Changes in Dielectric Constant as a Measure of Frying Oil Deterioration

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ABSTRACT

A soybean oil, a hydrogenated vegetable frying shortening and an animal-vegetable shortening were heated at 190 C for 8 hours each day for 4 days with and without the frying of potatoes. Samples were taken periodically and analyzed for various changes normally used to measure frying oil deterioration. The changes in the dielectric constant were determined with a patented instrument called the Food Oil Sensor. This instrument is standardized with a sample of the fresh oil, and it then measures the change in the electric capacitance of the heated oil samples. The dielectric constant of all three shortenings increased linearly with heating time. The greatest change occurred in the soybean oil sample and the smallest change in the hydrogenated vegetable shortening. For each shortening the increase was somewhat greater during frying than during heating without frying. Statistically significant correlations were obtained between instrument readings and increase in the total polar materials, the color, the peroxide values, the diene content, and the free fatty acids and the decrease in the iodine values.

INTRODUCTION

During deep fat frying, oxidation and hydrolysis occur in the frying shortening which changes its functional, sensory and nutritional quality. How long a frying shortening can be used to produce a high quality food depends on a number of factors (1,2). For example, a liquid vegetable oil high in polyunsaturates will deteriorate more rapidly than a hardened vegetable shortening. A frying shortening will deteriorate less rapidly in a fryer which has a small surface area than in one which holds the same volume but has a larger surface area (3). In most food-frying operations, some or all of the shortening in the fryer is dumped and replaced with fresh shortening at some point in time. Various criteria are used to judge when the shortening needs to be dumped. In a restaurant, the shortening may be dumped when the color becomes too dark, when it foams or smokes too much, when the odor of the smoke becomes too strong, or when the food has a greasy texture or odor. In a food-processing operation, where laboratory analysis can be carried out, judgment may be made on the shortening's viscosity, acidity, content of carbonyls or conjugated double bonds. Unfortunately, none of the above criteria are completely satisfactory, especially when different foods are prepared in the same operation or when the shortening used varies in its composition. Deterioration of frying shortenings can also be measured by its polymer content (4,5) or total polar content (6); however, these methods are not routine quality control procedures. The dielectric constants of most fresh edible fats and oils or their free fatty acids lie in the range of 3.0 to 3.2 (7). The more saturated fats are on the lower end of this range and the more unsaturated oils on the upper end. Cis and trans isomers of the same fatty acid have the same dielectric constant (8). Hydroxy fatty acids such as those of castor oil have a dielectric constant of ca. 4.0 (9). Oxidation increases the dielectric constant of oils through the introduction of polar groups (10). Changes in the dielectric constant have been used to study the oxidation kinetics of oleic acid (11). Northern Instrument Corporation (6680 North Highway 49, Lino Lakes, MN 55014) has developed an instrument called the Food Oil Sensor, which measures changes in the dielectric constant of insulating liquids. The instrument is a small compact unit which can be operated by anyone after reading a few simple instructions. Changes in the instrument response were compared to other analytical values obtained on oil samples collected during the frying of potatoes in three different shortenings.

EXPERIMENTAL PROCEDURES

Frying Experiments

Twice each day Russet potatoes were peeled and pressed through a die with 8 x 8 mm openings. The raw French fries were stored in cold water until used for frying. About 2500 g of shortening was placed into a 5 quart deep fat fryer. Controls were adjusted to maintain a shortening temperature of 190 C. About 45 min after the heat had been turned on, a batch of 100 g potatoes was fried for 10 min. The temperature dropped to 168 C after about 5 min of frying, then started to rise again. Before the next batch was fried, the temperature returned to 190 C. Two batches were fried each hour for 8 h hr each day. At the end of the day the heat was shut off and samples taken. This procedure was repeated each day for four days. At the end of the second day, 500 g of fresh shortening was added to maintain a good frying level. On the fifty day, the shortening was heated to 190 C and allowed to remain at that temperature for 8 hr without any frying.

The following week, fresh shortening was heated in the same manner but no frying was carried out.

Instrument Measurements

A food Oil Sensor, Model NI-20 was used. The instrument is a patented device for detecting, measuring and

TABLE I

Fatty Acid Pattern of Shortenings Used for Frying Experiments

Fatty acid	Percent in SBO[a]	HVS[b]	AVS[c]
12:0	—	.4	—
14:0	.3	.3	4.1
16:0	12.4	12.0	26.9
16:1	.1	.2	4.6
17:0	—	—	1.5
17:1	—	—	.8
18:0	4.4	11.7	17.6
18:1	23.1	70.6	38.0
18:2	52.2	2.5	4.0
18:3	6.9	.6	—
20:0	.1	.5	.6
20:1	—	—	1.2
20:4	—	—	.7
22:0	.5	1.3	—

[a]Bleached and refined soybean oil.

[b]Hydrogenated vegetable frying shortening.

[c]Animal-vegetable shortening blend.

TABLE II

Instrument Response to Soybean Oil Spiked with Various Compounds

Compounds added	Instrument reading at concentration of						
	0%	1%	2%	3%	5%	6%	10%
Oleic acid	4.0	4.0	---	3.9	---	3.6	2.9
Palmitic acid	4.0	3.9	---	3.8	---	3.4	2.8
Lauric acid	4.0	3.9	---	3.8	---	3.6	3.1
Octanoic acid	4.0	4.0	---	3.9	---	3.8	3.6
Glyceryl-2,3-dipalmitin	1.00	---	1.32	---	1.87	---	---
Glyceryl-1,3-dipalmitin	1.00	---	1.28	---	1.70	---	---
Glyceryl-1-monopalmitin	1.00	---	2.12	---	3.87	---	---
Glyceryl-2-monopalmitin	1.00	---	1.97	---	3.43	---	---
Monoolein (Technical)	1.00	---	1.93	---	3.36	---	---

reporting small changes in the dielectric constant of insulating liquids. A few drops of the test liquid are placed in an open type test cell which has a heater and temperature controller. The bottom of the cell is formed by two coplanar electrodes imbedded in a low permittivity, insulating material. The electrodes are connected to a comparison circuit designed to be optimally sensitive to small changes in electrical capacitance. The comparison circuit contains a variable capacitor for balancing the capacitance of the test cell and a null meter for detecting this balance condition.

Since the dielectric constant varies somewhat with different oils, the instrument must be calibrated with the fresh oil of the sample to be tested. With a medicine dropper, 5 drops of the fresh oil were placed into the instrument's cup. When a solid shortening was used, 5 to 10 g were placed into a 30 ml beaker and melted on a hot plate so it could be put dropwise into the instrument. When the liquid in the cup had reached the operating temperature, as indicated by the green light on the instrument, the "operate" button was depressed and the instrument calibrated to a 1.0 reading. The instrument's calibration was rechecked at least once every half hour. The oil in the cup was then removed with tissue paper (Kimwipes). The instrument's response to test oils were then determined. For room temperature oil samples, about 30 sec, were required to reach the operating temperature. For hot oils taken from the fryer, the temperature light came on immediately but went off and on several times for two to three minutes before constant operating temperature was reached.

Foam Height

A 250 ml graduated cylinder (35 mm id) cutoff at the bottom was lowered into the hot oil so that it almost touched the bottom of the fryer. The reading on the surface was recorded. Raw potato slices were cut with an apple cutter to obtain disks 25 mm in diameter and 10 mm in height. A potato disk was dropped into the cylinder when the shortening temperature was 190 C. The maximum foam height was observed. Each cc mark on the cylinder corresponded to one mm. The foam height in mm was the final reading minus the initial reading.

Total Polar Material

The method used was a modification of the one reported by I.P. Freeman (6). About 0.6 g of oil was accurately weighed and transferred with 10 ml toluene to a nylon column (15 cm × 2 cm id) packed to 4.5 cm with Woelm neutral alumina activity III. The neutral oil was eluted with an additional 30 ml of toluene. The column was then washed with 20 ml of hexane and visualized with UV 254 nm radiation. The fluorescence was quenched to 0.5 cm from the origin. The column was cut with a razor and the polar material eluted from the first 1.3 cm of alumina with 50 ml 85:15 chloroform/methanol. The washing was concentrated to dryness on a rotovap and the residue weighed and recorded as percent polar material.

Other Analytical Procedures

AOCS methods (12) were used for the determination of free fatty acids (Ca 5a40), peroxide values (Cd 8-53), iodine values (Cd-25), AOM (Cd 12-57), diene content (Ti 1a-64) and Karl Fisher moisture (Tb 2-64). Color was measured as absorbance at 420 nm of one mg oil per ml of isooctane.

Shortening Samples

Three samples with different AOM stabilities were selected for this study. For the low stability sample, refined and deodorized soybean oil with no antioxidants was used. The sample had an IV of 122.8, an initial PV of 1.3 and an AOM of 10 hr. The other two samples were commercial frying shortenings. The high stability sample was a hydrogenated vegetable oil which contained dimethyl silicone as an antifoamer. It has an IV of 70.2, initial PV of 0.9, a capillary mp of 41.0 C, and an AOM of over 200 hr. The other sample was an animal-vegetable blend which was found to contain 10 ppm BHA and 30 ppm BHT. It has an IV of 49.3, an initial PV of 0.9, a capillary mp of 45.5 C and an AOM of 65 hr. The fatty acid pattern of these samples as determined by gas chromatography is shown in Table 1.

RESULTS AND DISCUSSION

Evaluation of Instrument Response

To obtain reproducible results, the particular instrument used required a warm up period of at least 4 hr. About eight drops of oil could be added to the cup before it overflowed. At least five drops were required to obtain reproducible results. Low readings were obtained with less sample.

When the instrument was calibrated to 1.0 with the fresh hydrogenated vegetable shortening (HVS), a reading of 1.2 was obtained for the fresh animal-vegetable shortening (AVS) and 2.9 for the soybean oil (SBO). Over a two week period 17 of such checks were made by two different operators. For the AVS, the mean was 1.18 with a standard deviation of 0.06 and a range of 1.1 to 1.3. For the SBO, the mean was 2.88 with a standard deviation of 0.16 and a range of 2.6 to 3.1.

To avoid recalibration of the instrument whenever one of these different oils were measured consecutively, the calibration was done with HVS, which had the lowest initial reading. To determine if the measurements on the other oils could be adjusted by subtraction of the initial differences, the linearity of the instrument was checked. Using HVS, the reading was set with the calibration switch to different points over the entire scale and each time corresponding measurements made for the other two samples. It was

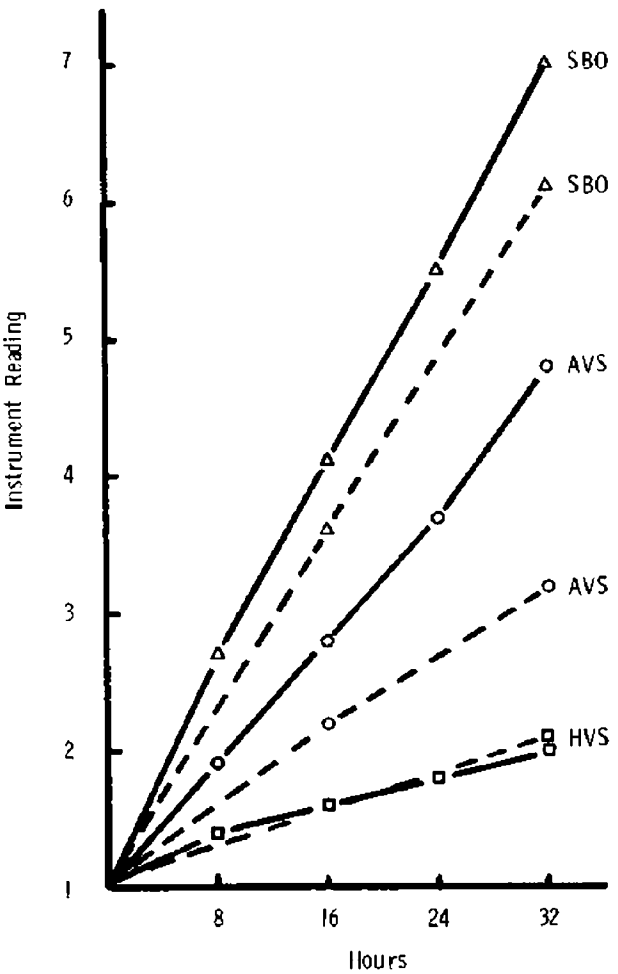

FIG. 1. Increase in instrument readings during the frying of potatoes (solid lines) and heating without frying (broken lines) of a soybean oil (SBO), of an animal-vegetable shortening blend (AVS), and of a hydrogenated vegetable shortening (HVS).

found that between 1 and 7 the instrument's response was linear. A linear response was also obtained when 6 samples of SBO with different amounts of monoolein (technical grade) were checked.

The regression equation was:

$$IR = 0.472\ C + 0.074$$

where:

IR = Instrument reading and
C = per cent monoolein in SBO.

The correlation coefficient was 0.9997.

The instrument response to SBO spiked with other mono- and diglycerides is shown in Table II. When fatty acids up to 1% were added to SBO, no significant change in the instrument readings were observed; however, higher concentrations resulted in a negative response as shown in Table II. When glycerine was added to SBO, an increase in the instrument readings was obtained, but the readings were not reproducible. With 0.2% glycerine dispersed in SBO the reading increased from 1.0 to somewhere between 2 and 3 and with 0.4% to between 5 and 7. After the glycerine-oil mixtures were allowed to stand for two days, sample from the top of the vials gave no increase in the instrument response; however, after the vials were shaken, the higher readings were again obtained which indicates a solubility problem. No change in the instrument reading was obtained when 100 ppm dimethyl silicone or 200 ppm each BHA and BHT were added to SBO.

During the AOM determination of safflower oil samples, instrument checks were carried out on the samples removed from the tubes for peroxide value determinations. With a reading of 1.0 for the fresh safflower oil, samples with a PV of 60 gave a reading of 1.4, PV of 90 a 2.1 and PV of 110 a 2.5. When the polar material isolated during the determination of total polar materials was mixed with fresh SBO, an increase in the instrument response was obtained.

During the frying experiment, instrument readings were taken at frequent intervals. It was noticed that when measurements were made on samples taken ca. 3 min after immersing a batch of potatoes, the values were from 0.7 to 1.3 higher than when they were rechecked 10 min after the potatoes had been removed from the fryer. No significant differences were obtained in readings between samples taken from the fryer between 10 and 60 min after a batch of potatoes had been fried. It is assumed that the higher readings were due to a somewhat greater moisture content of the oil during the frying compared to after frying. Samples for analysis and corresponding instrument readings were taken 15 min after the completion of frying. It was also observed that SBO in a beaker which had sat open all day on a humid day gave a reading of 0.3 higher than when a portion of this oil was placed into another beaker and heated for 20 min at 80 C.

Frying Experiments

In Figure 1, the increase in instrument readings during the frying of potatoes in the SBO, in the AVS, and in the HVS, which in the trade is often referred to as "heavy duty frying shortening," are shown. From experience, one would expect the SBO to show the greatest deterioration and the HVS the least. The instrument readings followed the same pattern. The increase in the instrument readings with respect to frying time was linear for all three shortenings. Regression analysis of hours of frying to instrument readings gave correlation coefficients above 0.98.

The increase in instrument readings during frying compared to just heating without frying was almost the same for the hydrogenated vegetable shortening, slightly higher for the soybean oil, and much higher for the animal-vegetable blend (Fig. 1). Similar results were obtained from the analysis of the total polar materials. The greater difference in the deterioration of the animal-vegetable shortening during frying than during just heating is attributed at least in part to the BHA and BHT in this sample. During heating, these antioxidants provide protection; however, during frying the antioxidants are rapidly lost by steam distillation.

In Table III, the increase in the instrument reading is compared to other analytical procedures frequently used for measuring frying oil deterioration. The first sections in these tables compare the results obtained during the four days (32 hr) of frying potatoes at 190 C. The second sections compare the results of the four days of frying plus an additional eight hours of heating with no frying. The third section shows the results obtained of the fresh oils heated in the same fryers at 190 C without frying and compares the results obtained in all three of these treatments. As can be seen, the correlations between instrument measurements and the other analytical procedures were very high and most of them statistically significant.

Regression analyses were also carried out between instrument readings and other analytical procedures combining the results obtained from the three different shortenings deteriorated both by frying of potatoes as well as by heating without frying (Table IV). Total polar materials yielded the highest correlation followed by the decrease in iodine values. This indicates that oxidation products are

TABLE III

Analytical Results

Treatment	Instrument reading	Free fatty acids	Peroxide value	Dienes % dienoic acid	Color absorbance at 420 nm	Total polar material %	Foam height mm	Iodine value	AOM hr.	Moisture %
A. Soybean oil										
Fresh oil	1.0	0.02	1.3	.400	.21	2.8	40	122.8	10	.35
Frying[a]—8 hr	2.7	.11	16.9	.623	1.01	8.5	50	---	---	---
Frying—16 hr	4.1	.18	21.9	.666	2.03	14.1	50	121.0	8	.02
Frying—24 hr	5.3	.27	21.3	.669	2.87	17.1	80	118.3	---	---
Frying—32 hr	7.0	.30	22.9	.690	4.31	21.2	80	---	---	---
r[b] =		.985***	.854*	.845*	.994**	.994**	.913**	-.934**		
Frying + heating[c]	8.0	.39	18.5	.713	7.48	26.8	---	112.6	18	.15
r[b] =		.991**	.720	.845*	.940**	.995**	---	-.953**	---	---
Heating[d]—16 hr	3.6	.11	12.1	.645	.55	13.4	---	121.5	8	---
Heating—32 hr	6.1	.17	9.9	.662	1.04	21.5	---	114.7	8	---
r[b] =		.931**	.599	.819*	.822**	.989**	---	-.938**	---	---
B. Hydrogenated vegetable shortening										
Fresh oil	1.0	.02	.9	.111	.08	3.7	30	70.2	200+	.01
Frying[a]—8 hr	1.4	.08	1.9	.152	.58	4.8	40	---	---	---
Frying—16 hr	1.6	.17	2.4	.183	.85	5.0	35	69.3	160	.02
Frying—24 hr	1.8	.28	3.4	.194	1.08	5.5	40	69.7	---	---
Frying 32 hr	2.0	.38	3.9	.224	1.42	7.6	25	---	---	---
r[b] =		.965**	.991**	.995**	.998**	.917**	-.120	-.763	---	---
Frying + heating[c]	2.4	.36	5.1	.246	1.51	8.5	---	69.3	18	.19
r[b] =		.938**	.995**	.989**	.976**	.959**	---	-.797	---	---
Heating[c]—16 hr	1.6	.05	1.9	.180	.23	4.5	---	70.4	130	---
Heating -32 hr	2.1	.09	2.2	.208	.39	7.3	---	69.6	80	---
r[b] =		.723	.858**	.979**	.717	.945**	---	0.648	---	---
C. Animal-vegetable blend shortening										
Fresh oil	1.0	.05	0.9	.391	.04	3.0	45	49.3	65	.11
Frying[a]—8 hr	1.9	.16	7.5	.426	.26	7.0	40	---	---	---
Frying—16 hr	2.8	.32	11.5	.490	.53	11.0	30	46.4	15	.31
Frying--24 hr	3.7	.50	12.5	.476	.74.74	13.4	40	46.3	---	---
Frying—32 hr	4.8	.78	14.5	.463	1.06	16.5	30	---	---	---
r[b] =		.991**	.937**	.739	.999**	.992**	-.711	0.954**	---	---
Frying + heating[c]	6.3	.85	8.2	.446	1.68	19.6	---	43.4	15	.25
r[b] =		.983**	.567	.480	.994**	.987**	---	-.983**	---	---
Heating[c]—16 hr	2.2	.13	6.4	.463	.17	6.5	---	47.7	15	---
Heating—32 hr	2.7	.23	5.8	.496	.36	9.0	---	47.2	10	---
r[b] =		.974***	.598	.317	.986***	.984***	---	-.985**	---	---

[a]Total hours of frying two 100 g batches of raw potatoes per hour in 2500 g oil at 190 C during the day and turning off heat at night.
[b]Correlation coefficient between all of the above analytical results and instrument readings.
[c]AFter frying potatoes for four days, the shortenings were heated for 8 hours with no frying.
[d]Total hours of heating fresh shortening in fryer with no frying.
*Significant at 5% level.
**Significant at 1% level.

primarily responsible for the observed increase in the dielectric constant.

Peroxide values are generally not used to measure frying oil deterioration. Peroxides are very unstable at frying temperatures; however, the extent of oxidation which has occurred during frying is reflected by the rate of peroxide formation after the sample is taken and allowed to cool before analysis. In this study the manner in which the samples were taken and the time elapsing before analyses was the same for all samples.

Free fatty acids yielded a much lower correlation when the regression was carried out on the combined data than on the data for each individual shortening. This is not unexpected, since the rate of free fatty acid increase was much greater for the AVS than for the other two shortenings. Acids during frying are produced by both hydrolysis and oxidation. The rate of hydrolysis can vary between different lots of the same shortening, between different types of shortenings, and is affected by the initial free fatty acids of the shortening (13). As the spiking experiments have shown, free fatty acids up to 1% have no effect on the instrument reading. The mono- and diglycerides formed during hydrolysis will increase the instrument reading; however, it was calculated that 1% free fatty acids and its corresponding mono- and diglycerides produced by hydrolysis would increase the instrument reading by not more than 0.4. The high correlation between free fatty acids and instrument reading obtained for each individual shortening was therefore an indirect correlation due to the simultaneous increase of oxidation products. An estimate of the formation of acids from oxidation was obtained by comparing the free fatty acid values obtained during the heating to that obtained during the frying. For SBO about half, for the AVS about one-third, and for the HVS about one-fourth of the acids produced during frying were due to oxidation.

Foam height was found to be a rather poor measure of frying oil deterioration. With the SBO the foam height

TABLE IV

Correlation between Instrument Response and Other Analyses of the Combined Date of Three Shortenings with Different Stabilities Deteriorated Both by Frying Potatoes and by Heating without Frying

Analysis	Number of samples	Correlation coefficient
Total polar materials	24	.991
Decrease in iodine value	18	.947
Color	24	.785
Peroxide value	24	.773
Diene content	24	.745
Free fatty acids	24	.569

increased with deterioration. With the other two shortenings the foam height either remained the same or actually decreased.

A logical question is: at what reading is the shortening no longer usable? Unfortunately, there is no definite answer. Oxidation of fats decreases their nutritional quality, but there is no consensus at what point an oxidized fat should not be consumed. The decrease in functional and sensory quality depends to a great extent on the type of food being fried. Informal sensory evaluations were carried out during the frying. In the opinion of the tasters, the French fries produced in shortenings with readings above 4 were poor quality fries.

The results of this study showed that changes in the dielectric constant of oils is a good measure of oil deterioration during frying or exposure to high temperatures for extended periods. Oxidation products were primarily responsible for this change; hence, such measurements should be most useful for shortenings containing some polyunsaturation. The Food Oil Sensor was found to provide these measurements simply the rapidly; however, some precautions had to be taken to obtain reliable results. The instrument had to be allowed to stabilize before readings could be taken. When melting the fresh shortening for the calibration of the instrument, the samples could not be allowed to overheat. Samples could not be taken from the fryer while food was being fried.

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