3	7.7[c]	7.4[c]
Description (FIV)[d]				
Bland	0.5	0.4	0.4	0.3
Buttery	0.9	0.9	0.9	0.9
Nutty		0.3	0.2	0.2
Grassy				0.2
Storage 4 days at 60 C				
Flavor score	6.5	6.8	6.8	6.5
Description (FIV)[d]				
Bland	0.8	0.8		
Buttery			0.9	0.9
Grassy		0.3		0.3
Beany	0.3			
Rancid	0.4	0.5	0.6	1.3
Storage 8 days at 60 C				
Flavor score	6.0	5.3[c]	5.5	5.2[c]
Description (FIV)[d]				
Buttery	0.8	0.6	0.5	
Grassy		0.5	0.3	
Beany		0.3		
Rancid	0.6	0.8	1.1	1.1
Painty			0.3	
Hydrogenated	0.4		0.4	0.4
Light exposure 4 hr				
Flavor score	6.1	6.0	5.6[c]	5.3[c]
Description (FIV)[d]				
Buttery	1.1	0.7	0.9	1.0
Grassy	0.5	1.0	0.8	0.6
Beany		0.3		
Rancid	0.4	0.6	0.4	0.6
Melony			0.3	
Light struck			0.3	
Initial (no storage)				
Room odor score	6.5	6.0	5.9	6.3
Description (OIV)[d]				
Heated/hot oil	0.9	0.7	0.8	1.0
Rancid	0.3	0.5	0.4	0.4
Fishy		0.2	0.3	0.3
Acrid			0.2	
Burnt		0.3		0.2

[a] HSBO = hydrogenated soybean oil.

[b] Flavor and odor scores were averaged on a 1 (low) to 10 (high) rating (24).

[c] Score differs significantly from Ni-CuCr-HSBO at the 0.05 level.

[d] Flavor intensity value (FIV) and odor intensity value (OIV) rated on a scale of 1 to 3, where 1 was a weak response, 2 was medium, and 3 was strong (16).

Because the cost to hydrogenate SBO is ca. 0.6 cent per pound of oil and the cost to winterize HSBO is ca. 0.4 cent per pound of oil, a total saving of 1 cent will be realized for each pound of unhydrogenated and winterized SBO used in a blended oil. For 100 pounds of 2% linolenate blend, which contains 29 pounds of unhydrogenated SBO, there would be a saving of 29 cents.

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REFERENCES

1. Kromer, G.W., "Fats and Oil Situation," Economic Research Service, USDA, Washington, DC, February, 1974, p. 3.
2. Evans, C.D., K. Warner, G.R. List, and J.C. Cowan, JAOCS 49(10):578 (1972).
3. Cowan, J.C., Soybean Dig. 26(12):48 (1966).
4. Cowan, J.C., Proc. Production and Technical Division Meeting of the Potato Chip Institute International, Las Vegas, Nevada, 1966, pp. 35-39.
5. Koritala, S., and H.J. Dutton, JAOCS 43:86 (1966).
6. Koritala, S., and H.J. Dutton, Ibid. 43:556 (1966).
7. Koritala, S., Ibid. 45:197 (1968).
8. Koritala, S., Ibid. 47:106 (1970).
9. Moore, D.J., and K.J. Moulton, Ibid. 45:639 (1968).
10. Moulton, K.J., Ibid. 46:662 (1969).
11. Moulton, K.J., R.E. Beal, and E.L. Griffin, Jr., Ibid. 48:499 (1971).
12. Moulton, K.J., R.E. Beal, and E.L. Griffin, Jr., Ibid. 50:450 (1973).
13. Evans, C.D., H.A. Moser, G.R. List, H.J. Dutton, and J.C. Cowan, Ibid. 48:711 (1971).
14. Cowan, J.C., H.A. Moser, G.R. List, C.D. Evans, Ibid. 48:835 (1971).
15. Cowan, J.C., C.D. Evans, H.A. Moser, G.R. List, S. Koritala, K.J. Moulton, and H.J. Dutton, Ibid. 47:470 (1970).
16. Butterfield, R.O., and H.J. Dutton, Ibid. 44:549 (1967).
17. "Official and Tentative Methods of the American Oil Chemists' Society," Vol. I and II, Third edition, AOCS, Champaign, IL, 1964 (revised to 1973), Method Cc 7-25.
18. Ibid. Method Cd 8-53.
19. Ibid. method Cd 12-57.
20. List, G.R., C.D. Evans, and W.F. Kwolek, JAOCS 48:438 (1971).
21. Beal, R.E., K.J. Moulton, H.A. Moser, and L.T. Black, Ibid. 46:498 (1969).
22. List, G.R., C.D. Evans, R.E. Beal, L.T. Black, and K.J. Moulton, Ibid. 51:239 (1974).
23. Moser, H.A., H.J. Dutton, C.D. Evans, and J.C. Cowan, Food Technol. 4:105 (1950).
24. Evans, C.D., JAOCS 32:596 (1955).
25. Evans, C.D., G.R. List, H.A. Moser, and J.C. Cowan, Ibid. 50:218 (1973).

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