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Effects of Hydrogenation and Additives on Cooking Oil Performance of Soybean Oil

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ABSTRACT

Soybean oil was continuously hydrogenated in a slurry system to investigate the effects of linolenate content and additives on cooking oil performance. Room odor evaluations carried out on oils heated to 190 C after frying bread cubes showed that the oils hydrogenated with Cu catalyst to 2.4% linolenate (Cu-2.4) and with Ni catalyst to 4.6 linolenate (Ni-4.6) had a significantly lower odor intensity score than the unhydrogenated soybean oil (SBO). Other hydrogenated oils (Cu-0.5 and Ni-2.7) were not significantly better than SBO. Oil hydrogenated with Ni (Ni-0.4) scored poorly because of its strong "hydrogenated-paraffin" odor. The performance of all partially hydrogenated oils (2.4, 2.7 and 4.6% linolenate) was improved by adding methyl silicone (MS), but the most hydrogenated oils (0.5 and 0.4% linolenate) were not improved. Although with tertiary butyl hydroquinone (TBHQ) no improvement was obtained, with the combination of TBHQ + MS all odor scores were lower, indicating a synergistic effect. Evaluations of bread cubes after intermittent heating and frying showed that the breads fried in most hydrogenated oils (Ni-0.4, Cu-2.4 and Ni-2.7) were rated significantly better in flavor quality than breads fried in SBO. The bread cubes fried in MS-treated oils had significantly higher flavor quality scores than breads fried in SBO or SBO containing TBHQ. Dimer analyses by gel permeation chromatography and color development after heat treatments also did not correlate with sensory analyses.

INTRODUCTION

Much work has been reported on thermal oxidation and deterioration of unsaturated fats when heated in air under deep fat frying conditions (1-12). However, little information is available on the effect of partial hydrogenation on the performance of soybean oil as a cooking oil and on the flavor and oxidative stability of foods fried in such oil.

Direct sensory evaluation of the effect of deep fat frying on oil quality is difficult because used heated fats have flavors and odors that are too intense to be measured reliably. To overcome this problem, Evans et al. (13) developed a useful test based on evaluation of the room odor produced by oils heated under standardized conditions. Recent studies based on this room odor test with samples heated statically at 190 C showed a significantly lower odor intensity from soybean oil partially hydrogenated with copper or nickel catalysts than from unhydrogenated oil (14). The use of combinations of citric acid (CA), methyl silicone (MS) and tertiary butyl hydroquinone (TBHQ) also lowered the odor intensity of the heated oils. These results are in contrast to those obtained in storage stability studies of similar samples evaluated as salad oils by tasting at 50 C after accelerated storage at 60 C (15,16). Salad oil evaluations showed no significant improvement in the flavor stability during storage by either partial hydrogenation or by the use of antioxidants such as BHA, BHT or TBHQ. However, the oxidative stability based on peroxide values showed an improvement by partial hydrogenation of the oils as well as by the use of these antioxidants.

In this paper we report the effect of hydrogenation to different linolenate contents, and of stabilizers such as MS and TBHQ, on cooking performance of soybean oil under deep fat frying conditions. A continuous slurry hydrogenation system (17,18) was used, and copper-chromite and nickel catalysts were compared. Methods were developed to evaluate the performance of hydrogenated oils under deep fat frying conditions by both sensory and instrumental techniques. The room odor test was modified to include evaluation of oils that had been used to fry bread cubes. The fried bread cubes also were evaluated after storage under different conditions.

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EXPERIMENTAL

Continuous Hydrogenation

The continuous slurry system used to hydrogenate soybean oil with copper-chromite (Cu) and nickel (Ni) catalysts was described previously (17). The hydrogenated oils were bleached, deodorized and stabilized with CA in combination with either MS or TBHQ. Analyses of the bleached and deodorized oils and their evaluations for flavor and oxidative stability are reported in another paper (19). The fatty acid compositions of these oils are summarized in Table I. Hydrogenated oils are designated by the catalyst used and % linolenate (e.g. Cu-0.5 = hydrogenated with Cu catalyst to 0.5% linolenate).

Frying Procedures

The following schedule was designed to test the performance of oils for frying bread cubes repeatedly and to evaluate room odor intensity, flavor quality and stability of the fried bread.

Day 1. Oil sample (600 g) weighed in a 2-qt deep fat fryer ("Electric Multi-Fry," Northland Aluminum Prods., Minneapolis, Minnesota) was heated to 190 C in 15 min. One-hundred g of white bread ("Butternut" sandwich style),

TABLE I

Fatty Acid Composition (Relative Area %) of Hydrogenated and Nonhydrogenated Soybean Oils (19)

Identifications (code)[a]	Fatty acid composition by GLC, %					Calc IV[b]	*Trans* %
	16:0	18:0	18:1	18:2	18:3		
Soybean oil (SBO)	10.3	4.4	22.7	54.1	8.5	139.5	0
Cu hydrogenated (Cu-0.5)	10.1	4.4	39.7	45.3	0.5	113.9	22.9
Cu hydrogenated (Cu-2.4)	10.4	4.2	30.4	52.6	2.4	123.7	8.4
Ni hydrogenated (Ni-0.4)	10.2	16.4	62.8	10.2	0.4	73.0	27.4
Ni hydrogenated (Ni-2.7)	10.2	7.1	49.3	30.7	2.7	102.6	15.0
Ni hydrogenated[c] (Ni-4.6)	11.2	3.5	37.8	42.9	4.6	119.3	16.5

[a](Catalyst-% linolenate).

[b]IV = iodine value calculated on the basis of GLC analyses.

[c]Commercial.

cut into 1-in. crust-free cubes, was fried in 10 g lots at 6-min intervals for one hr. To avoid contamination, a separate fryer was dedicated to those oils containing methyl silicone. Fried bread was drained and stored at 0 C in glass jars until tasting. The used oil was subjected to room odor evaluation in duplicate, each involving a 1-hr heating period at 190 C (total heating and frying = 3 hr). Suitable samples were saved for instrumental tests.

Day 2. Used oil was mixed with 10% by weight, fresh make-up oil in the fryer and heated six more hr at 190 C, followed by one hr frying of 100 g bread cubes as above (total heating = 7 hr).

Day 3. Used oil was again mixed with 10% fresh make-up oil and heated an additional 6.5 hr followed by 0.5 hr frying of 50 g bread cubes. Drained fried bread cubes were stored, and the used oil was submitted to room odor evaluation in duplicate involving two more hr of heating (total heating = 9 hr). According to this schedule, oils were subjected to heating at 190 C for a total period of 19 hr (3 + 7 + 9) and to frying bread cubes for 2.5 hr (1 + 1 + 0.5).

Sensory Evaluations

Room Odor. Evaluations were conducted by a panel of 16 members in two identical and specially designed rooms as described previously (20). Odors were generated by heating an oil sample (200 g) in a 500 ml glass crystallizing dish on a hot plate at 190 C for 30 min before, and 30 min during evaluation. Samples were evaluated in duplicate. Odors produced in the individual hoods were vented into the rooms during each test period. To eliminate any room order bias, half the panelists rated room No. 1 first and the other half rated room No. 2 first, and the sample location was reversed at the duplicate session. Oil odor was rated for overall intensity and individual descriptions by using a score sheet with interval scales (20). Line scores were converted into a numerical scale of 0 to 10 with 0 = no odor and 10 = strong intensity. Odor descriptions included fruity, hydrogenated, musty, acrid/pungent, fishy, smoky and doughy.

Fried Bread. A 15-member panel experienced in tasting vegetable oils was trained to evaluate fried bread quality. Bread cubes were tasted after frying (initial, 1 hr) and after 17 hr of oil usage. Fried bread cubes were then stored at 60 C for four days in wide-mouth 4-oz glass jars, and at 25 C for six weeks in 6 × 6 in. plastic bags ("zip-lock"). A control bread sample was fried in cottonseed oil and stored at 0 C until testing. The flavor quality of the bread cubes was evaluated on fresh and stored samples. Before tasting, individual bread cubes were placed in 50-ml beakers covered with watch glass and maintained at 50 C over a heated aluminum plate. A flavor quality scale from 1 to 10 was used with 10 = excellent and 1 = extremely poor. Control bread cubes rated as good quality were given an average score of 8 by the panel. Each evaluation was done by comparing two samples of bread cubes with the control. Flavor descriptions included fried food, stale, hydrogenated, grassy, acrid, fishy, rancid and painty.

Instrumental Evaluation

Nonsensory evaluations included dimer analyses, color, and headspace volatiles by gas chromatography. The results of headspace volatiles are reported in another paper (21).

Dimers. Previous methods have been reported for the separation of dimeric and high-molecular weight materials in heated and polymerized fats by gel permeation chromatography (GPC) (22-24). For the present study, we developed a GPC procedure to separate the methyl esters of the heated fat on "ultrastyragel" columns obtained from Waters Associates (Milford, Massachusetts) with tetrahydrofuran (THF) as solvent. A Waters high pressure liquid chromatograph (HPLC) was used with refractive index detector. Oil samples were transesterified with sodium methoxide, and the resulting methyl esters were injected as 1:1 solutions in methylene chloride (0.5 μl). The pressure was 600 psi, and the flow rate 0.5 ml/min. The procedure was standardized with known mixtures of commercial dimer ester (Emery Empol 1010, Emery Industries, Inc., Cincinnati, Ohio) and methyl oleate as monomer. A linear plot was obtained between observed (X-axis) and actual dimer (Y-axis) content in the 0 to 17% range (Y = 0.8395X). When standard mixtures of commercial dimer esters and methyl oleate were used, adequate dimer-monomer separation was obtained with one column of 100 Å ultrastyragel (30 cm × 7.8 mm). However, when a heated fat was used, adequate separation between dimer and monomer required two columns connected in series (Waters 500 Å "microstyragel" and 100 Å ultra-styragel, 30 cm × 7.8 mm each).

Color. A Brinkman PC-600 Probe colorimeter (Brinkman Instrument Co., Westbury, New York) was used to follow the effect of repeated heating and frying of bread on oil color. A 545 nm filter and 20 mm stainless steel probe were used to measure percent transmittance in samples of 20 g oil in a 25 ml vial at ambient temperature. Highly hydrogenated oils were melted at 40 C before measurement. A clear paraffin oil was used as a blank giving 100% transmittance.

RESULTS AND DISCUSSION

Sensory Evaluations

In previous studies oil samples were heated for room odor evaluation either after a single use (13,15,16) or after an extended period of time (14) without food frying. In this study the effect of frying bread cubes for varying times was determined under standardized conditions before room odor evaluation. Bread cubes proved to be a suitable model food because of availability, uniform size and moisture content (35%). Bread cubes are stored conveniently after frying and easily evaluated by our vegetable oil panel.

The effects of hydrogenation and additives were tested by a chain block experimental design (25) shown in Table II. With six hydrogenation and four additive treatments there were 24 combinations of treatments possible with each oil paired with all others. Each oil-additive combination was tested against two different samples by room odor evaluation, thus giving two replicates per sample. Bread samples were evaluated two at a time by the same plan. With this

TABLE II

Testing Design for Room Odor and Fried Bread Evaluations[a]

Run	Room/Bread 1	Room/Bread 2
1	SBO + CA	Cu-0.5 + CA
2	Cu-2.4 + CA	Ni-0.4 + CA
3	Ni-2.7 + CA	Ni-4.6 + CA
4	SBO + CA + TBHQ	Cu-2.4 + CA + TBHQ
5	Cu-0.5 + CA + TBHQ	Ni-2.7 + CA + TBHQ
6	Ni-0.4 + CA + TBHQ	Ni-4.6 + CA + TBHQ
7	SBO + CA + MS + TBHQ	Ni-0.4 + CA + MS + TBHQ
8	Cu-0.5 + CA + MS + TBHQ	Ni-4.6 + CA + MS + TBHQ
9	Ni-2.7 + CA + MS + TBHQ	Cu-2.4 + CA + MS + TBHQ
10	SBO + CA + MS	Ni-2.7 + CA + MS
11	Ni-0.4 + CA + MS	Cu-0.5 + CA + MS
12	Cu-2.4 + CA + MS	Ni-4.6 + CA + MS
13	Ni-4.6 + CA + MS + TBHQ	SBO + CA + MS + TBHQ
14	Cu-2.4 + CA + MS + TBHQ	Cu-0.5 + CA + MS + TBHQ
15	Ni-0.4 + CA + MS + TBHQ	Ni-2.7 + CA + MS + TBHQ
16	Cu-0.5 + CA + MS	SBO + CA + MS
17	Ni-4.6 + CA + MS	Ni-0.4 + CA + MS
18	Ni-2.7 + CA + MS	Cu-2.4 + CA + MS
19	Ni-4.6 + CA	SBO + CA
20	Ni-0.4 + CA	Ni-2.7 + CA
21	Ni-0.5 + CA	Cu-2.4 + CA
22	Ni-2.7 + CA + TBHQ	SBO + CA + TBHQ
23	Ni-4.6 + CA + TBHQ	Cu-0.5 + CA + TBHQ
24	Cu-2.4 + CA + TBHQ	Ni-0.4 + CA + TBHQ

[a]See Table I for sample identification.

Additives: CA, citric acid, 100 ppm; MS, methyl silicone, 5 ppm, and TBHQ, tertiary butyl hydroquinone, 200 ppm.

plan there is equal precision among all oil treatments. Analysis of variance was used to determine statistical significance.

All samples listed in Table III contained CA as metal inactivator. In the presence of CA alone, after the initial 1 hr of bread frying the oils partially hydrogenated with Cu to 2.4% linolenate and with Ni to 4.6% linolenate gave the lowest odor scores of 4.1 and 4.2, respectively. Intermediate odor scores were obtained with unhydrogenated oil (4.9) and with the oils hydrogenated with Ni to 2.7% linolenate (5.2) and with Cu to 0.5% linolenate (4.7). The highest odor score of 6.4 was obtained with the oil hydrogenated with Ni to 0.4% linolenate. After 19 hr of heating and bread frying essentially the same trend was obtained in odor scores and descriptions. Odor intensities increased in the order (catalyst-% linolenate): Cu-2.4, Ni-4.6, Cu-0.5 = Ni-2.7, control, Ni-0.4. Again, the oil most highly hydrogenated with Ni gave the highest odor intensity. These odor intensity scores can be explained by the description responses. The unhydrogenated oil gave the highest fishy responses, whereas the oil highly hydrogenated with Ni to 0.4% linolenate gave the highest "hydrogenated-paraffin" response. Therefore, the oils partially hydrogenated with either Cu or Ni performed best under these experimental conditions.

In the presence of MS and CA, all partially hydrogenated oils (2.4, 2.7 and 4.6% linolenate) performed better initially than the unhydrogenated soybean oil control in giving a significantly lower odor intensity score. However, the highly hydrogenated oils (0.5 and 0.4% linolenate) were not significantly different from the unhydrogenated control. In the presence of TBHQ and CA, the oil hydrogenated with Ni to 4.6% linolenate was initially better (3.7) than the control (4.5) but not as good when hydrogenated to 0.4% linolenate (5.8). The other samples were not significantly different. After 19 hr of heating and bread frying, all but one of the hydrogenated oils were not significantly better than the control; the oil hydrogenated with Ni to 0.4% linolenate was poorer than the control. In the presence of MS, TBHQ and CA, all odor scores were lower, showing a synergistic effect. There was no apparent effect of partial hydrogenation. However, the oil most highly hydrogenated with Ni (0.4% linolenate) produced the highest odor score (4.5 and 4.6). As before, the oil highly hydrogenated with Ni was scored poorly because of the strong hydrogenated-paraffin odor it generated.

TABLE III

Effect of Hydrogenation and Additives on Room Odor Scores[a] after Initial (I) and Final (F) Heating and Frying[b]

	CA		CA + MS		CA + TBHQ		CA + MS + TBHQ	
Samples[c]	I	F	I	F	I	F	I	F
SBO	4.9a	5.8a	4.9a	5.0a	4.5a	5.2a	3.8a	3.8a
Cu-0.5	4.7ab	5.5ab	4.6ab	4.7a	4.7a	4.7a	4.0ab	4.1a
Cu-2.4	4.1b	4.7b	4.1b	4.3ab	4.4a	4.5a	3.5a	3.9a
Ni-0.4	6.4c	6.5c	4.6ab	4.8a	5.8b	6.7b	4.5b	4.6b
Ni-2.7	5.2a	5.6a	3.9b	3.9b	4.4a	5.1a	3.4a	3.5a
Ni-4.6	4.2b	5.2ab	4.2b	4.3ab	3.7c	5.0a	4.0ab	3.9a

[a]Statistical comparison of scores should be made within each heating treatment (I and F) and additive type in going vertically. Scores with letters not in common are significantly different at the 95% confidence level. Scale 0-10, 0 = none, 10 = strong intensity.

[b]Initial = 1 hr frying, final = 16.5 hr heating + 2.5 hr frying (total 19 hr).

[c]See Table I for sample description.

Flavor evaluations of bread cubes after initial 1 hr frying showed no effect of hydrogenation with oils containing CA alone when evaluated fresh (0-time) or after storage six weeks at 25 C (Table IV). Storage of the initial fried bread cubes (1 hr) for four days at 60 C showed significant improvement in flavor quality with hydrogenated oils Cu-2.4, Ni-0.4 and Ni-2.7 over the unhydrogenated oil. Frying bread cubes for one hr in oils containing CA + MS showed improvements in flavor quality scores by using hydrogenated oils Cu-0.5, Cu-2.4, Ni-2.7 and Ni-4.6 when evaluated at 0-time. After storage for six weeks at 25 C, the flavor quality of bread fried in hydrogenated oils Cu-0.5, Cu-2.4, Ni-2.7 and Ni-4.6 was significantly more stable than that of bread fried in unhydrogenated oil. With a few exceptions the same results were obtained when oils containing CA + TBHQ or CA + MS + TBHQ were used for frying bread cubes.

When oils used 17 hr were used for frying, the quality of the bread cubes was higher with most hydrogenated oils than with unhydrogenated soybean oil when tested at 0-time storage. However, after storage four days at 60 C or six weeks at 25 C, the flavor quality scores decreased significantly with all oils containing CA and CA + TBHQ. On the other hand, those oils containing CA + MS or CA + MS + TBHQ generally imparted stability to the fried bread cubes after storage.

Our results show that if bread cubes are fried in fresh, good quality soybean oil, they can be stored without much loss in quality. On the other hand, if bread cubes are fried in repeatedly used oils, they can be consumed immediately after frying only if the oils are partially hydrogenated. However, they cannot be stored without marked decrease in quality. It appears, therefore, that fried bread cubes may prove useful as a quality control method for processors of fried products consumed after storage (e.g. potato chips), to measure the abuse of an oil by tasting them after storage under standardized conditions.

Instrumental Evaluations

To determine cooking performance by independent instrumental methods, soybean oil was compared to hydrogenated oils subjected to the same frying conditions used above for sensory evaluations.

TABLE IV

Effect of Hydrogenation on Flavor Quality Scores[a] of Fried Bread Cubes After Initial (I) and Final (F) Heating and Frying[b]

Samples[c]	Storage[d]	CA		CA + MS		CA+TBHQ		CA + MS + TBHQ	
		I	F	I	F	I	F	I	F
SBO	0-time	5.6	5.5	5.3	4.8	5.5	5.4	5.8	4.8
	4d-60 C	4.9	2.7	5.4	3.8	5.5	2.0	6.0	4.3
	6w-25 C	5.6	<2	4.9	5.6	5.6	<2		
Cu-0.5	0-time	5.3	6.1	6.3	6.8	6.6	6.1	7.3	6.7
	4d-60 C	5.4	3.8	5.9	5.5	6.3	2.2	7.0	5.6
	6w-25 C	5.5	<2	6.8	6.2	7.0	<2		
Cu-2.4	0-time	6.3	6.5	7.2	6.4	7.1	6.6	6.8	6.4
	4d-60 C	6.0	2.4	6.8	4.9	6.3	2.0	7.0	5.0
	6w-25 C	6.0	<2	6.4	6.1	6.9	<2		
Ni-0.4	0-time	6.1	5.9	5.9	5.9	6.6	6.4	6.0	5.5
	4d-60 C	6.2	2.8	6.7	4.5	6.4	2.0	5.8	5.2
	6w-25 C	5.7	6.1	5.8	5.5	6.6	4.3		
Ni-2.7	0-time	6.1	6.6	6.7	7.0	7.0	6.6	6.9	6.5
	4d-60 C	6.5	3.0	6.4	6.4	5.7	1.9	7.0	5.0
	6w-25 C	6.1	1.9	6.8	5.7	6.8	2.4		
Ni-4.6	0-time	6.0	6.5	6.8	6.6	6.9	6.8	6.0	6.2
	4d-60 C	5.6	3.8	5.6	4.8	6.4	2.0	5.8	5.1
	6w-25 C	6.1	<2	6.6	5.6	6.4	<2		

[a]Least significant difference (LSD) = 1.0. Scale 1-10, 10 = excellent, 1 = extremely poor.

[b]Initial = 1 hr frying, final = 2.5 hr frying + 14.5 hr heating (total 17 hr).

[c]See Table I for sample identification.

[d]d = days, w = weeks.

TABLE V

Dimer Analyses by Gel Permeation Chromatography[a], %

Samples[b]	Heat treatment[c]		Increase
	Initial	Final	
SBO	0.5	5.3	4.8
Cu-0.5	0.7	6.0	5.3
Cu-2.4	1.0	6.0	5.0
Ni-0.4	0.3	3.0	2.7
Ni-2.7	0.2	4.2	4.0
Ni-4.6	0.5	6.1	5.6

[a]Averages of 2-4 analyses. Calculated average standard deviation ± 0.05 for initial values, and ± 0.3 for final values.

[b]See Table I for sample identification.

[c]Initial = 1 hr frying, final = 2.5 hr frying + 16.5 heating (total 19 hr).

TABLE VI

Color Development in Heated Oils—% Transmittance[a] (increase)

Samples[b]	CA		CA + MS		CA + TBHQ		CA + MS + TBHQ	
	I[c]	F[c]	I	F	I	F	I	F
SBO	95	75 (20)	96	82 (14)	97	75 (22)	97	86 (11)
Cu-0.5	97	90 (7)	97	88 (8)	97	82 (15)	99	99 (8)
Cu-2.4	95	80 (15)	96	88 (8)	97	78 (19)	99	88 (11)
Ni-0.4	94	87 (7)	98	85 (13)	98	85 (13)	97	84 (13)
Ni-2.7	97	70 (27)	98	84 (14)	97	74 (23)	98	85 (13)
Ni-4.6	96	75 (21)	96	85 (11)	97	74 (23)	97	87 (10)

[a]By probe colorimeter using 545 nm filter. Calculated average standard deviation ± 0.5.

[b]See Table I for sample identification.

[c]I = initial, 1 hr frying; F = final, 2.5 hr frying + 16.5 hr heating.

Previous work has shown that dimers and high molecular weight compounds could be separated and determined by GPC in fats used for deep fat frying (24). Analyses by GPC of used oils obtained after one hr of bread frying showed the least amount of dimer (0.2-0.3%) in the Ni-0.4 and Ni-2.7 hydrogenated oils (Table V). The other oils varied from 0.5 to 1% in dimer content. After 19 hr of heating and bread frying, the Ni-0.4 and Ni-2.7 hydrogenated oils developed the least amount of dimer (2.7-4.0%). However, the increased dimer content in the other hydrogenated samples was in the same range (5.0-5.6%) as the unhydrogenated control (4.8%). The effect of additives such as MS was inconsistent in showing either a decrease or no effect on the dimer content of soybean oils used for frying. Therefore, our GPC analyses for dimers are not sufficiently sensitive to differentiate between thermal deterioration of hydrogenated and unhydrogenated oils under our conditions of frying.

Color measurements in used oils after one hr initial frying showed little or no difference among the different oils and additive combinations with transmittance ranging from 94 to 99% (Table VI). After 19 hr of heating and bread frying, the oils containing CA alone showed the least change when hydrogenated with Cu to 0.5% linolenate and with Ni to 0.4% linolenate. The oils hydrogenated with Ni to 2.7 and 4.6% linolenate and the unhydrogenated soybean oil showed the most change. Oils containing CA + MS and CA + MS + TBHQ remained lighter after 19 hr of heating and frying and showed only small improvement by hydrogenation with Cu to 0.5% linolenate but not with Ni catalyst. Oils containing TBHQ had the least color protection and showed no effect by hydrogenation. Therefore, MS afforded the most color protection. In the absence of MS, hydrogenation to 0.4-0.5% linolenate was the most effective means to reduce color formation.

Results of color formation do not correlate either with dimer formation or with sensory evaluations in samples containing CA alone (Tables III-V). Hydrogenated oils Cu-0.5 and Ni-0.4 rated poorly because of their high hydrogenation-paraffin responses observed by our panels. In another paper (21) we report the same discrepancy between the sensory evaluations and GC headspace volatile analyses when soybean oils are compared with hydrogenated oils. Therefore, these instrumental analyses can provide useful information on the extent of thermal deterioration of oils. This information must be accompanied, however, by sensory evaluations because of the poor correlations as demonstrated in this paper with the strong odor intensity observed with certain highly hydrogenated soybean oil samples.

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♣Film Forming and Foaming Behavior of Food Proteins

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ABSTRACT

The current state of understanding of protein structure as it relates to its function in foaming has proven to be of sufficient accuracy to predict the effects of particular modifications in soy proteins. Comparative whipping studies performed on egg white, casein, Bovine serum albumin and soy protein showed important differences both in the development and subsequent stability of foams produced from these proteins. Our understanding of the structures of soy proteins and the alterations induced by reductive modification and heating implied that similar modifications would have dramatic impact on the foaming properties specifically of the 11S protein. The foaming ability and stability of the 11S protein were enhanced dramatically by cleavage of intersubunit disulfide bridging. Computerized lamellar measurement techniques developed in this laboratory indicated that these modifications enhanced the ability of the protein to foam rapidly and then to stabilize surface films at the rate typically encountered in the whipping of foams.

INTRODUCTION

The unique structural properties of certain proteins is largely responsible for the proliferation of diverse foods with highly desirable texture, flavor and stability characteristics. Foods such as foams (whipped toppings, cakes, ice cream), gels (meats, cheeses) and emulsions (dressings, sausage) are dependent on specific protein components typically present at relatively low levels (1). As food sources, processing methods and consumer tastes evolve, the need to understand and predict the behavior particularly of the protein components of these foods becomes increasingly acute. Foams, in particular, constitute systems in which the protein component plays a highly 'functional' role (1). Considerable research in recent years has begun to unravel the structural basis of the foaming properties of different proteins and even to predict means by which this functionality can be improved.

A foam can be defined loosely as a two-phase system in which a distinct gas bubble phase is surrounded by a continuous liquid lamellar phase. A consequence of this dispersion is a very large gas-liquid interface. Since interfaces between non-miscible phases are under tension, the expansion of these interfaces requires energy, i.e., work is performed in forming them and energy is released on their relaxation, hence foams are highly unstable. Surfactants, being amphiphilic, orient at an interface and lower the energy or tension of that interface (2). In a dynamic, energetic system such as the formation of a foam, the ability of a foaming agent (surfactant) to rapidly reach an interface, effectively lower the interfacial tension and stabilize new surface determines its capacity to form foams. Once formed, each bubble is separated by a very thin column of liquid and must be stabilized by the film surrounding the gas. The role of a foaming agent at this stage must be to associate into a cohesive network or membrane which can withstand minor physical perturbations and repel the approach of adjacent films (1, 3,4). This introduces a basic paradox in the requirements of an effective foaming agent. That is, a perfect amphiphile should be soluble, small and flexible enough to rapidly absorb to and coat fresh surfaces as it is exposed, then interact immediately among adjacent molecules sufficiently to form a stable film.

Ideally, proteins as amphiphilic, structurally dynamic macromolecules are able to fulfill both roles in the chemistry of foams. They typically lower the surface tension of the air-water interface by up to 50%, facilitating rapid expansion of the surface (5). Also, by virtue of their ability to associate into a multimolecular matrix, proteins form surface films which retard the coalescence and collapse of the bubbles. Not all proteins possess this capacity, and different proteins of varying sizes, structures and flexibilities differ dramatically in their ability to form and stabilize foams (1, 3,6). It is the relationship between the structure of proteins and their ultimate role in the diverse processes of film and foam formation which new research techniques and more complete information on protein structure are beginning to elucidate.

Foam Formation

In terms of foam formation, certain general principles have been found. Several studies have described a parallel between a protein's foaming behavior and its capacity to lower surface tensions rapidly (1,3,6,7). This tendency is related to the ability of the protein to reach, absorb and 'unfold' rapidly at the interface. The rate at which a protein reaches a clean interface is related primarily to its diffusion coefficient; generally, the smaller the protein the faster it will move to an interface (4). A clean surface is very rapidly covered by a thin monolayer of protein. Subsequent association of proteins with the interface is related to their ability to adsorb onto and insert themselves into a preexisting film rather than disrupt the film's integrity via repulsive interactions or return to the bulk aqueous phase. This would re-

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