Changes in the Characteristics and Composition of Oils During Deep-Fat Frying

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ABSTRACT: Refined, bleached, and deodorized soybean oil and vanaspati (partially hydrogenated vegetable oil blend consisting of peanut, cottonseed, nigerseed, palm, rapeseed, mustard, rice bran, soybean, sunflower, corn, safflower, sesame oil, etc., in varying proportions) were used for deep-fat frying potato chips at 170, 180, and 190°C. Refractive index, specific gravity, color, viscosity, saponification value, and free fatty acids of soybean oil increased with frying temperature, whereas the iodine value decreased. The same trend was observed in vanaspati, but less markedly than in soybean oil, indicating a lesser degree of deterioration. Iodine values of soybean oil and vanaspati decreased from their initial values of 129.8 and 74.7 to 96.2 and 59.6, respectively, after 70 h of frying. Polyunsaturated fatty acids decreased in direct proportion to frying time and temperature. Losses were highest in soybean oil with a 79% decrease in trienoic acids and a 60% decrease in dienoic acids. Levels of nonurea adduct-forming esters were proportional to the losses of unsaturated fatty acids. Butylated hydroxyanisole and tertiary butylhydroquinone did not affect deterioration of soybean oil at frying temperatures.

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KEY WORDS: Butylated hydroxyanisole, deterioration, nonurea adduct-forming esters, polyunsaturated fatty acids, soybean oil, tertiary butylhydroquinone, vanaspati.

Deep-fat frying enhances the sensory properties of foods; however, repeated use of frying oils produces undesirable constituents that may pose health hazards (1,2). During deep-frying, fats and oils are repeatedly used at elevated temperatures in the presence of atmospheric oxygen and receive maximum oxidative and thermal abuse. Heating in the presence of air causes partial conversion of fats and oils to volatile chain-scission products, nonvolatile oxidized derivatives, and dimeric, polymeric, or cyclic substances (3,4). There is some evidence that highly oxidized and heated fats may have carcinogenic properties because of potentially toxic substances (5–11). On the other hand, investigations of commercial frying have generally indicated that these oils have no deleterious effects upon human health (12–18). Apart from this, the nutritional value of frying fats is affected by loss of polyunsaturated fatty acids (PUFA), which supplement the essential fatty acids' requirement in human metabolism (19,20). Soybean oil, because of its high content of PUFA, is considered to be superior to many vegetable oils and hydrogenated fats from a nutritional standpoint, but it is inferior in thermal stability at high temperatures. Furthermore, partially hydrogenated fats and oils may have adverse nutritional effects due to the presence of *trans* isomers (21–23). Butylated hydroxyanisole (BHA) and tertiary butylhydroquinone (TBHQ), alone or in combination, are commonly added to fats and oils to retard oxidative deterioration due to storage and heat. Recent studies have found lack of agreement on the effectiveness of antioxidants in retarding deterioration of oils during frying (24–29). Besides this, there are numerous analytical and chromatographic methods for assessment of frying fat deterioration, but no one analytical technique can evaluate frying fat quality. Most of these methods are tedious and time-consuming. Therefore, it is important to have simple, objective methods for assessing frying fat quality. This study investigated the changes in oil quality characteristics and fatty acid composition of refined, bleached, and deodorized (RBD) soybean oil with and without antioxidants under frying conditions by a combination of the most effective analytical and instrumental analysis. The amount of deterioration in soybean oil was evaluated by periodically monitoring the analytical characteristics and was compared with identical frying experiments with vanaspati as a reference frying medium.

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EXPERIMENTAL PROCEDURES

Materials. RBD soybean oil and vanaspati (partially hydrogenated vegetable oil blend, consisting of peanut, cottonseed, nigerseed, palm, rapeseed, mustard, rice bran, soybean, sunflower, corn, safflower, and/or sesame oil, with a melting point of 37°C) were obtained from Britannia Industries Limited (Calcutta, India) and Lipton India Limited (Ghaziabad, India), respectively. BHA and TBHQ were obtained from Sigma Chemical Company (St. Louis, MO) and Aldrich Chemical Company (Milwaukee, WI), respectively. Potatoes, procured daily from a local market, had an average moisture content of 77.5%. All analytical-grade reagents were obtained from S.D. Fine-Chem Pvt. Ltd. (Boisar, Maharastra, India).

Frying experiments. Potatoes were peeled and sliced into elliptical chips (3.0–4.0-cm diameter; 1.0-mm thickness) and submerged in water until needed. Potato chips were fried in

soybean oil without antioxidants (Medium A), soybean oil with BHA and TBHQ used in combination, 0.01% each, w/w (Medium B), and in vanaspati without antioxidants (Medium C).

The oil (1.2 kg) was placed in a 2-L capacity stainless-steel pan with thermostatic control (1.5 KVA) and heated to 170, 180, and 190°C. Potato chips were fried in 20-g batches at constant frying temperature. The batches were fried at half-hour intervals for 10 h on the first day and then 6 h/d for ten consecutive days. At the end of each day, 40 mL of frying oil was filtered into a screw-cap vial and stored under nitrogen in the dark at 4°C until analyzed. The volume of oil was not replenished during frying operations. Frying experiments were conducted in single replicates on each frying medium.

Oil analyses. American Oil Chemists' Society methods were used for determining acid value (Method Cd 3a-63), peroxide value (PV) (Method Cd 8-53), iodine value (IV) (Method Cd 1-25), saponification value (SV) (Method Cd 3-25), color (Method Cc 13b-45), refractive index (RI) (Method Cc 7-25), specific gravity (Method Cc 10a-25), conjugated dienoic acids (Method Cd 7-58), and isolated *trans* isomers (Method Cd 14-61) (30). Viscosity was determined by Gardner-Holdt Tube (31). All fresh and used frying oils were saponified, fatty acids recovered, and converted to methyl esters (32). The methyl esters of fatty acids were subjected to urea fractionation by the decreasing solvent method (33) to isolate adduct-forming esters from nonadduct-forming (NAF) esters. The adduct-forming esters were then evaluated for their fatty acid composition, and NAF esters were quantitatively determined. Duplicate analyses of each chemical test were averaged.

Fatty acid composition. Fatty acid composition was determined by gas–liquid chromatography of methyl esters with a gas chromatograph (model 85 PRO; Chromatograph Instrument Company, Baroda, India) with a flame-ionization detector and 2 m × 3.2 mm stainless-steel columns packed with 20% diethylene glycol succinate on chromosorb W (60–80 mesh, HP grade). Nitrogen was used as a carrier gas at a flow rate of 40 mL/min. The oven and injector temperatures were 190 and 230°C, respectively. The percentages of fatty acids were obtained from a computerized data processor.

Statistical analyses. For statistical analyses, a completely randomized design was used for the analysis of variance by methods outlined by Cochran and Cox (34) and Goulden (35).

RESULTS AND DISCUSSION

Physical and chemical changes in frying oil. Characteristics of RBD soybean oil and vanaspati (Table 1) showed no deviation from normal values of Indian soybean variety and vanaspati produced in India (36,37). Changes in physical properties of frying oils during frying are shown in Figure 1. Vanaspati had the lowest values for RI and specific gravity, irrespective of frying temperature or duration of frying. Soybean oil with or without antioxidants showed the highest values at each frying temperature. On the other hand, color and viscosity of oils increased periodically and were highly influenced by frying temperature rather than frying medium. As the oxidation accelerated by heat proceeded, the values of these properties progressively increased. These results clearly indicated the higher deteriorative effect of oxidation and polymerization of soybean oil compared to vanaspati because the former contained larger quantities of trienoic and dienoic acids. Changes in physical characteristics of the three frying media were significantly different with respect to frying temperature (Table 2). Data on these properties of soybean oil with or without antioxidants indicated that these values are not significantly different at $P \leq 0.05$.

TABLE 1
Initial Characteristics[a] of Soybean Oil and Vanaspati

Characteristic	Soybean oil	Vanaspati
Iodine value (Wijs)	129.8	74.7
Saponification value	194.9	195.5
Peroxide value (meq/Kg)	3.2	3.7
Acid value (mg KOH/g)	0.08	0.26
Viscosity[b] (s)	1.0	1.0
Specific gravity (30/30°C)	0.912	0.897
Refractive index (40°C)	1.4688	1.4517
Lovibond color (10-mm cell; Y + 5R)	5.1	2.8
NAF esters[c] (%)	3.8	0.8
Conjugated acids (%)		
Dienoic	0.14	0.80
Trienoic	0	0
Trans isomers (%)	0	26.7
Fatty acid composition (% wt)		
14:0	0.1	0.1
16:0	10.9	13.2
16:1	<0.05	0
18:0	3.3	11.2
18:1	26.7	62.9
18:2	52.3	12.6
18:3	6.7	0

[a]Average of two determinations.
[b]Determined by Gardner-Holdt tube at 40°C.
[c]NAF = nonurea adduct-forming.

The effect of frying time on chemical properties are shown in Figure 2. Free fatty acid (FFA) of fresh soybean oil was 0.04 and reached 1.51 after 70 h of frying at 190°C, whereas that of vanaspati increased from 0.13 to 2.45 in the same period. The steady rise in the formation of FFA can be attributed partly to the hydrolysis and partly to the component carboxylic groups present in polymeric products of frying (38,39). The higher value of FFA in vanaspati during frying could be due to the higher initial concentration of FFA (0.13%) in original vanaspati, which tend to catalyze the hydrolysis reaction (40). These higher values of FFA observed in vanaspati are not indicative of a higher degree of deterioration and can be supported by the work of Melnick *et al.* (13) when hydrogenated fats were used for frying.

One measure for the degree of autoxidation of oils is PV. However, this measure is deceptive in heat-oxidized oils and cannot be relied upon in deep-fat frying of oils that contain PUFA. In PUFA-rich oils, the formation of peroxides takes

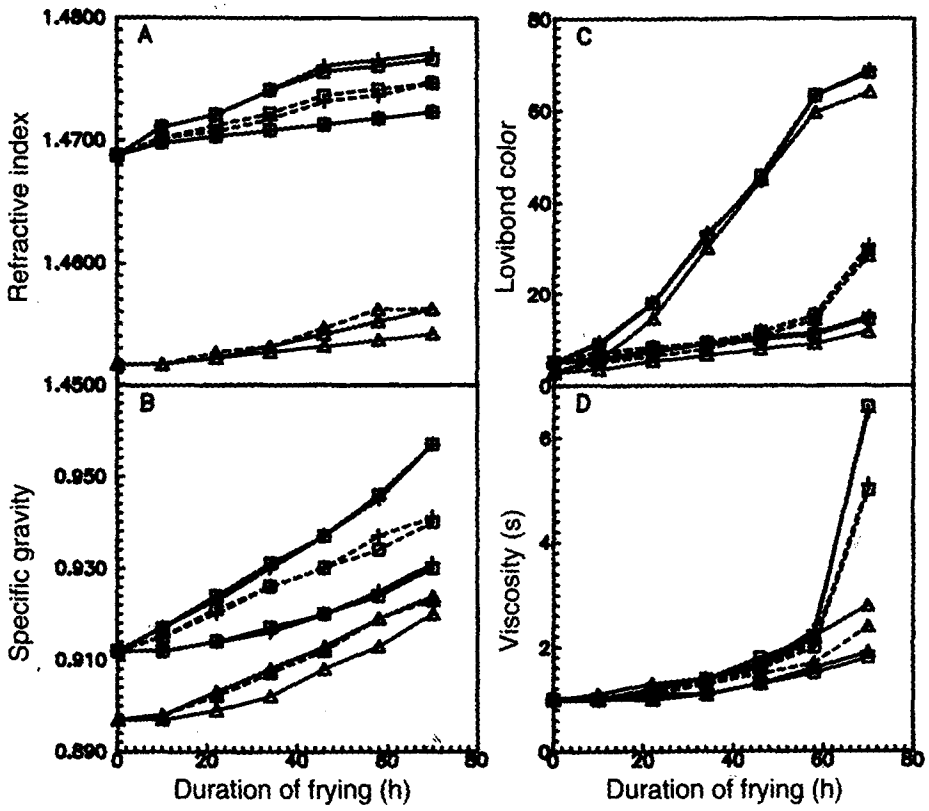

FIG. 1. Effect of duration and temperature of frying on physical characteristics: A, refractive index; B, specific gravity; C, color; D, viscosity of frying media. △, Vanaspati; +, soybean oil without antioxidants; □, soybean oil with antioxidants: ———, 170°C; — — —, 180°C; - - -, 190°C.

place through the oxidation of free radicals obtained from abstraction of protons from methylene-interrupted fatty molecules. These peroxides decompose much faster by means of labile hydrogen, obtained from the active methylene group of another molecule, which causes free radical polymerization. The higher the temperature of deep-fat frying, the stronger the tendency for decomposition of peroxides. A similar trend was seen with antioxidant-containing soybean oil with minor variations. The picture was entirely different for vanaspati with no triene. The trend of rise in PV of vanaspati indicated less tendency to decomposition of peroxides, thereby indicating a lesser degree of polymerization (41). The presence of *trans* isomers in vanaspati could possibly also inhibit the free radical polymerization by restricting the decomposition of peroxides.

Measurement of unsaturation is somewhat more reliable in assessing the deterioration of frying oils than other analytical methods. During frying, a progressive decrease in unsaturation was observed in all oils by the determination of IV. This decrease in unsaturation can be attributed to the destruction of double bonds by oxidation, scission, and polymerization (42,43). Soybean oil provided more active methylene groups, which were more prone to oxidative deterioration, and resulted in faster loss of unsaturation than the control vanaspati. IV of soybean oil decreased from an initial level of 129.8 to 106.7, 97.4, and 96.2 in 70 h at 170, 180, and 190°C, respectively. Almost the same IV, with minor variations, were observed with antioxidant-containing soybean oil. IV for vanaspati under similar frying conditions decreased from 74.7 for fresh vanaspati to 63.0, 61.0, and 59.6 at 170, 180, and 190°C, respectively. The decrease of IV of vanaspati showed its higher stability at the frying temperatures (44).

The SV of soybean oil and vanaspati increased significantly with frying temperature (Fig. 2); however, the effect of antioxidant addition to soybean oil was not significant. The higher SV observed in soybean oil, particularly at 180 and 190°C, could be related to the formation of a comparatively larger number of secondary oxidation products (e.g., carbonyl compounds) by the conversion of primary oxidation products, and agrees with the work of Perkins and Van Akkeren (45) on frying fats.

Data represented in Table 2 show the effects of frying temperature, frying media, and duration of frying obtained by combining different factors in two-way classification for different characteristics. Hence, the reported mean values of a factor have been obtained by averaging over the other factor(s). The observed data revealed the significant effect of frying temperature. The average values of most of the characteristics increased significantly with frying temperature, except for the IV, which decreased significantly with the rise in temperature. No significant difference, however, was observed for PV when frying temperature was increased to 190 from

TABLE 2
Mean Values of the Combined Data at Different Levels of the Different Factors for Various Characteristics

Factor	Level	Characteristic							
		Refractive index	Specific gravity	Color	Viscosity	Free fatty acids	Peroxide value	Iodine value	Saponification value
Frying temperature (°C)	170	1.4649^{c}	0.9143^{c}	8.6^{c}	1.27^{c}	0.57^{c}	12.5^{a}	102.1^{a}	199.7^{c}
	180	1.4661^{b}	0.9207^{b}	12.0^{b}	1.68^{b}	0.71^{b}	10.4^{b}	99.3^{b}	201.6^{b}
	190	1.4672^{a}	0.9252^{a}	35.8^{a}	1.90^{a}	0.80^{a}	9.1^{b}	97.5^{c}	205.4^{a}
SEM ± CD at 0.05		0.0001	0.0003	0.1	0.06	0.01	0.6	0.2	0.3
		0.0002	0.0009	0.3	0.16	0.03	1.8	0.4	0.7
Frying medium[a]	A	1.4724^{a}	0.9261^{a}	19.7^{a}	1.70^{a}	0.52^{b}	4.5^{b}	115.2^{a}	203.2^{a}
	B	1.4723^{a}	0.9260^{a}	19.6^{a}	1.69^{a}	0.51^{b}	4.4^{b}	115.6^{a}	203.2^{a}
	C	1.4535^{b}	0.9081^{b}	17.2^{b}	1.45^{b}	1.05^{a}	23.0^{a}	68.3^{b}	200.3^{b}
SEM ± CD at 0.05		0.0001	0.0003	0.1	0.06	0.01	0.6	0.2	0.3
		0.0002	0.0009	0.3	0.16	0.03	1.8	0.4	0.7
Duration of frying (h)	0	1.4631^{h}	0.9070^{l}	4.3^{l}	1.00^{g}	0.07^{l}	3.4^{e}	111.4^{a}	195.1^{i}
	10	1.4641^{g}	0.9090^{k}	6.5^{k}	1.01^{g}	0.17^{k}	4.8^{e}	108.6^{b}	197.9^{h}
	16	1.4645^{f}	0.9111^{j}	7.7^{j}	1.08^{f,g}	0.25^{j}	6.3^{d,e}	106.9^{c}	198.9^{g,h}
	22	1.4649^{e}	0.9133^{i}	10.5^{i}	1.14^{f,g}	0.37^{i}	9.3^{c,d}	104.5^{d}	199.4^{f,g}
	28	1.4652^{e}	0.9158^{h}	12.9^{h}	1.20^{f,g}	0.44^{h}	13.6^{a,b}	102.8^{e}	200.2^{f,g}
	34	1.4649^{d}	0.9181^{g}	16.4^{g}	1.27^{e,f,g}	0.53^{g}	15.4^{a}	100.8^{f}	200.8^{e,f}
	40	1.4664^{c}	0.9203^{f}	19.3^{f}	1.39^{d,e,f}	0.69^{f}	14.6^{a,b}	99.0^{g}	201.6^{e}
	46	1.4670^{b}	0.9230^{e}	22.1^{e}	1.52^{d,e}	0.79^{e}	13.8^{a,b}	96.9^{h}	203.5^{d}
	52	1.4674^{a}	0.9261^{d}	27.0^{d}	1.70^{c,d}	0.94^{d}	12.5^{a,b,c}	94.6^{i}	205.1^{c}
	58	1.4677^{a}	0.9291^{c}	29.2^{c}	1.91^{b,c}	1.17^{c}	12.4^{a,b,c}	92.7^{j}	206.2^{c}
	64	1.4680^{a}	0.9322^{b}	33.0^{b}	2.39^{b}	1.36^{b}	11.6^{b,c}	90.4^{k}	208.1^{b}
	70	1.4683^{a}	0.9359^{a}	36.8^{a}	3.78^{a}	1.54^{a}	9.9^{c,d}	87.2^{l}	210.1^{a}
SEM ± CD at 0.05		0.0001	0.006	0.2	0.11	0.021	1.3	0.3099	0.5
		0.0004	0.0019	0.6	0.32	0.062	3.7	0.8834	1.4

[a]Frying Medium A, soybean oil without antioxidants; B, soybean oil with antioxidants; C, vanaspati (control) without antioxidants; CD, critical difference. Figures bearing the same superscripts do not differ significantly at $P < 0.05$.

180°C. Mean values for soybean oil and antioxidant-containing soybean oil were not statistically different for all characteristics. Average values for all characteristics for vanaspati were significantly lower than soybean oils, except for FFA and PV, which were significantly higher. Mean values of almost all characteristics increased with frying time, except IV, which decreased significantly in successive frying. However, no definite pattern was observed for PV.

Conjugated fatty acids and trans *isomers.* Conjugated fatty acids as dienes were initially present in small quantities in all oils, whereas conjugated trienes were absent (Table 1). *Trans* isomers were present in significant amounts in vanaspati, as expected (46,47). Deep-fat frying for 70 h at 170, 180, or 190°C produced an increase in the conjugated fatty acids from initial values; the higher temperature of frying yielded somewhat higher quantities of conjugated dienes (Table 3). The highest levels of conjugated dienes were observed in vanaspati, whereas antioxidant-containing soybean oil showed the least rise in the conjugated dienes. Conjugated trienes, which were initially absent in all oils, were found in traces in soybean oil samples at all three temperatures after 70 h of frying. No conjugated trienes were observed in vanaspati, which does not contain any trienoic acid.

Trans fatty acids, which were initially absent in both soybean oil samples, were present after 70 h of frying at 170, 180, and 190°C, which agrees with the work of Sebedio *et al.* (48) on frying oils. No differences were found between *trans* isomers content of soybean oils at 170 and 180°C; however, at 190°C, *trans* isomers increased in soybean oils. In vanas-

TABLE 3
Percentage of Conjugated Fatty Acids and *trans* Isomers of the Frying Medium After Deep-Fat Frying of Potato Chips

Frying temperature (°C)	Frying[a] medium	Level of fatty acids after 70 h of frying		
		Conjugated dienes	Conjugated trienes	*Trans* isomers
170	A	3.09	<0.01	1.68
	B	2.58	<0.01	1.72
	C	4.46	0	28.8
180	A	4.26	<0.01	1.83
	B	2.74	<0.01	1.72
	C	5.36	0	31.1
190	A	4.39	<0.01	2.60
	B	2.84	<0.01	2.41
	C	6.08	0	31.7

[a]A, Soybean oil without antioxidants; B, soybean oil with antioxidants; C, vanaspati.

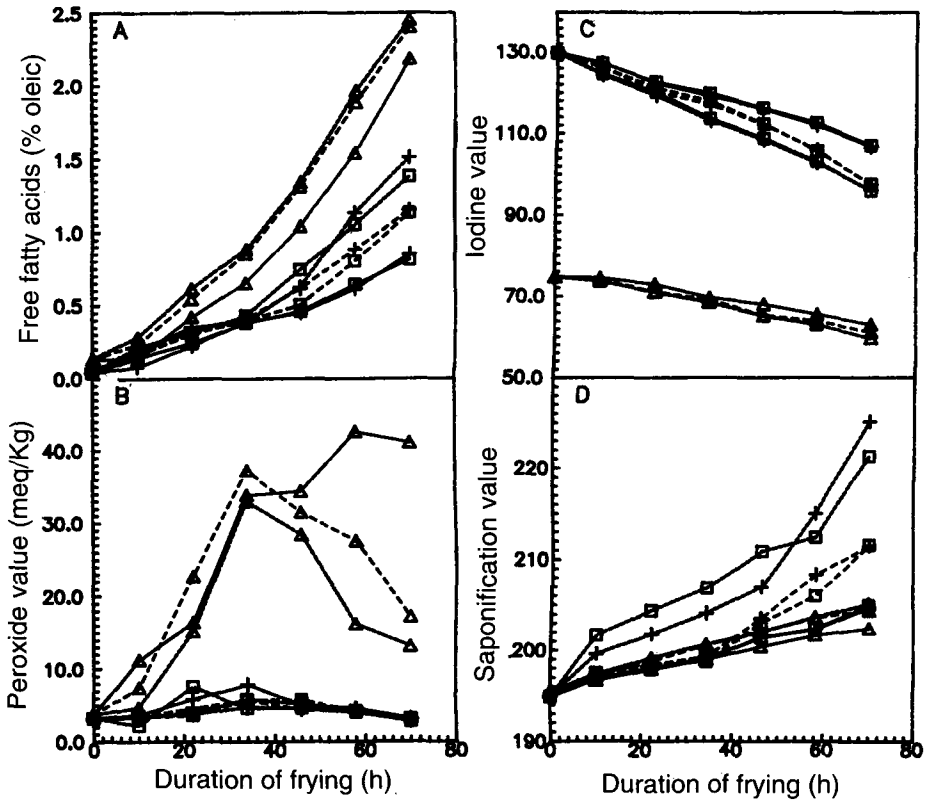

FIG. 2. Effect of duration and temperature of frying on chemical characteristics: A, free fatty acid; B, peroxide value; C, iodine value; D, saponification value. △, Vanaspati; +, soybean oil without antioxidants; □, soybean oil with antioxidants: ———, 170°C; — — —, 180°C; - - -, 190°C.

pati, after 70 h of frying, the *trans* isomers increased from the initial value of 26.7 to 28.8% at 170°C, to 31.1% at 180°C, and to 31.7% at 190°C. These data showed the tendency for both geometrical and positional isomerization during frying, which is not unusual at such high temperatures (49–52). However, higher dienes observed in vanaspati may be because of less reliability of ultraviolet spectroscopy in the presence of *trans* isomers (13).

Change in fatty acid composition. Changes in fatty acid profile of all oils during frying were basically among the unsaturated fatty acids (Table 4), whereas the saturated fatty acids (myristic, palmitic, and stearic) remained constant (data not shown). The fatty acid composition was determined by gas–liquid chromatography of the methyl esters of fatty acids not destroyed during deep-fat frying. Although the calculations were made by the integrator of the gas chromatograph on the basis of the fractional peak areas, there was an apparent increase in saturated fatty acid content and a decrease in polyenoic acid content as frying time increased. The percentage of fatty acids was recalculated while taking palmitic acid as a reference, which could not have been altered under any circumstances during deep-fat frying (53), while keeping myristic and stearic acid percentages also constant. The resulting fatty acid composition left large gaps in the total fatty acid composition by percent weight, which was due to oxidative polymerization, scission, cyclization, and other side reactions that would have taken place during the course of frying. It was separately categorized as loss of fatty acids during frying.

Hexadecenoic acid ($C_{16:1}$), present in fresh soybean oil only in trace amounts, disappeared totally after deep-fat frying for 16 h at 170 and 180°C, and after 10 h at 190°C. Octadecenoic acid ($C_{18:1}$) showed a gradual decrease from 10 h of frying period and decreased to 23.3% at 170°C, to 20.7% at 180°C, and to 19.7% at 190°C in 70 h, which amounted to a loss of about 12.7, 22.5, and 26.2% in monoenes. Octadecadienoic acid ($C_{18:2}$) deteriorated much faster than the monoenes. After 70 h of frying, the content of octadecadienoic acid decreased to 29.5% at 170°C, to 24.4% at 180°C, and to 21.0% at 190°C. This loss of dienes amounted to about 44, 53, and 60%. Losses in triene content ($C_{18:3}$) of soybean oil were much higher than monoenes and dienes and amounted to about 64, 73, and 79% after 70 h. The losses in unsaturated fatty acids during frying were separately categorized to indicate the damage of unsaturated fatty acids during frying. After 70 h of frying, the losses of fatty acids ranged from 30.5 to 43.6% at the three temperatures.

Fatty acid profiles of soybean oil with antioxidants were not different from soybean oil without antioxidants, except for a few minor variations (Table 4). The ineffectiveness of antioxidants in frying operations may be attributed to their volatilization through evaporation, decomposition (54,55), and to the scavanging reaction (56) involved in deep-fat fry-

TABLE 4
Fatty Acid Composition of Frying Media During Deep-Fat Frying

Frying temperature (°C)	Duration of frying (h)	Frying media[a]										
		Medium A				Medium B				Medium C		
		Major fatty acids, %wt			Loss of fatty acids (%)	Major fatty acids, %wt			Loss of fatty acids (%)	Major fatty acids, %wt		Loss of fatty acids (%)
		18:1	18:2	18:3		18:1	18:2	18:3		18:1	18:2	
170	0	26.7	52.3	6.7	0.0	26.7	52.3	6.7	0.0	62.9	12.6	0.0
	10	25.4	46.3	5.0	9.0	25.6	46.1	5.0	9.0	61.7	11.8	2.0
	22	25.0	42.9	4.4	13.4	25.1	43.4	4.4	12.8	61.1	10.9	3.5
	34	24.6	39.6	4.0	17.5	24.5	39.6	4.0	17.6	59.8	9.4	6.3
	46	24.4	35.4	3.4	22.5	24.4	35.5	3.5	22.3	59.0	7.6	8.9
	58	23.8	32.3	2.9	26.7	24.0	32.1	2.9	26.7	58.1	5.8	11.6
	70	23.3	29.5	2.4	30.5	23.3	29.8	2.5	30.1	57.1	3.9	14.5
180	10	25.1	44.2	4.6	11.8	25.2	44.8	4.6	11.1	62.0	11.4	2.1
	22	24.7	42.0	4.2	14.8	24.7	41.9	4.2	14.9	60.7	9.9	4.9
	34	23.9	37.7	3.4	20.7	24.4	37.9	3.2	20.2	59.8	7.9	7.8
	46	23.7	33.6	2.8	25.6	24.0	33.8	2.8	25.1	58.3	5.9	11.3
	58	22.8	29.3	2.3	31.3	23.0	29.9	2.4	30.4	57.4	3.4	14.7
	70	20.7	24.4	1.8	38.8	20.4	23.9	1.8	39.6	56.7	1.3	17.5
190	10	25.3	42.8	4.5	13.1	25.3	43.2	4.6	12.6	62.2	11.1	2.2
	22	24.7	38.9	3.9	18.2	24.8	39.7	3.8	17.4	60.8	8.7	5.0
	34	24.1	35.5	2.9	23.2	23.9	36.3	3.1	22.4	59.4	8.0	8.1
	46	23.2	31.3	2.4	28.8	22.8	31.0	2.4	29.5	57.6	5.2	12.7
	58	21.8	26.5	1.8	35.6	21.2	25.9	1.8	38.8	56.5	2.8	16.2
	70	19.7	21.0	1.4	43.6	19.0	20.4	1.4	44.9	56.3	0.7	18.5

[a]Medium A, soybean oil without antioxidants; medium B, soybean oil with antioxidants; medium C, vanaspati (control) without antioxidants.

ing. On the other hand, vanaspati showed a gradual reduction in monoenes, less than observed in soybean oil with or without antioxidants, and amounted to a loss of 9, 10, and 10.5%, respectively, after 70 h of frying. The loss in dienes of vanaspati was 69% at 170°C, 90% at 180°C, and 94% at 190°C, which was much higher than the losses in soybean oil, even for trienes. The percentages of unsaturated fatty acids in soybean oil, particularly those for dienes and trienes, were high, whereas in vanaspati, monoenes were high and dienes were much less, and trienes were totally absent. Thus, the deterioration of dienes in vanaspati was high because only these fatty acids could provide the active methylene groups or conjugated double bonds that could have a deteriorative effect on the fatty acid content.

Formation of NAF esters in frying oils. The NAF esters indicate the presence of cyclic, polymerized, or partially polymerized fatty materials in the oil, which do not form adducts with urea. The percentages of NAF esters (Fig. 3) do not agree with the loss in fatty acids during frying as given in Table 4. However, the percentages of NAF esters were proportionately close to losses in fatty acids during deep-fat frying, which indicates that all the losses in fatty acids were not entirely due to the formation of cyclic or such NAF compounds as polymers. Fatty acids that were lost still retained straight aliphatic chains capable of forming urea adducts. The mean values of NAF esters at different levels are shown in Table 5. The data confirmed that NAF esters increased significantly with frying temperature and duration of frying. Amounts of NAF esters were not statistically different in soybean oil with or without antioxidants. NAF esters formed in vanaspati were significantly lower than the levels in soybean oil, which indicates the greater frying stability of hydrogenated oil compared to soybean oil.

Correlation between analytical methods during frying. Correlation coefficients (r) between each pair of analytical values were calculated to study the degree of association between any two characteristics taken under consideration (Table 6). Among these analytical methods, specific gravity and IV showed high positive correlation with RI ($r >$ 0.82–0.85); RI showed a low negative correlation ($r > -0.75$) with PV and no correlations with color, viscosity, SV, and FFA. However, specific gravity showed a high positive correlation ($r > 0.87$) with SV and low positive correlations with color, viscosity, FFA, and IV, whereas it showed a negative correlation with PV. Color correlated positively with SV, viscosity, and FFA and negatively with PV and IV. Viscosity showed positive correlations with FFA and SV and was negative with PV and IV. FFA had no correlations with PV, IV, and SV. PV showed a high negative correlation with IV and a low negative correlation with SV. On further interpretation of data, it was revealed that RI increased with specific gravity and IV, whereas it decreased with PV. Also, specific gravity increased with SV and remained almost ineffective with color, viscosity, FFA, PV, and IV. Color and viscosity also in-

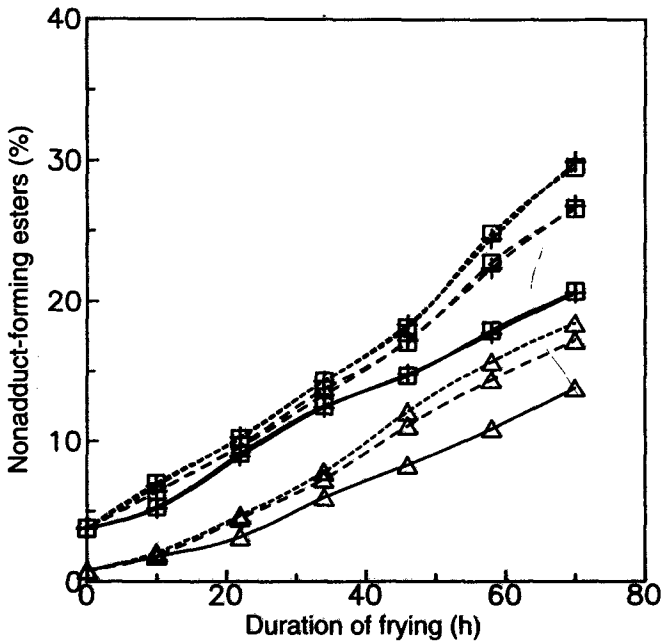

FIG. 3. Effect of duration and temperature of frying on formation of nonadduct-forming esters. △, Vanaspati; +, soybean oil without antioxidants; □, soybean oil with antioxidants, ———, 170°C; — — —, 180°C; – – –, 190°C.

creased with SV. These results indicate that specific gravity, IV, SV, are good indicators for oil quality assessment, whereas RI, PV, FFA, color, and viscosity analyses require other auxiliary tests for assessing frying oil deterioration.

The changes in characteristics and composition of different frying media showed that vanaspati was more stable during frying than soybean oil, as expected. This work also confirmed that antioxidants BHA and TBHQ did not prevent deterioration of soybean oil during frying, which has also been observed by other workers (57).

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TABLE 5
Mean Values of the Combined Data at Different Levels of the Different Factors for Nonadduct-Forming (NAF) Esters

Factor	Level or type	NAF esters
Frying temperature (°C)	170	10.61[c]
	180	12.75[b]
	190	13.79[a]
SEM ± CD at 0.05		0.07
		0.21
Frying medium[a]	A	14.45[a]
	B	14.45[a]
	C	8.25[b]
SEM ± CD at 0.05		0.07
		0.21
Duration of frying (h)	0	2.80[l]
	10	4.76[k]
	16	6.37[j]
	22	7.80[i]
	28	9.10[h]
	34	11.28[g]
	40	13.02[f]
	46	14.63[e]
	52	16.54[d]
	58	18.97[c]
	64	20.74[b]
	70	22.61[a]
SEM ± CD at 0.05		0.15
		0.43

[a]Medium information and abbreviation as in Table 2. Figures for each factor bearing the same superscripts do not differ significantly at $P < 0.05$.

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TABLE 6
Correlation Matrix for the Different Characteristics Taken Pairwise

	Refractive index	Specific gravity	Color	Viscosity	Free fatty acids	Peroxide value	Iodine value	Saponification value
Refractive index	1.00	0.82[a]	0.24[a]	0.27[a]	−0.28[a]	−0.75	0.85[a]	0.44[a]
Specific gravity		1.00	0.68[a]	0.69[a]	0.32[a]	−0.41[a]	0.34[a]	0.87[a]
Color			1.00	0.66[a]	0.57[a]	−0.05	−0.18	0.81[a]
Viscosity				1.00	0.54[a]	−0.09	−0.15	0.83[a]
Free fatty acids					1.00	0.54[a]	−0.65[a]	0.53[a]
Peroxide value						1.00	−0.77[a]	−0.13
Iodine value							1.00	−0.07
Saponication value								1.00

[a]Significant at $P < 0.05$.

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