Effects of Antioxidants, Methyl Silicone and Hydrogenation on Room Odor of Soybean Cooking Oils

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ABSTRACT

Room odor characteristics produced by heated soybean oil (SBO) and soybean oils hydrogenated with copper (CuHSBO) and nickel (NiHSBO) catalysts were evaluated by a trained panel. Oils were intermittently heated to 190 C for total heating periods of 5, 15 and 30 hr. Oil additives investigated included methyl silicone (MS), tertiary butylhydroquinone (TBHQ) and a polymeric antioxidant in various combinations with citric acid (CA). In room odor tests directly comparing SBO, CuHSBO and NiHSBO, panelists rated the hydrogenated oils as having significantly less odor intensity than the SBO. The combination of CA+MS had the greatest effect in lowering odor intensity of the heated oils, followed by the mixture of CA+MS+TBHQ. The low odor intensity of the MS-treated oils remained fairly constant throughout the tests, while the higher intensity associated with all the other additive-treated oils decreased with increasing heating times, possibly as the result of formation of more volatile decomposition products in the initial heating stages. Methyl silicone had the strongest effect of any additive in decreasing objectionable room odors in the oils. Partially hydrogenated SBO treated with up to 5 ppm of MS produced cooking oils with low room odor intensity and low color development during prolonged heating.

INTRODUCTION

The cooking performance and quality of vegetable oils at elevated temperatures are of interest to oil processors and commercial fry operators as well as individual consumers. Oil performance, stability and quality can be measured by sensory analyses as well as by chemical and instrumental techniques. A variety of oil treatments, including hydrogenation and additives, have been used to maintain oil quality during frying. The effect of hydrogenation was investigated by a number of researchers. Evans et al. (1,2) reported that commercially hydrogenated, winterized soybean oil had significantly better room odor scores than those for soybean salad oil. Moulton et al. (3) reported no significant differences in room odor scores between oils hydrogenated with CuCr or CuCr-Ni catalysts. Chemical and instrumental analysis of soybean oil (iodine value = 123) and hydrogenated vegetable shortening (iodine value = 70) showed significant differences after the oils were either heated or used for frying potatoes for 32 hr at 190 C (4,5). The SBO sample in both heating and frying tests was not as stable as the hydrogenated product as judged by color, iodine value, dielectric constant, and the development of polar materials.

Additives such as silicones and antioxidants have been used to improve the stability of oils during heating and frying. However, antioxidants tend to be lost through volatilization. Augustin and Berry (6) reported that after 8 hr of heating, palm olein lost 70% of the original BHT (butylated hydroxytoluene) and 60% of BHA (butylated hydroxyanisole). Results of chemical and instrumental tests such as peroxide value, anisidine value and absorbance as 232 and 268 nm showed few differences between untreated palm olein and the same oil treated with 200 ppm or less of BHA or BHT. Freeman et al. (7) statically heated sunflower oils containing 200 ppm of BHT or 1 ppm methyl silicone. They reported no protective effect from the antioxidant, whereas silicone had a significant protective effect in preventing oxidation. Martin (8) and Babayan (9) have patents for the use of methyl silicone, showing it to protect the oil against oxidative deterioration and to raise the smoke point of oils.

Many techniques have been used to evaluate the effects of deep fat frying on oil quality by actual frying of foods, simulated frying and static heating. Static heating of oil was applied as an evaluation technique for room odor stability by Evans et al. (1) and was found to be sufficiently sensitive for measuring relative quality differences among a variety of vegetable oils at elevated temperatures. Other investigators used this method to evaluate differences between types of oil (2,3,10) and processing conditions (11). In these tests, room odors were generated during a single use of the test oil. This paper reports a room odor evaluation study on soybean oil to evaluate the effect of hydrogenation and of additives, such as citric acid, antioxidants and methyl silicone, alone or in combination, after extended periods of heating.

EXPERIMENTAL PROCEDURES

Materials

A sample of commercially refined and bleached soybean oil (SBO) was hydrogenated with either copper (CuHSBO) or nickel catalyst (NiHSBO) and deodorized as described previously (12). Fatty acid composition of the oils is given in Table I. Stabilizers, added on the cooling side of deodorization, included 100 ppm citric acid (CA); 100 ppm CA + 5 ppm methyl silicone (MS) (Antifoam A, Dow Corning Corp., Midland, Michigan); 100 ppm CA + 200 ppm tertiary butylhydroquinone (TBHQ) (Eastman Chemical Products, Kingsport, Tennessee); 100 ppm CA + 5 ppm MS + 200 ppm TBHQ; 100 ppm CA + 200 ppm polymeric antioxidant (polymeric AO) (Dynapol, Palo Alto, California).

Methods

Procedures to evaluate room odor are based on modifications of methods of Evans et al. (1,2). Two 8 ft × 5 ft × 10 ft rooms were constructed, each with two entry chambers (3.8 ft × 2.8 ft × 10 ft) which served as air locks to prevent premature exposure to odors (13). The odor rooms, panelled with non-porous material, were maintained at 24 C ± 1 C. A 200 g sample of oil was heated in a 500 ml glass crystallizing dish (100 mm diameter × 80 mm high). A temperature of 190 C was maintained for 30 min prior to the 30 min panel evaluation period. One tester was allowed in a room at a time. To avoid bias from order of testing, one-half of the panelists rated the odor in room #1 first and the other half evaluated the odor in room #2 first. Panelists

TABLE I

Composition of Oils (wt %)

Fatty acid	Unhydrogenated soybean oil (SBO)	Nickel-hydrogenated soybean oil (NiHSBO)	Copper-hydrogenated soybean oil (CuHSBO)
16:0	10.6	10.7	10.7
18:0	3.7	3.5	3.8
18:1	22.6	37.4	42.4
18:2	55.4	47.8	39.7
18:3	7.7	0.6	3.3
Calc iodine value	133	114	113

evaluated the odor of the oils during initial heating and after 5, 15 and 30 hr of intermittent heating. Heating of the oils was continued immediately after each 0 (initial), 5 and 15 hr evaluation to increase the oil usage time. After each heating period, the oils were cooled and placed in 250 ml narrow-mouth glass bottles with N_2 in the headspace and stored at 0 C until the next scheduled evalution. Panelists rated the room odor for overall intensity as well as for specific odor components and their intensities by modified quantitative descriptive analysis (14). A scale of 0 to 10 was used with 0 = no odor and 10 = strong intensity for both overall intensity and individual description intensity. Descriptions listed on the score sheet included doughy, fried food, burnt, acrid, fishy, fruity, hydrogenated, musty, smoky and woody.

RESULTS AND DISCUSSION

Panelists evaluated the oils in sample pairings from a modified chain block experimental design (15). Within each oil type, five additive combinations and a control with no additives were compared. Each of the oil-additive combinations was evaluated in both of the odor rooms (I and II), pairing two different additive treatments in separate trials. Each oil also was tested at four heating times of 0, 5, 15 and 30 hr. Table II presents the design for comparing the room odor of the oil treatments tested in two odor rooms at four heating times.

The effect of hydrogenation was evaluated by comparing the three oil types which contained citric acid only, in a randomized complete block design at 0 and 5 hr of heating. Odor scores were examined by analysis of variance, tests of interactions and main effects, and regression analysis (16).

The room odor scores for the three oil types with the five additive combinations at four heating times are shown in Figure 1. In comparing the scores for the four heating times, a stronger room odor intensity was noted by the panelists at the initial evaluation, with a gradually decreasing intensity through the subsequent heating times of 5, 15 and 30 hr. Although volatile compounds continue to be generated throughout the heating periods, it does appear that more volatiles may be formed initially, as judged by differences in room odor intensity.

Recommendation of an optimum heating time at which to evaluate an oil is dependent on the oil type. The 15 hr heating time is recommended for evaluation of the SBO sample because of the wide range of scores, whereas either the 0, 5 or 15 hr times would be appropriate for either of the hydrogenated oils. The 30 hr heating time is not recommended for evaluation of any of the oils because of the range of scores for the oils showed smaller differences between additive types.

In all oils tested, the additive treatment responsible for the largest decrease in room odor intensity was MS in combinations with either CA or CA + TBHQ. Evans et al. (1) noted the improvement of room odor scores of soybean oil containing 8% linolenate (Ln) and hydrogenated soybean oil (1.2% Ln) during a single heating by the addition of 5 ppm of MS. They also reported that mixtures of BHA, BHT and MS gave results not significantly different from oils with MS alone. In this study, the efficacy of MS was retained during repeated heatings of the oil up to the 30 hr period, at which our testing stopped. This observation was also reported by Frankel et al. (17) during repeated fryings in MS-treated soybean oil. When vegetable oils were used at elevated temperatures, addition of MS at a level of 5 ppm significantly improved oil performance and quality.

The addition of other stabilizers, CA, TBHQ or Polymeric AO, without MS did not affect the room odor intensity in most of the tests as compared to the intensity of the control

TABLE II

Test Design for Comparing Room Odor of Oils with 6 Treatments at 4 Heating Times

		Heating time (hr)							
		0		5		15		30	
Trial	Room =	I	II	I	II	I	II	I	II
		Sample codes[a]							
A		1	2	1	3	1	4	1	4
B		2	3	3	5	4	3	4	2
C		3	4	5	2	3	6	2	6
D		4	5	2	4	6	2	6	3
E		5	6	4	6	2	5	3	5
F		6	1	6	1	5	1	5	1

[a] Codes: 1, no additives; 2, 100 ppm citric acid (CA); 3, 100 ppm CA + 200 ppm tertiary butylhydroquinone (TBHQ); 4, 100 ppm CA + 5 ppm methyl silicone (MS); 5, 100 ppm CA + 200 ppm TBHQ + 5 ppm MS, and 6, 100 ppm CA + 200 ppm polymeric antioxidant.

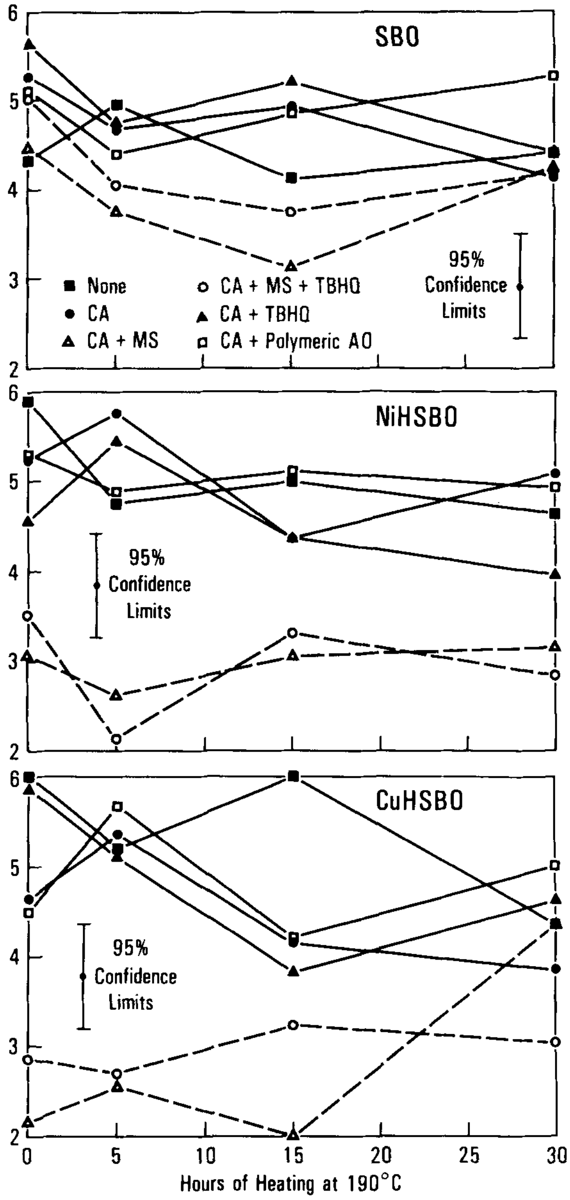

FIG. 1. Effect of additives and hydrogenation on room odor intensity of heated oils.

oils (Fig. 1). A few exceptions exist, as in tests with CuHSBO at 0 and 15 hr heating and with NiHSBO at 0 hr heating time, in which the controls had the strongest odor, but there were no consistent trends.

Table III presents pooled data showing the effects of MS and TBHQ in each of the three oil types. Within each oil type, data from tests were divided first into those containing MS and those without MS. All of the data were pooled again and redivided into groups with and without TBHQ. Significant differences between oils with and without MS were observed in room odor intensities at 0, 5 and 15 hr heating for all three oil types. At 30 hr, only NiHSBO showed an improvement with MS. The antioxidant TBHQ did not significantly improve the room odor scores of the oils.

The mechanism by which MS protects oil is not completely understood. Methyl silicone has been reported to form a surface protective film on the oil to prevent oil deterioration (7,8,18,19). Freeman (7) has suggested that in addition to preventing oxygen from reaching the oil, the MS monolayer also inhibits convection currents. The effect of MS as described in this study of statically heated oil has also been observed in repeated frying tests with sunflower oil (7,19) and vegetable shortening (8), even when the protective film is physically disrupted at various intervals.

Color development of the oils during repeated heatings was monitored visually. Oils with MS developed a medium yellow color after 30 hr of heating, whereas the oils without MS were dark orange. Sims et al. (18) reported that MS retards color development in oils by acting as a polymerization inhibitor.

Odor descriptions are of importance in evaluating oil quality. The types of room odor descriptions and their intensities for the three oil types are presented in Figure 2. As expected, the SBO had the highest intensity of fishy odors, whereas hydrogenation odor was typical of the NiHSBO, but slightly less in CuHSBO. Other predominant odors de-

TABLE III

Overall Room Odor Intensity Scores for Oils With and Without Methyl Silicone (MS) and Tertiary Butylhydroquinone (TBHQ)

		Heating time (hr)			
Oil	Additives	0	5	15	30
SBO	MS present[a]	4.7 *[b]	3.9 *	3.5 *	4.3
	MS absent[c]	5.4	4.7	5.2	4.3
	TBHQ present[d]	5.3	4.4	4.5	4.4
	TBHQ absent[e]	4.9	4.2	4.0	4.2
CuHSBO	MS present	2.5 *	2.6 *	2.6 *	3.7
	MS absent	5.3	5.2	4.0	4.2
	TBHQ present	4.4 *	3.9	3.0	4.0
	TBHQ absent	3.4	3.9	3.5	3.8
NiHSBO	MS present	3.3 *	2.6 *	3.2 *	3.0 *
	MS absent	4.9	5.6	4.4	4.5
	TBHQ present	4.0	3.8	3.9	3.4
	TBHQ absent	4.2	4.2	3.7	4.0

[a] Combined scores of citric acid (CA) + MS and CA + MS + TBHQ.

[b] Significant at 95% confidence level.

[c] Combined scores of control; CA; CA + TBHQ and CA + polymeric AO.

[d] Combined scores of CA + TBHQ and CA + TBHQ + MS.

[e] Combined scores of control; CA; CA + MS and CA + polymeric AO.

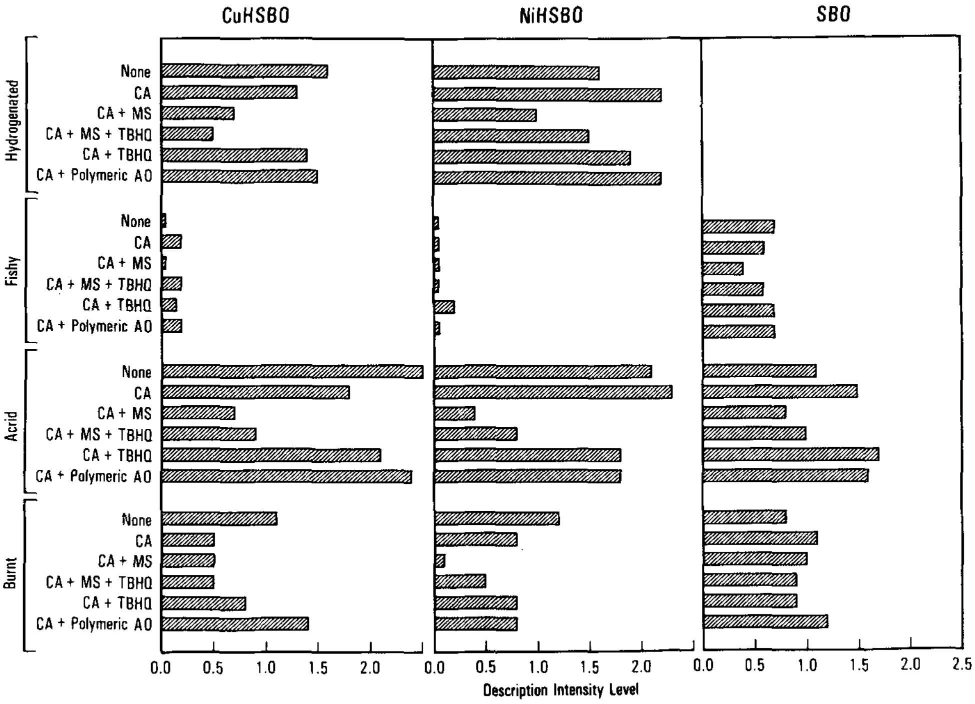

FIG. 2. Effect of additives and hydrogenation on room odor descriptions of heated oils.

tected by the panelists were burnt and acrid. The effect of methyl silicone can be seen in the description intensity levels, especially for NiHSBO and CuHSBO. The acrid, burnt and hydrogenated odor intensities are significantly reduced, due to the methyl silicone effect. Generally, the combination of CA + MS has a slightly greater effect in suppressing odor intensities than does the combination of CA + MS + TBHQ.

The effect of hydrogenation on room odor scores is shown in Table IV with oils which contained only CA as an additive and which were evaluated only at the initial and 5 hr periods. These tests directly compared the three oils in the following pattern at each heating time: SBO vs CuHSBO; SBO vs NiHSBO, and CuHSBO vs NiHSBO. The duplicate room odor scores were pooled. At the initial heating, SBO had a significantly stronger odor than either of the two hydrogenated oils. The oil with the least room odor intensity initially was CuHSBO. At the 5 hr heating time, no significant difference was noted between the two hydrogenated oils but both had significantly lower odor intensity than the SBO sample.

As noted earlier, Evans et al. (1) showed improvement of room odor scores of SBO during single heatings by addition of MS and no effect from antioxidants. These results indicate that the effect of MS is retained during repeated heatings of SBO and hydrogenated SBO. The efficacy of hydrogenation of soybean oil to a linolenic acid content of 3.3 or less to improve room odor stability also has been confirmed. Partially hydrogenated SBO treated with up to 5 ppm of MS produced cooking oils with low room odor intensity and low color development during prolonged heating.

TABLE IV

Effect of Hydrogenation at Room Odor Scores[a] of Oils Containing Citric Acid

	Oils[b]				
			Hydrogenated soybean oils		
Heating at 190 C (hr)	SBO		CuHSBO		NiHSBO
0	6.6	*	4.8	*	5.5
			*		
5	5.8	*	4.8	NS	4.7
			*		

[a]Based on 0-10 scale with 0 = none, 10 = strong intensity.

[b]Significance levels: * = 95% confidence level; NS = not significant.

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REFERENCES

1. Evans, C.D., H.A. Moser, G.R. List, H.J. Dutton and J.C. Cowan, JAOCS 48:711 (1971).
2. Evans, C.D., K. Warner, G.R. List and J.C. Cowan, JAOCS 49: 578 (1972).
3. Moulton, K.J., R.E. Beal, K. Warner and B.K. Boundy, JAOCS 52:469 (1975).
4. Fritsch, C.W., D.C. Egberg and J.C. Magnuson, JAOCS 56:746 (1979).
5. Fritsch, C.W., JAOCS 53:272 (1981).
6. Augustin, M.A., and S.K. Berry, JAOCS 60:1520 (1983).
7. Freeman, I.P., F.B. Padley and W.L. Sheppard, JAOCS 50:101 (1973).
8. Martin, J.B., U.S. Patent 2,634,213 (1953).
9. Babayan, V.K., U.S. Patent 2,998,319 (1961).
10. Cowan, J.C., S. Koritala, K. Warner, G.R. List, K.J. Moulton and C.D. Evans, JAOCS 50:132 (1973).
11. List, G.R., C.D. Evans, R.E. Beal, L.T. Black, K.J. Moulton and J.C. Cowan, JAOCS 51:239 (1974).
12. Mounts, T.L., K. Warner, G.R. List, J.P. Friedrich and S. Koritala, JAOCS 55:345 (1978).
13. Mounts, T.L., JAOCS 56:659 (1979).
14. Stone, H., J. Sidel, S. Oliver, A. Woolsey and R.C. Singleton, Food Technol. 28:24 (1974).
15. Cochran, W.G., and G.M. Cox, "Experimental Designs," 2nd ed., John Wiley and Sons, Inc., New York, NY (1957).
16. Snedecor, G.W., "Statistical Methods," 5th ed., The Iowa State University Press, Ames, IA (1956).
17. Frankel, E.N., K. Warner and K.J. Moulton, JAOCS (in press) (1985).
18. Sims, R.J., J.A. Fioriti and M.J. Kanuk, Lipids 8:337 (1973).
19. Zwoboda, F., Rev. Fr. Corps Gras 26:534 (1979).

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