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☘ A Technique for Monitoring the Quality of Used Frying Oils

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The objective of this work was to develop a practical method for monitoring the quality of oils during the frying process. A special effort was made to find a technique that would not be affected by dilution, since replenishment with fresh oil to varying degrees is a frequent necessity. Nine analytical methods, i.e., measurements of viscosity, polymers, change in dielectric constant, polar compounds, dimers, free fatty acids, smoke point, carbonyls and cyclic monomers, as well as certain combinations of these measurements were evaluated. Since each single method was influenced by replenishment with fresh oil, combinations of two methods were studied in an attempt to produce a single value unaffected by dilution. The ratio polymer/FOS (polymers according to Peled's technique of methylation and extraction and change in dielectric constant by Foodoil Sensor readings) proved not only to be adequate for monitoring the quality of the used oil, but also was affected minimally by replenishment.

Deep-fat frying is one of the most commonly used procedures for the preparation of foods. Desirable texture and flavor can be generated during the frying operation; however, when the oil is used repeatedly at elevated temperatures in the presence of air, thermal oxidation occurs and the oil deteriorates. Severe decomposition of frying oils not only compromises the quality of the food being fried, but also poses a potential hazard to human health and nutrition. The importance of establishing simple, objective methods for quality evaluation of used frying oil cannot be overemphasized.

The purpose of the present work was to develop such methodology. A special effort was made to find a technique whose applicability would not be affected by dilution, since replenishment with fresh oil to varying degrees is a frequent necessity.

MATERIALS AND METHODS

Nine analytical methods were chosen to evaluate the quality of used oils. These were measurements of viscos-

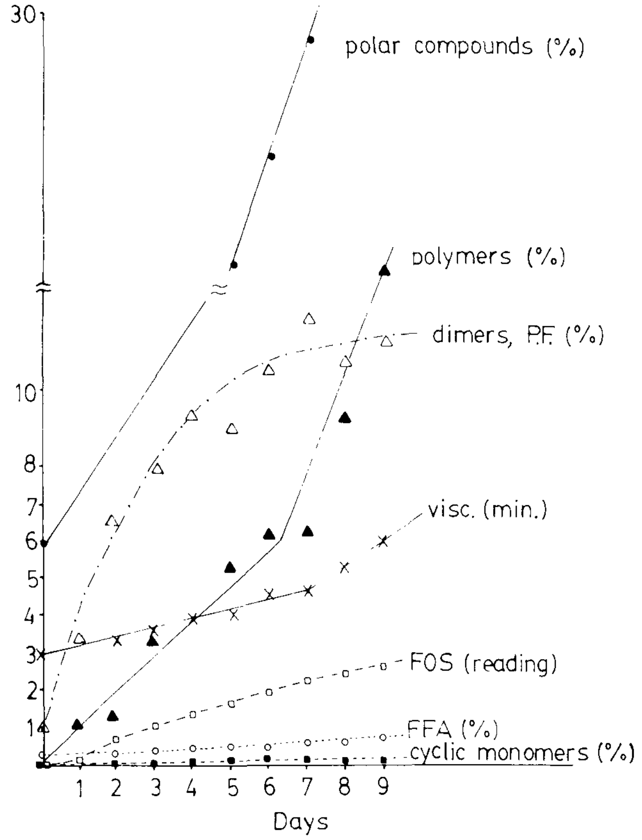

FIG. 1. Monitoring corn oil heated at 185 C by different methods.

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ity, free fatty acids, carbonyl value, smoke point, cyclic monomers, change in dielectric constant (measured by the Foodoil Sensor [Northern Instruments Co., Minneapolis, Minnesota]), dimer esters by gas chromatography (GC), polar compounds by column chromatography and determination of polymers by methylation followed by the separation of a relatively insoluble fraction.

The change in dielectric constant was measured with the Foodoil Sensor and expressed as Foodoil Sensor (FOS) readings. The fresh corn oil used for heating or frying was also used to calibrate the zero point. The operational procedure followed was as outlined in the manual.

The Fisher capillary viscometer #300 was used to measure viscosity. Time for the oil to flow through a marked distance was recorded, and the viscosity was expressed in terms of time or centipoises according to Nelson (1).

Polar compounds were measured by the column chromatography method described by Billek and coworkers (2).

Dimer esters were analyzed by GC according to the method developed by Paradis and Nawar (3). The method of Peled et al. (4) was used, with minor modifications to determine polymers. One g of oil was added to 125 ml methanol containing 1% (v/v) H_2SO_4. The mixture was boiled under a reflux condenser for 2 hr and cooled to room temperature. The methanol insolubles then were filtered and the insolubles washed with methanol until no sulfuric acid remained. The washed insolubles were dissolved in 25 ml petroleum ether and transferred to a preweighed flask. The solvent then was evaporated under a stream of nitrogen until constant weight was obtained.

Cyclic monomers were analyzed according to the method reported by Meltzer et al. (5) with some modifications. The analysis of carbonyl value was based on the method described by Bhalerao et al. (6).

Free fatty acids and smoke points were measured according to AOCS official methods (7).

RESULTS AND DISCUSSION

After several preliminary experiments, the determination of smoke points and carbonyl values was abandoned due to either lack of reproducibility or failure to reflect the extent of abuse. Therefore, only the results from the other seven methods are presented here. When corn oil was continuously heated at 185 C for nine days, values obtained by all seven methods increased with increased heating time (Fig. 1). Obviously the slopes of the curves differ from method to method. It is noteworthy that after seven days of heating, an inflection can be observed in the curves for polymer and viscosity, beyond which the rate of increase rises rapidly. The dimers in the polar fraction followed the progress of lipid deterioration during the early stages of heating and then reached a plateau after six days. Since the quantitative analysis of cyclic monomers is time-consuming and cumbersome, this method is not suitable for routine quality evaluation of used frying oils and was not considered further.

To study the effect of dilution on measurement by the remaining six methods, samples of corn oil were heated for seven days and then diluted with different amounts of fresh corn oil prior to analysis (Table 1). As expected, all six methods were affected by dilution, albeit to different extents. It was thus reasoned that while a value obtained from a simple method changes with dilution, the ratio of values obtained from two methods may not be affected. If, for example, one measurement gives a value of *a*, while measurement by another method gives *b*, the ratio of the values obtained from the two tests, i.e., *a/b*, would remain the same after dilution with fresh oil. However, such a ratio can only be useful as an indicator of oil quality if it correlates well with frying time. To test this hypothesis, 85-g batches of raw potato were each fried in 1 l of corn oil for 3 min every 15 min over an 8-hr period for five consecutive days. At the end of each day, the fryer was turned off. The following day, fresh corn oil was added for replenishment to the original volume. This required an average of 18% replenishment each day.

TABLE 1

Effect of Replenishment with Fresh Oil, After Seven Days of Continuously Heating Corn Oil, on Values Obtained by Different Methods

	Fresh oil added			
	0	30%	50%	70%
Viscosity (min)	4.7	4.6	4.2	3.9
Polymer (%)	6.3	5.3	3.1	2.8
FOS	2.3	1.6	1.1	0.6
Polar (%)	26.3	19.1	16.4	12.4
Dimer ester in polar fraction (%)	12.0	7.6	7.5	5.7
FFA (%)	0.7	0.6	0.4	0.3

TABLE 2

Effect of Daily Replenishment with Fresh Oil (18%) on Values Obtained During the Frying of Potato in Corn Oil[a]

	Fresh oil	2-Days frying		4-Days frying		5-Days frying	
		B	A	B	A	B	A
Viscosity (min)	2.6	3.1	3.0	3.7	3.5	3.8	3.6
Polymer (%)	0	0.2	0.05	1.5	1.3	2.2	1.5
Polar (%)	4.9	17.0	15.4	23.7	20.2	25.6	21.9
Polymer ÷ polar	0	0.01	0.003	0.06	0.06	0.08	0.07

B, before replenishment; A, after replenishment.

TABLE 3

Polymer/Polar and Polymer/FOS Ratios in Heated Corn Oil

		2-Days heating		4-Days heating		6-Days heating		8-Days heating	
	Fresh	B	A	B	A	B	A	B	A
Viscosity (min)	2.5	3.0	2.9	3.3	3.1	3.3	3.2	3.5	3.4
Polymer	0	0	0	0.3	0.2	0.6	0.5	0.7	0.6
FOS	0	0.8	0.7	1.2	1.1	1.6	1.4	1.8	1.5
Polar (%)	5.0	11.8	10.1	16.9	14.9	20.0	17.7	22.7	18.8
Polymer ÷ polar	0	0	0	0.02	0.02	0.03	0.03	0.03	0.03
Polymer ÷ FOS	0	0	0	0.2	0.2	0.4	0.4	0.4	0.4

B, before replenishment; A, after replenishment.

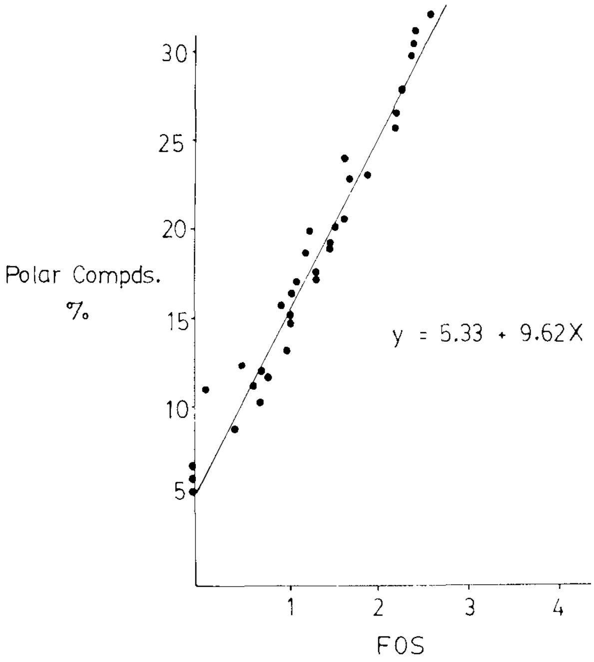

FIG. 2. Relationship of FOS to polar compound content of corn oil heated at 185 C.

The oils were analyzed after two days, four days and five days of frying, before and after replenishment; the results are given in Table 2. Again, the values from each method decreased with dilution. However, the ratio polymer/polar compounds in the replenished oil was relatively close to that of the unreplenished. In the meantime, this ratio increased with longer frying time indicating its validity as an objective means of quality assessment.

Since both FOS and column chromatography of polar compounds reflected increase in polar compounds in the used oil, and since FOS analysis is much simpler and quicker than polar compound analysis by column chromatography, we attempted to investigate the possibility of combining FOS with polymer analysis to follow the progress of lipid deterioration. In the next experiment the same conditions were used as in the previous potato frying system, except that no food was fried. The oil was tested after two, four, six and eight days of heating, before and after replenishment (Table 3). As seen before, the polymer/polar compound ratio was hardly affected by dilution, and such value increased with heating time. In addition, the ratio polymer/FOS was minimally affected by dilution and also increased with longer heating times. The measurement combining FOS with polymer analysis is thus considered of greater practical value.

Since both FOS and column chromatography reflect the increase in polar compounds in the used oil, correlation between these two methods was investigated. Data of FOS and polar compounds obtained from the previous heating experiments where corn oil was used were plotted as shown in Figure 2, and a regression equation, $y = 5.33 + 9.62\,x$, was derived, where x = FOS and y = polar compound content. Polar content can thus be calculated for a given FOS reading. It should be pointed out that, in this case, only a single oil, corn oil, was used in a controlled experiment. When we studied the relationships between FOS and polar compounds in seven other frying oils, we found the slopes of the curves of the different oils to be different. Regression equations for these oils will be published later. As we reported earlier, FOS values are influenced by several other factors. FOS values do not always agree with other parameters of oxidation, and therefore extreme caution must be exercised when this method is used.

In another experiment, measurements were made on batches of corn oil in which other foods were fried, i.e., hake and herring. The frying operation was similar to that of the previous potato frying study, except that no fresh oil was added during the frying operation. After four days the frying oils were sampled for analysis. The oils were also diluted with 10% fresh oil and analyzed. The results are shown in Table 4. The reduction in individual values resulting from the 10% dilution with fresh oil ranged from 8–14%, with an average of 10.88 ± 2.08. However, both polymer/polar compound ratio and polymer/FOS ratio were minimally affected by dilution for all three foods.

As concluded previously, the measurement of polymer/FOS appears to be more convenient and time-saving than that of polymer/polar compound. However, since polymer analysis requires 2 hr of refluxing, an attempt was made to minimize the time of analysis even further by reducing the time of refluxing required for polymer analysis. A refluxing period of 30 min was chosen. While sufficient for complete hydrolysis of the nonpolymerized triacylglycerols (using 30 min refluxing, polymer value in fresh oil was zero), the shorter reflux-

TABLE 4

Effect of Replenishment (10% Fresh Oil Added After Four Days) on the Evaluation of Corn Oil in Which Different Foods Were Fried

	Potato		Hake		Herring	
	B	A	B	A	B	A
Polymer (%)	7.7	6.7	3.7	3.4	0.7	0.6
FOS	6.2	5.5	6.2	5.4	0.9	0.8
Polar (%)	43.3	39.4	37.9	35.1	14.3	13.5
Polymer ÷ polar	0.18	0.17	0.10	0.10	0.05	0.04
Polymer ÷ FOS	1.23	1.21	0.60	0.63	0.81	0.75

B, before replenishment; A, after replenishment.

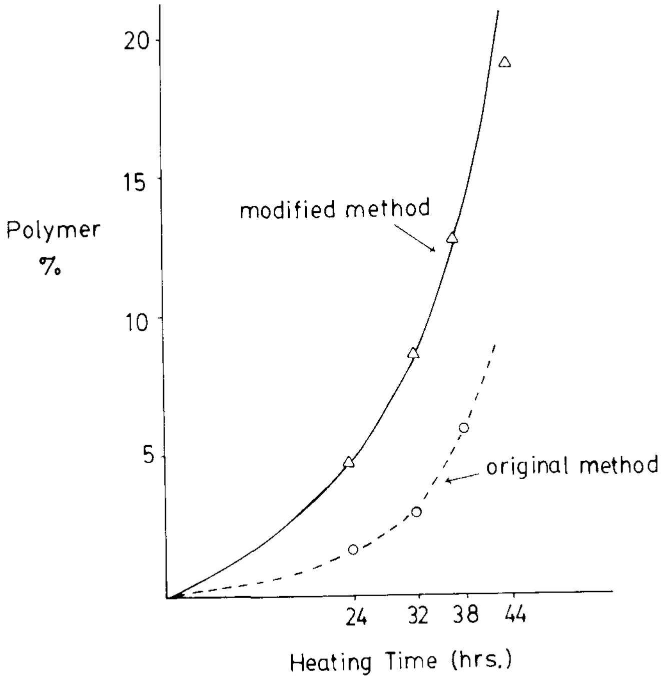

FIG. 3. Polymer formation by original and modified methods.

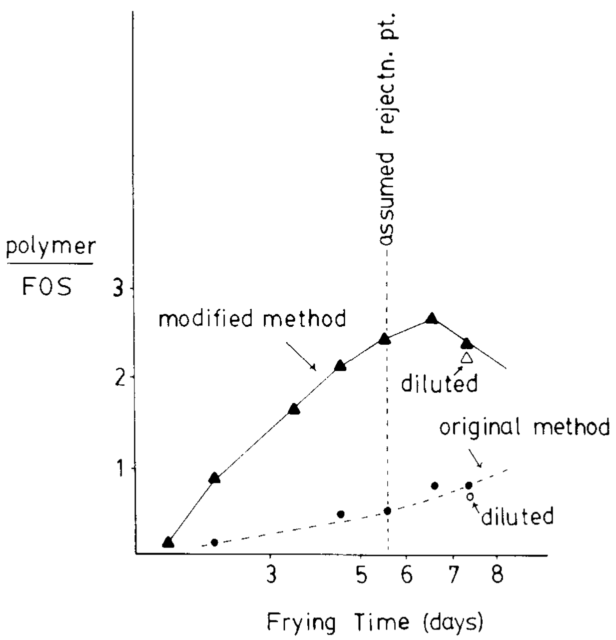

FIG. 4. Effect of frying on polymer/POS values of corn oil used for potato frying.

ing time gives rise to higher polymer values since polymeric acids are less readily methylated and thus remain insoluble. When a heated corn oil with an FOS of 2.6 was analyzed by the modified method (30 min refluxing), its polymer content was 13% as compared to 6% after 2 hr refluxing. In our laboratory polymer values obtained with the shorter refluxing time were closer to those obtained by high pressure size exclusion chromatography. Figure 3 shows polymer formation as determined by both the original and modified methods. In both cases, the rate increased significantly after about 30 hr of heating, a stage in this course of heating which coincides with a polar compound content of approximately 27% as measured by column chromatography.

When polymer/FOS ratios were plotted against frying time (Figure 4), both measurements increased with frying time. The modified method gave higher values, but these reached a maximum and then declined. Therefore the modified method for polymer determination can be used in combination with FOS to follow the extent of oxidation, but only up to a point above which the decline in polymer/FOS value may be misleading. This decline, however, occurs beyond the usual rejection point and would be obvious from the higher FOS at that stage.

It is clear from the above that the use of a single datum derived from measurements by two different tests as described here provides a more reliable means for the evaluation of used frying oils. A major advantage is that values obtained as such are minimally affected by replenishment with fresh oil. The technique is simple and requires a relatively short time, i.e., approximately one hour.

On the other hand, caution must be exercised in the application of any test, including the method proposed here. It must be realized that the changes which take place during frying are numerous, complex, gradual and variable.

No single test can thus be expected to reflect the total decomposition pattern or to determine, accurately and precisely, a sharp "endpoint" beyond which the frying oil is to be rejected. The accuracy and/or precision obtained if two tests are used, as proposed above, will naturally depend on the accuracy and precision of these two tests.

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Indian Ricebran Lecithin

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In view of the high potential of ricebran oil in India, lecithins recovered from crude and dewaxed Indian ricebran oil were analyzed and different classes characterized with the objective of effectively utilizing this valuable by-product. Lipid classes and individual phospholipid components were identified and estimated. Dewaxing was found to have a considerable effect on composition of the derived lecithin. The lecithin obtained from crude or dewaxed Indian ricebran oil consisted mainly of phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol and triglycerides, along with carbohydrates, free fatty acid, sterols and waxes (in case of crude oil). The major fatty acids of individual phospholipids were found to be palmitic, oleic and linoleic. Analytical characteristics of ricebran lecithin were shown to be comparable to local soybean lecithin. It can be expected that the gummy materials in the oil, presently lost with the soapstock during refining, could find important applications.

Some 0.15 million tons of ricebran oil are recovered in India annually, and the untapped potential is about four times this figure (1). The present potential of ricebran lecithin (which amounts to roughly 1% of the oil) is approximately 6,000 tons; this will rise with the planned increases in rice production. The objective of this investigation was to assess the suitability of upgrading this highly valuable by-product of ricebran oil to edible grade. Since all lecithin used in India is imported, this locally produced product would be attractive.

Egyptian workers have studied the phospholipid range (1.2-1.94%) of local solvent extracted ricebran oils and composition of the isolated lecithin (2). Fatty acid compositions of total phospholipid and cephalin and lecithin fractions were determined.

The objective of the present study was to determine more completely the composition of ricebran lecithin. Lecithin obtained from crude and dewaxed ricebran oil of Indian origin was analyzed for the different lipid classes present. Each class was identified by different techniques and estimated. Since phospholipids constitute the most important class, the phospholipid components were further resolved, identified and quantified using TLC techniques.

Fatty acid compositions of the total lecithin and each individual phospholipid also were determined. Finally, analytical characteristics of ricebran lecithin were determined and compared with those obtained with local soybean lecithin and with U.S. specifications.

MATERIALS AND METHODS

A commercial ricebran oil[1] obtained through Hindustan Vegetable Oils Corporation Ltd. was used throughout the investigation and had a phosphatide content of 0.6% (AOCS Method) (3).

The oil drawn from ambient temperature storage (30-33 C) was centrifuged to remove impurities like sludge, mucilage, tissue particles and fibers.

For dewaxing, the clarified oil was mixed with n-hexane in 1:1 ratio (v/v) and kept at 10 C with occasional mild stirring for 4 hr, filtered free of wax, and the oil desolventized (4).

TABLE 1

Composition of Ricebran Lecithin (wt %)

	From crude oil	From dewaxed oil
Phosphatidylcholine	20.4	23.1
Phosphatidylethanolamine	17.8	20.2
Phosphatidylinositol	5.8	6.6
Other phosphatides	9.4	10.8
Triglycerides	39.2	35.2
Wax	3.1	—
Carbohydrates, sterols, FFA	4.0	3.8
Moisture	0.3	0.3

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[1] Characteristics of the oil: acidity, expressed as % oleic acid, 8.4; color (1/4″ cell, Lovibond), 1.2 R/18.0Y; fatty acid composition, myristic and lower, 0.5, palmitic, 16.5, stearic, 1.5, oleic, 44.5, linolenic, 36.0, linolenic, 0.1, others, 0.9 (wt %).