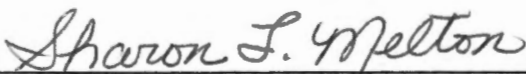


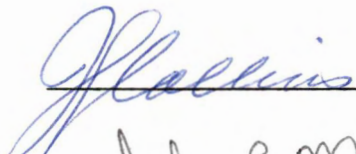
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DETERIORATION OF PALM OIL OLEIN AND PARTIALLY HYDROGENATED
SOYBEAN OIL DURING DEEP-FAT FRYING

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Norsaadah Husain

August 1986

AG-VET-MED.

Thesis

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ACKNOWLEDGEMENTS

The author wishes to acknowledge her major professor, Dr. S. L. Melton, for her invaluable assistance, guidance, patience and encouragement throughout the entire graduate program and in the preparation of this thesis.

The author also wishes to express her sincere appreciation to Dr. J. L. Collins and Dr. J. R. Mount for their assistance and guidance in serving on the graduate committee.

The author also wishes to thank all the teachers, staff members and friends in the Food Technology Department for their warm friendship and assistance throughout the author's educational experience at The University of Tennessee, Knoxville. You all will be dearly missed.

The author wishes to thank the Public Services Department of Malaysia for the financial support throughout the entire university program. The last but not least sincere gratitude is expressed to the author's parents, brothers and sisters for their love, understanding and support throughout her life.

ABSTRACT

The deterioration of palm oil olein (P00) and partially hydrogenated soybean oil (PHS0) during deep-fat frying of fish and potato was compared. Deterioration of the oils during use was assessed by fast analytical tests (dielectric constant, DC, and foam height, FH, measurements) and changes in the fatty acid composition, smoke point (SP), levels of free fatty acids (FFA), dienoic acids (DA) and total polar materials (TPM). The study consisted of four treatments: (1) potatoes fried in P00, (2) fish fried in P00, (3) potatoes fried in PHS0, and (4) fish fried in PHS0. The statistical design of the experiment was a 4 x 4 Latin Square with a split in each square. The design was represented by four replications and four fryers with the split being sampling time from each fryer. The frying oils were used in the following manner. The oil in each fryer was held at 180 C for 8 hours a day for 5 consecutive days with a batch of food being fried every 2 hours starting 1 hour after the fat had reached 180 C. At the end of each day the frying oil was cooled, filtered through cheese cloth and stored covered until the next day. DC and FH were measured on all frying oils every day, and SP, FFA, DA, TPM and fatty acid composition of the frying oils were determined after 1, 3 and 5 days of use. Moisture and fat levels were measured in the last batch of food fried each day at 1, 3 and 5 days of use.

Levels of DA, FH, FFA, and SP were significantly affected by the type of frying oil used and the type of product fried.

Across 5 days of frying, PHS0 had higher levels of FH, DA and SP and a lower level of FFA than P00. The frying of fish in either oil resulted in a higher DC, FH, DA, FFA and SP than did the frying of potatoes. DC was not affected ($P < 0.05$) by type of frying oil used. Levels of TPM did not differ ($P < 0.05$) between types of oil used or types of product fried.

The fatty acid composition of the frying oils was affected by the type of oil used and the type of product fried. Used P00 had higher levels of saturated fatty acids (12:0, 14:0, 16:0 and 18:0) and lower concentrations of the unsaturated fatty acids (18:1 ω 9, 18:1 isomers, 18:2 ω 6 and 18:2 isomers) than the used PHS0. The frying of fish caused higher concentrations of 18:2 ω 6, 18:3 ω 3 and 20:0 than did the frying of potatoes.

All measurements of the frying oils were significantly affected by the amount of time the frying oils were used. Levels of DC, FH, DA, FFA and TPM generally increased in a curvilinear fashion with increasing time of frying oil use while the SP decreased. The level of TPM was 30.7 percent by the third day of use which is higher than the 27 percent recommended as the point at which a frying oil should be discarded. The average percentage of 18:0, an 18:1 isomer, an 18:2 isomer and 20:2 ω 6 increased significantly across frying time, while the average percentage of 18:2 ω 6, 18:3 ω 3, 20:1 ω 9, 18:2 ω 7 (diene) and 24:0 decreased.

Results of this study indicate that both oils deteriorated during use; however, compared with PHS0, P00 had higher levels

of FFA, a lower smoke point and might cause problems in commercial frying operations. Results also indicate that the frying of fish caused a greater deterioration of frying fats than the frying of potatoes. Results also confirm that 27 percent TPM as a level at which a frying fat should be discarded is probably applicable to most frying fats and situations, since the level of TPM was not affected by the type of frying fat used or the type of product fried. Although other measurements such as levels of DC, FH and FFA were highly correlated with levels of TPM, they were affected by one or both of these parameters.

TABLE OF CONTENTS

CHAPTER		PAGE
I.	INTRODUCTION	1
II.	REVIEW OF THE LITERATURE	4
	Degradative Reactions of Fat During Deep-Fat Frying. . .	4
	Oxidation.	6
	Hydrolysis	9
	Polymerization	11
	Measurements of Frying Oil Deterioration	13
	Cut-off level.	13
	Rapid Tests for Determination of Frying Fat	
	Deterioration.	15
	Dielectric constant.	15
	Foaming.	17
	Color.	18
	Smoke point.	19
	Dienoic acid	21
	Free fatty acids	22
	Total polar materials.	24
	Fatty acid composition	25
III.	MATERIALS AND METHODS.	27
	Source of Data	27
	Analysis of 0-day frying oil samples	28
	Analysis of frozen food samples.	28
	Frying Procedure and Sampling.	28
	Physical Measurements.	30
	Foam height.	30
	Dielectric constant.	31
	Smoke point.	31
	Chemical Measurements.	32
	Conjugated dienoic acid.	32
	Free fatty acid.	32
	Total polar materials.	33
	Fatty acid composition	33
	Analyses of Raw and Fried Food Samples	35
	Statistics	36
	Experimental design.	36
	Statistical analysis	37
IV.	RESULTS AND DISCUSSION	38
V.	SUMMARY.	74

CHAPTER	PAGE
LITERATURE CITED	79
APPENDIX	84
VITA	94

LIST OF TABLES

TABLE	PAGE
1. Experimental Design.	36
2. Orthogonal Contrasts for Treatment Effects	37
3. Analysis of Variance for the Effects of Treatment, Fryer and Days of Frying on Dielectric Constant and Foam Height.	39
4. Analysis of Variance for the Effects of Treatment, Fryer and Days of Frying on Diene Content, Free Fatty Acids, Polar Materials and Smoke Point.	40
5. Mean Values for Dielectric Constant for Each Treatment During 5-Day Frying Period	42
6. Mean Values for Measured Characteristics of Each Frying Oil Averaged Across Product and Frying Time.	45
7. Mean Values for Measured Characteristics Across Frying Oil and Frying Time for Each Product Fried	46
8. Mean Values for Foam Height (mm) of Frying Oils for Each Treatment During 5-Day Frying Period	47
9. Mean Values for Percentage of Dienoic Acids for Each Treatment During 5-Day Frying Period	50
10. Mean Values for Percentage of Free Fatty Acids for Each Treatment During 5-Day Frying Period	53
11. Mean Values for Characteristics of Frying Oils Across Treatments for Days of Frying Time	55
12. Fatty Acid Composition of Used Frying Oils Across Days of Frying.	58
13. Mean Percentages of Fatty Acids in Frying Oils Affected Significantly by Product Fried.	60
14. Mean Values for Percentage Fatty Acids Affected Significantly by Oil x Product Interaction	61
15. Mean Percentages of Fatty Acids of Frying Oils Affected by Days of Frying Fish and Potato.	64

TABLE	PAGE
16. Equations for the Effect of Days of Frying Fish and Potato on Fatty Acid Concentrations of Frying Oils.	65
17. Analysis of Variance of the Effects of Fryer, Treatment and Days of Frying on the Moisture and Fat Contents of Fried Fish and Potato.	66
18. Mean Values for Percentage Moisture and Fat in Fried Fish and Potato for Each Treatment.	68
19. Means for Percentage Moisture and Percentage Fat in Products Before and After Frying	69
20. Correlation Coefficients Among Measurements for Palm Oil Used for Frying (N=24)	70
21. Correlation Coefficients Among Measurements for Soybean Oil Used for Frying (N=24)	71
22. Simple Correlation Coefficients Among Measurements of Frying Oil Across Oil Sources (N=48)	73
A-1. Means for the Characteristics of Fresh Palm Oil Olein and Soybean Oil.	86
A-2. Partitioning of the Dielectric Constant Sum of Squares for Days of Frying and Each Treatment.	87
A-3. Partitioning of the Foam Height Sum of Squares for Days of Frying for Each Treatment.	88
A-4. Partitioning of the Sum Squares for Days of Frying Effect Across Treatment for Percentage Total Polar Materials and Smoke Point.	89
A-5. Partitioning of the Percentage of Dienoic Acids Sum of Squares for Days of Frying for Each Treatment.	90
A-6. Partitioning of the Percentage of Free Fatty Acids Sum of Squares for Days of Frying for Each Treatment.	91
A-7. Mean Percentage of Fatty Acids in 0-Day Frying Oils. . . .	92
A-8. Analysis of Variance for Percentage Fatty Acids in Used Frying Oils Affected Significantly by Products or Days of Frying	93

CHAPTER I

INTRODUCTION

Deep-fat frying is one of the most widely used methods of food preparation used at home and on the commercial scale. The tremendous amount of deep-fried snack foods consumed annually reflects the popularity of foods prepared by deep-fat frying compared with foods prepared by other methods. Also, the ever-increasing number of fast-food restaurants involved in the selling of fried items such as fried chicken, fish and chips, and french fried potatoes further increase the consumption of deep-fat fried foods. According to Chang et al. (1978), a major portion of the ten billion pounds of edible fats and oils consumed each year in the United States is used in fried foods out of which over 200 million pounds are used for doughnut production and over 500 million pounds are used for potato chip production.

Edible fats and oils used for deep-fat frying have two important roles. One, as a medium of heat transfer that cooks the food quickly and efficiently, and two, being absorbed by the food fried, becomes an important ingredient of the fried food (Alim and Morton, 1974; Weiss, 1983). During deep-fat frying, a myriad of physical and chemical changes occur in the frying medium and in the food being fried. These changes affect the quality of the frying fat and the product fried. As these chemical reactions proceed, the functional, sensory and nutritional quality of the fat changes

and may eventually reach a point where it is no longer suitable for frying foods and the frying fat will have to be discarded. Therefore, it is important to use a good quality frying fat and to maintain it in good condition as long as possible since the quality of the fried product depends on the fat in which the food is fried. A frying fat that is well maintained will cook the food efficiently and produce a highly acceptable and nutritious fried product. On the other hand, foods fried in a deteriorated fat will result in a greasy product with poor texture and unappealing odor and flavor.

In most deep-fat frying operations, the decision to discard a frying fat is usually based on physical tests measured subjectively such as color, foam height, smoke point and odor and flavor of the frying medium as well as the flavor and color of the fried product. These tests alone are not reliable because sometimes, the frying fat has already been exposed to prolonged abuse before the adverse changes are detected. The determination of total polar materials and petroleum ether insoluble oxidized fatty acids provide the most reliable measures of the extent of deterioration, but these methods are complicated and are only possible for frying operations with laboratory facilities such as those found in major food processing plants.

Studies conducted on abused frying fats during the past several decades have contributed to the development of several methods for assessing deterioration of frying fats. A number of simple methods that enables on-the-site testing have evolved from

these studies. At the present time, however, there is no rapid, reliable and widely accepted method for determining the point at which frying fat should be discarded. If an existing test could be proven to be reliable, it should produce substantial savings to deep-fat frying operations, yet provide consumers with highly palatable and nutritious fried foods. More information is needed on existing tests for measurement of frying oil deterioration to assess the reliability of the different tests. In addition, the two most inexpensive frying fats in the market today are partially hydrogenated soybean oil and palm oil olein. Little information, however, is available for comparing the frying performance of these two oils, particularly with fish that increase the deteriorative rate. Such information would be useful for commercial users.

CHAPTER II

REVIEW OF THE LITERATURE

A. DEGRADATIVE REACTIONS OF FAT DURING DEEP-FAT FRYING

During deep-fat frying, the frying fat undergoes several physical and chemical changes as a result of continuous or repeated exposure of the fat to the high frying temperatures and to the atmosphere. According to McGill (1980) and Roth and Rock (1972a), the frying fat is subjected to three different environmental conditions during the frying process, namely the frying period, the standby period and the storage period. Each of the environmental conditions contributes to the deterioration of the frying fat.

Heating and frying changes the composition of the frying fat. The amount of decomposition products in the frying fat increases the longer the fat is heated. According to Chang et al. (1978), the thermal and oxidative reactions that the fat undergoes during frying results in the formation of both volatile and non-volatile decomposition products. Although the volatile and non-volatile products are produced simultaneously, most of the volatile decomposition products (VDP) are removed from the frying fat by the steam generated during frying (Weiss, 1983; Robertson, 1968) while the non-volatile ones remain in the frying fat (Stevenson et al., 1984b). Chang and co-workers (1978) collected, fractionated and identified the volatile decomposition products produced

by corn oil, hydrogenated cottonseed oil, trilinolein, and triolein under simulated frying conditions. The investigators reported a total of 220 compounds that were identified as VDPs produced during frying, and many of them had known toxic properties. Among the VDPs identified, the γ -lactones with unsaturation at the 2- or 3-position, when added to cottonseed oil, were found to impart a characteristic deep-fat fried flavor described by a taste panel as nutty, fried fat and butter-like. Due to the low volatility of the VDPs, there is a possibility that these compounds are inhaled by the fryer operator during frying operations (Kawada et al., 1967) and thus could have some effect on the health of these individuals. Krishnamurthy et al. (1965) collected volatile decomposition products produced during the frying of moist cotton balls in corn oil under simulated restaurant conditions. The investigators found that part of the degradation products, particularly those of higher boiling points, remained in the frying oil. Consequently, foods fried in the oil could retain some of the degradation products thereby affecting the flavor and oxidative stability of the fried products. Non-volatile decomposition products (NVDP) are composed of higher molecular weight compounds formed by thermal oxidation and polymerization of the unsaturated fatty acids present in the fat (Perkins, 1967). The NVDPs are the major concern in frying fat studies since these products are less volatile than the VDPs and so tend to accumulate in the frying fat. According to Chang et al. (1978), the presence of NVDPs in a frying oil can cause

12/5/68
Chang

foaming when foods containing moisture are deep-fried in the oil. The presence of NVDPs in fats can also cause other physical changes in the frying fat such as increases in viscosity and color, as well as chemical changes, such as increases in the free fatty acid and polymer content (Stevenson et al., 1984b). Unlike the VDPs, all the NVDPs, due to their high molecular weight, remain in the frying fat and, therefore, can promote further degradation of the fat. In addition, the NVDPs are also absorbed by the food fried in the fat containing these products thus entering the consumer's diet. The formation of these decomposition products in a frying fat and the resulting changes in the physical and chemical characteristics of the fat are due to the oxidation, hydrolysis and polymerization processes that the frying fat undergoes during the heating, frying and storage periods.

Oxidation

Oxidation occurs when the double bonds in the triglycerides are attacked by oxygen present in the air. Oxidation of fats proceeds through a free-radical chain mechanism to form hydroperoxides which may decompose to form other secondary oxidation products. This process causes rancidity in fats and has been cited in the literature as the major factor in the deterioration of frying fats (Baeuerlen et al., 1968; DeMan, 1980; Gray, 1978; Rossell, 1984; Roth and Rock, 1972a).

According to Gray (1978), the unsaturated fatty acids, particularly oleic, linoleic and linolenic are the principal fatty

acids involved in oxidation. Gray also reported that the susceptibility and rate of oxidation of fatty acids increases with their degree of unsaturation. The oxidative stability of fats, however, can be improved by reducing the amount of unsaturation. Landers and Rathmann (1981), in a review of vegetable oil production and use, mentioned that partial hydrogenation of soybean oil to reduce its linolenic acid content increases the stability of the soybean oil against oxidation.

Oxidation of frying fats is unavoidable under normal frying conditions as long as the fat is exposed to air. According to McGill (1980) and Roth and Rock (1972a), the addition of oxygen and the formation of free-radicals are slow in fats under storage conditions. During the standby and frying periods, when the fat is heated to about 180 C, the oxidation process becomes more rapid than at lower temperatures. The accumulation of oxidation products that are formed during normal frying changes the characteristics of the frying fat. Free fatty acids are formed as a result of cleavage and oxidation of double bonds (Perkins, 1967). Hydroperoxides which are formed also can undergo further degradation of three major types: fission to form alcohols, aldehydes, acids and hydrocarbons, which cause darkening of the frying fat; dehydration to form ketones; and free-radical formation which leads to dimers, trimers, epoxides, alcohols and hydrocarbons that cause increases in viscosity and polymer content (Fritsch, 1981; Stevenson et al., 1984b).

The use of synthetic antioxidants such as butylated hydroxy toluene (BHT) and butylated hydroxy anisole (BHA) protect vegetable oils from oxidation during long periods of storage at ambient temperatures (Weiss, 1983). However, these antioxidants have proven ineffective in protecting oils during frying (Augustin and Berry, 1983; Peled et al., 1975).

Several other factors also influence the rate of oxidative deterioration of a frying fat. These include exposure of the frying fat to air, deposition of unsaturated food fat in frying fat, and length of heating and cooling periods (Bracco et al., 1981; McGill, 1980; Peers and Swoboda, 1982).

Peers and Swoboda (1982) studied the changes which occur in sunflower seed oil under simulated frying conditions and during potato chip frying at 180 C. In the simulated frying experiment, either argon or air, with or without steam, was bubbled through the oil held at 180 C. For the frying experiment, 40 batches of potato chips were fried in the sunflower oil either with the oil continuously maintained at frying temperature or intermittently with a temperature cycle of cooling and re-heating between frying periods. By monitoring the changes in fatty acid composition, triglyceride content, octanoate content, titratable acidity and color of the oil, the investigators found that whenever the hot oil was exposed to air, whether during simulated frying (air and air plus steam) or during continuous or intermittent frying, there was evidence of oxidative deterioration. They concluded that exposure of the frying fat to oxygen was the main cause for deterioration.

According to McGill (1980), foods such as chicken or fish that tend to deposit their raw unsaturated fats in the frying medium, increase the oxidation rate resulting in quicker breakdown of the frying fat. This deposition can be decreased by battering the food to be fried. On the other hand, Bracco et al. (1981), studying the performance of palm olein, reported that the surface of the oil volume exposed to air rather than the interaction of the oil with the foods that controls the degradation of a frying oil.

McGill (1980) also reported that an oil that received 62 hours of total heating time during a 223 hour period of cycles of heating 7 hours followed by cooling and storage for 12 hours at room temperature had the same concentration of breakdown products as an oil heated continuously 166 hours.

Hydrolysis

Hydrolysis occurs when food is fried in the hot oil. The moisture which is present in the food being fried causes hydrolysis of the ester linkage thus liberating free fatty acids, mono- and diglycerides and glycerine. Free fatty acids are produced by both oxidation and hydrolysis during the frying of foods; however, whether they adversely affect the odor and flavor of the fried foods and the frying fat is dependent upon the fatty acid composition of the frying fat. Fritsch (1981) reported that hydrolytically generated free fatty acids up to at least 2 percent from nonlauric acid oils such as soybean, cottonseed, peanut and palm oil have no

adverse effect on the odor and flavor of foods. On the other hand, the free fatty acids of lauric acid oils, such as coconut oil will produce a soapy flavor at approximately 0.5 percent.

Several factors other than the actual frying of food can increase the rate of hydrolysis. According to McGill (1980), the presence of caustic soda and other alkalis used for cleaning and chemicals such as baking powder in the food being fried also promote hydrolysis. Moreover, the surface of foods to be fried such as potatoes should be dry to reduce hydrolysis during frying (McGill, 1980). In addition, a frying fat with a higher level of initial free fatty acids will deteriorate faster due to increased hydrolysis than a frying fat with a lower initial free acid content (Baeuerlen et al., 1968; Fritsch, 1981). Although the presence of moisture in the food to be fried tends to cause hydrolysis, there are also advantages associated with the presence of moisture. According to Landers and Rathmann (1981), the presence of moisture has a positive effect by creating a blanket of steam over the fryer, thereby protecting the frying fat against oxidation by minimizing contact with the air. Also, the escaping steam helps to remove the volatile by-products which would otherwise accumulate in the frying fat and cause adverse odor and flavor, thus making it unfit for frying. In the study of Peled et al. (1975), cottonseed oil was exposed to heating at 180 C in the presence of low and high water levels under strict controlled conditions. Evaluation of the cottonseed oil indicated that thermal oxidation and hydrolytic

cleavage of cottonseed oil were considerably lessened by the presence of large amounts of water. The investigators concluded that water had a protective effect on the cottonseed oil if it was present in amounts sufficient to generate such volume of steam which could effectively act as an inert gas blanket over the frying oil. Jacobson (1967) conducted a series of tests (Active Oxygen Method) to determine the effect of water on the heat stability of two frying fats. The investigator concluded that the addition of 24 percent water to the frying fat improved the overall performance of the fat compared with the addition of 6 percent water. The investigators also demonstrated that the frying of potatoes in the heat stability test improved the performance even more.

Polymerization

Polymerization causes a frying fat to thicken and become more viscous with progressive heating. The presence of gum or resin-like substance on the fryer is due to a polymerized fat. An increase in the viscosity of the frying fat tends to reduce the rate of heat transfer thereby increasing the cooking time of the food fried in the fat. Also a viscous oil causes food to absorb more oil resulting in a greasy and possibly undercooked food. According to Firestone (1963), polymers are formed in fats and oils through either the thermal polymerization process or the oxidative polymerization process. Thermal polymerizations proceed in the absence of oxygen. They involve Diels-Alder addition of the double bond system at the 1,4-position of a conjugated diene structure

to form hydroaromatic cyclic compounds. On the other hand, oxidative polymerizations occur by free-radical mechanisms. Hydroperoxides that are formed initially at low temperatures decompose upon heating to form dimeric products whose monomeric units are linked through carbon. According to Melnick (1957b), the formation of dimers and higher polymers are only possible if linoleic acid is present in the frying fat. Heating causes conjugation of linoleic acid which then reacts with a natural linoleic acid to form a dimer in the process of which the number of double bonds is reduced from four to two. Thus, the amount of unsaturation in a fat decreases with polymerization. According to Cowan (1954), since iodine value indicates the amount of unsaturation in triglycerides, a drop in iodine value is an indication that polymerization changes have occurred.

Polymerization causes adverse changes that results in a decline in the quality of a frying fat. The presence of dimers and cyclic compounds in a polymerized fat results in deteriorative changes such as increases in viscosity, foaming, gum accumulation and color darkening (McGill, 1980; Stevenson, 1984b). Melnick et al. (1957a) conducted a survey of the frying oils used in the potato chip industry. They suggested that the major concern for fats and oils used commercially should be directed at thermal polymers since oils containing a relatively small amount of oxidative polymers possess an objectionable flavor, whereas a measurable amount of thermal polymers may be present without unfavorable organoleptic

indication. They concluded that the oils used in the production of potato chips were free of thermal polymers.

Methods proposed for evaluating the effects of heat and oxygen on vegetable fats and oils include determinations of materials not eluted in the gas liquid chromatography (Walting, 1975; Walting et al., 1975; Zielinski, 1964) and the measurement of polymers by non-urea-adduct forming fraction (Bennion and Park, 1968; Jacobson, 1967; Peled et al., 1975; Thompson and Aust, 1983).

B. MEASUREMENTS OF FRYING OIL DETERIORATION

Cut-off Level

In 1973, a deteriorated fat or one that should be discarded was defined as (1) one without any doubt had unacceptable odor and taste, (2) one if in the case of doubtful sensory assessment had a concentration of 0.7 percent petroleum ether insoluble oxidized fatty acids (PEIOFA) and a smoke point of less than 170 C, or (3) one with a PEIOFA concentration of 1 percent or higher (Billek et al., 1978; Fritsch, 1981). Fritsch (1981) pointed out that for routine quality control, taste evaluations alone were unreliable, and that the rejection point of a frying oil should be established by a quantitative method such as PEIOFA or equivalent. The PEIOFA method, however, requires considerable skill and time, and suitable alternate methods of quantitation have been studied as a replacement with determination of polar materials emerging as the best substitute for PEIOFA (Billek et al., 1978; Fritsch,

1981). Billek and co-workers (1978) showed that for palm oil, hydrogenated soybean oil (IV=100) and soybean oil, 27 percent total polar materials were equivalent to 1 percent PEIOFA.

The time in hours required for heating an oil at 180 C to reach a concentration of 1 percent oxidized fatty acids is also called its frying stability (Bracco et al., 1981). Bracco and co-workers (1981) heated either palm oil liquid fraction (POLF) or peanut oil in a household fryer (3000 ml capacity) continuously for 100 hours with the frying of potato slices after 0, 50 and 100 hours of heating. Peanut oil had a frying stability of 72 hours, which is approximately the same as that of POLF.

Many tests beside the determination of total polar materials and PEIOFA have been used to measure deterioration of frying oils. Among these are the change in dielectric constant, free fatty acid content, peroxide values, diene/triene content, ultraviolet spectrophotometry, iodine value, changes in fatty acid composition, color measurement of the oil, foam height, active oxygen method, smoke point, flash point, viscosity, polymer content and non-eluted materials (Billek et al., 1978; Bracco et al., 1981; Fritsch, 1981).

High correlation coefficients have been reported among several of these tests. Bracco et al. (1981) reported that polymer content, non-eluted materials and oxidized fatty acids showed parallel values for frying oils during deterioration and were all highly correlated.

C. RAPID TESTS FOR DETERMINATION OF FRYING FAT DETERIORATION

Although many tests are available for assessment of frying oil abuse, most of them require laboratory facilities and/or highly skilled personnel. These requirements could be easily met by major food processors but for most fast food frying operations, the use of quick and reliable on-site tests would be more practical due to time and economic reasons.

Dielectric Constant

The dielectric constant of a substance is its ability to transfer electrical energy. The instrument (Food Oil Sensor) used to measure the change in the dielectric constant of fats has been marketed as a rapid test to ascertain the point at which the frying fat should be discarded.

In the Food Oil Sensor, the shortening is allowed to become the dielectric substance in a patented capacitor sensor. In this sensor, only the shortening is allowed to change, all other parameters remain fixed. A very sensitive bridge detects minute but important changes which are directly attributable to the dielectric constant in the used shortening (Fritsch, 1981; Graziano, 1979).

Oxidation increases the dielectric constant through the introduction of polar groups and hydrolysis of glycerides to free fatty acids. Fritsch et al. (1979) evaluated the change in dielectric constant of a soybean oil (IV=122), a hydrogenated vegetable

shortening (IV=70) and an animal-vegetable shortening (IV=49) subjected to a frying regimen consisting of frying potatoes or heating without frying at 190 C for 8 hours each day for 4 consecutive days. The investigators found that the dielectric constant for the three shortenings increased linearly with frying or heating. Soybean oil showed the greatest increase in dielectric constant while hydrogenated vegetable shortening showed the smallest increase.

Fritsch (1981) reported significant correlation coefficients (r ranging from 0.7 to 0.9) between the change in the dielectric constant and the following tests: total polar materials, decrease in iodine value, color, peroxide value and diene content. The correlation coefficient between the change in dielectric constant and free fatty acid content was much lower ($r = 0.569$). Paradis and Nawar (1981) analyzed oils collected from various commercial frying operations. The investigators reported that the Food Oil Sensor readings represent the net balance between polar and non-polar components present in heated fats. They also reported that for a given frying operation, methods of assessment of frying oils by column chromatography, dielectric constant and GLC of triglycerides dimers correlated well with each other and with frying time.

Although the Food Oil Sensor enabled rapid measurement of frying oil quality, some precautions have to be taken to obtain reliable results. According to Fritsch et al. (1979), the instrument must be stabilized before readings can be obtained, fresh shortening must be melted without overheating and samples must not be taken from the fryer while food is being fried.

Foaming

The amount of foaming in the frying oil is one of the most common indicators used in deep-fat frying operations in determining the condition of a frying fat. Foaming in a frying fat is caused by the presence of polymers and is indicative of a deteriorated fat. According to Roth and Rock (1972b), foam is an unstable colloidal system formed by the dispersion of gas in a liquid. In a frying fat, the dispersed phase is supplied by the frying food product in the form of steam, air and, in the case of leavened products, carbon dioxide. According to McGill (1980), the compounds which cause foaming in a heated fat are formed by oxidation and hydrolysis, and these compounds act on the surface of the oil by allowing a stable foam to develop. In the absence of these compounds, the bubbles of steam and carbon dioxide from the frying food escape from the surface without forming a foam. Roth and Rock (1972b) also stated that the formation of a stable foam in a frying fat is caused by low surface tension, creation of molecular species capable of hydrogen bonding, increased viscosity and accumulation of polymer and fall-off materials which add structural strength to the bubble.

Since the degree of polymer formation increases with frying oil usage, the longer the oil is used, the more it is expected to foam. Bracco et al. (1981) measured the foam index of heat abused peanut oil and palm oil liquid fraction by comparing the time taken by the heat-abused frying oil to reach the 80 mm level against the time taken by the fresh oil to reach the same level. The peanut oil that had been heated for 72 hours at 180 C gave a foam index

of 9.75 while the palm oil liquid fraction that had been heated for 78 hours at 180 C gave a foam index of 9.4. Fritsch et al. (1979) reported that foam height is a poor measurement of frying oil deterioration. With soybean oil, the foam height increased with increased deterioration but with hydrogenated vegetable shortening and animal-vegetable shortening, the foam height either remained the same or actually decreased.

Several factors other than accumulation of polymers influence the foam height of a frying fat. According to Weiss (1983), the frying of food dipped in egg batter or doughnuts containing a high level of egg yolk solids can cause early foaming from lecithin leaching into the shortening. Also, a high fat turnover rate maintains a polymer level below that which would cause high foam formation. Foaming in fat during frying can cause problems with the fried foods. It can cause spotting of the fried food and a non-uniform crust color (McGill, 1980; Roth and Rock, 1972b). According to McGill (1980), the presence of foaming compounds in the oil also causes the oil to penetrate the fried food more easily, thereby increasing fat absorption.

Color

As frying progresses, the color of the frying fat changes from light yellow to a dark shade of brown. In most food frying operations, subjective measurement of color is one of the criteria used to determine the use end-point of a frying fat. According

to Roth and Rock (1972b), the darkening of the color of a frying fat is a result of oxidation which forms a variety of compounds that can absorb energy over a wide range of the visible spectrum. Oxidation of natural pigments such as carotenes and xanthophyll present in fats also account for the observed color changes. Other factors also contribute to darkening of a frying fat. Compounds formed in the frying food by caramelization dissolve in the oil and tend to darken the frying medium. In addition, very fine carbon particles which remain suspended in the frying oil will also darken the oil (McGill, 1980; Roth and Rock, 1972b).

Stevenson et al. (1984a) measured the color changes of liquid canola and soybean oil using the Hunterlab Color Difference Meter at 0, 37.5 and 75 hour intervals of frying french fries in the liquid fats. The investigators found that the color of the fats darkened with continued heating and that the correlation of the change in color, ΔE , with hours of frying was 0.97.

The color of the food product fried is affected by the color of the frying oil in which the product is fried. A fresh oil produces a light colored product while an oil that has been used repeatedly produces a product with darker color.

Smoke Point

The smoke point is the temperature at which a frying oil begins to emanate continuous wisps of thin smoke (A.O.C.S., 1983). Smoke point is a common method used in deep-fat frying operations

as an indicator of the condition of a frying fat. A highly deteriorated frying fat creates an unfavorable frying condition by producing an acrid and objectionable odor.

The amount of smoke emanating from a fryer is directly proportional to the temperature and the amount of low molecular weight decomposition products present in the frying fat (Roth and Rock, 1972b). A fresh fat has a smoke point of 218 C or higher (Weiss, 1983). As free fatty acids and other volatile compounds formed by oxidation or hydrolysis continue to increase during progressive heating and frying, the frying fat begins to smoke at a lower temperature. A badly deteriorated frying fat will smoke even at temperatures below the frying temperature, 180 C. Consequently, where a deteriorated fat is used, the food has to be cooked below the frying temperature to avoid smoking, thus resulting in a longer frying time for the food. The use of smoke point as an indicator of frying fat abuse has several limitations. According to Stevenson et al. (1984b), the smoke point test relies heavily on the ability of the technician to determine the point at which the frying fat actually begins to smoke. In addition, the temperature of the testing room also affects the smoke point.

Bracco et al. (1981) measured the smoke point of palm oil liquid fraction and peanut oil used for frying potato slices at 0, 50 and 100 hours of frying at 180 C. The results of their study suggested that the smoke points of the oils decreased with increased heating and frying time at relatively the same rate.

Stevenson et al. (1984a) found negative correlations between smoke point and hours of frying for canola and soybean fats used for frying french fries at 180 C for 37.5 hours in solid fats and 74 hours in liquid fats. The investigators also reported that the smoke points for all the fats dropped below 170 C after 15 to 20 hours of frying.

Dienoic Acid

Oxidation of linoleate or more highly unsaturated fatty acids results in the formation of conjugated diene systems that can be measured by ultraviolet absorption at 233 nm (Gray, 1978). According to Melnick (1957a), conjugated dienes are a precursor to the formation of polymers.

Augustin and Berry (1983) studied the effectiveness of BHA and BHT in retarding the deterioration of palm olein during static heating (180 C) and during frying of french fried potatoes for 4 hours a day on two consecutive days. The investigators found that the diene content of the used palm olein increased with heating and/or frying. Peled et al. (1975) studied the effects of water and BHT on cottonseed oil used for frying under controlled conditions at 180 C and under a constant air or nitrogen flow. The investigators concluded that water in the form of steam provided protection of the frying oil against oxidation as reflected in the lower amounts of conjugated diene compounds in the presence of water. Fritsch et al. (1979) found the greatest increase in the conjugated diene content of soybean oil, hydrogenated vegetable shortening and

an animal-vegetable shortening (heated at 190 C for 8 hours a day for 4 days with and without frying) to occur during the first day of frying. The changes in the dienoic acid content during the subsequent days were relatively small. Their results agreed with the findings of Augustin and Berry (1983).

Free Fatty Acids

During frying, free fatty acids are formed in the frying fat due to both oxidation and hydrolysis. Measurement of the free fatty acid content is one of the most common methods used by large commercial food frying operations for quality control evaluation of frying fats. The standard method of determining free fatty acids by titration does not differentiate between the free fatty acids formed by oxidation and those formed by hydrolysis of the fat (Fritsch, 1981; Peers and Swoboda, 1982). Fritsch (1981) suggested that the amount of free fatty acids produced by hydrolysis is too small to affect the quality of the food and that the adverse effects on the frying oil are due to oxidation. This is in disagreement with McGill (1980) who reported that free fatty acids from hydrolysis of frying fat causes the fat to develop off-flavors. Peers and Swoboda (1982) studied the types of deterioration which sunflower oil undergoes under simulated frying conditions at 180 C for 22.5 hours. The investigators found that oxidation caused a higher increase in acidity of the oils than did hydrolysis (argon plus steam). They also reported that in the presence of air plus

steam, the titratable acidity was the sum of acids due to hydrolysis and those due to oxidation.

Maintaining the free fatty acids of a frying fat at low levels will prevent early smoking and foaming. Weiss (1983) suggested that a free fatty acid level of 0.5 to 0.8 percent is normal for frying fat in use. Also a proper turnover rate of a frying fat will maintain the amount of free fatty acids in a frying fat at a sufficiently low level. Thompson and Aust (1983) found that replenishment of a lightly hydrogenated soybean oil used for frying french fried potatoes at 20.5, 45 and 60 hours of frying lowered the free fatty acid levels in the frying fat. Chen (1984) analyzed the free fatty acid contents of a vegetable shortening used for frying chicken parts for a total of 12 days in two commercial fried chicken outlets. The investigators found that the free fatty acid contents increased continuously throughout the 12-day frying period. Besides air and moisture, other factors can also increase the rate of free fatty acid formation. Bennion and Park (1968) studied the effect of various ingredients in a fritter type batter on the physical and chemical changes in corn oil and a hydrogenated vegetable shortening. The investigators reported that a highly significant increase in the percentage of free fatty acids and a marked darkening of the color of the oils after 8 hours frying were associated with the presence of egg yolk in the batter being fried for both frying fats.

Total Polar Materials

The deteriorative reactions that occur during deep-fat frying causes the production and accumulation of highly polar compounds. Polar materials include free fatty acids, monoglycerides, diglycerides and other polar transformation products formed during heating and frying (Walting and Wessels, 1981).

Determination of total polar materials using column chromatography has been shown to be reliable as an indicator of the extent of frying fat deterioration by Billek et al. (1978). They assessed four blends of frying oils collected from various commercial frying operations for total polar materials by gel permeation chromatography, liquid chromatography and column chromatography, Petroleum ether insoluble oxidized fatty acids (PEIOFA) levels were also measured. The investigators concluded that the determination of total polar materials by column chromatography produced good correlation with PEIOFA content. They found that 1 percent PEIOFA was equivalent to 27 percent total polar materials for all the frying oils studied.

Good correlations between total polar materials and other rapid tests have been reported by other investigators. Fritsch et al. (1979) found high correlations ($r > 0.9$) between total polar materials and dielectric constant for three different frying fats heated with or without frying of potatoes. Stevenson et al. (1984a) reported high correlations between total polar materials and hours of frying french fried potatoes in canola and soybean fats. The

investigators also found high correlations ($r > 0.9$) between total polar and free fatty acids for all the fats.

Fatty Acid Composition

Oxidation and polymerization of fats that occur during deep-fat frying result in the loss of polyunsaturated fatty acids since these fatty acids are more susceptible to oxidative breakdown. Thompson et al. (1967) found lower amounts of linoleic acid in fats and oils used for commercial deep-fat frying compared with the fresh fats and oils. Gas liquid chromatography is a widely used method for determining the exact fatty acid composition of fats and oils. In the work by Waliking and Zmachinski (1970), several fatty acid methodologies of heated fats were described. Kilgore and Bailey (1970) studied the changes in linoleic acid composition of safflower oil, corn oil, cottonseed oil and a highly unsaturated shortening after repeated frying of potatoes at 180 C for 5 days. The investigators found a significant decrease in the linoleic acid content in all the fats. They concluded that the decrease was due to degradation of linoleic acid in the oils during frying. Peers and Swoboda (1982) studied the changes in sunflower seed oil under simulated frying conditions and during potato chip frying. Gas liquid chromatography was used to analyze the changes in palmitic, oleic and linoleic acids of the used oils. The investigators concluded that in both the simulated or actual frying condition, oxidative deterioration resulted in a decrease in the oleic acid and linoleic acid

contents. They also reported that due to higher unsaturation, linoleic acid showed a greater decrease in content than oleic acid.

Replenishment of a frying oil with fresh oil maintains the frying oil in a satisfactory condition for a longer time. Thompson and Aust (1983) employed gas liquid chromatography using an internal standard method to determine the changes in the fatty acid composition of a lightly hydrogenated soybean oil used for frying potatoes over a 100-hour frying period. The frying oil was replenished three times during the course of the frying period. They reported that the oleic acid content of the frying oil increased initially and then decreased with no net effect.

CHAPTER III

MATERIALS AND METHODS

A. SOURCE OF DATA

For this study, 19 liters of partially hydrogenated soybean oil and 19 liters of palm oil olein were obtained from Kraft, Inc., Memphis, TN, and Palmco, Inc., Portland, OR, respectively. Each type of oil was shipped to the Department of Food Technology, The University of Tennessee, Knoxville, in a 20-liter bulk container. Prior to the beginning of the frying experiment, each oil was mixed thoroughly by mechanical agitation of the cans containing the oil. After mixing, the oils were poured into labeled, airtight, two-quart plastic containers, flushed with nitrogen and sealed until used. This ensured homogeneity among the different lots for each type of oil which would be used to complete the four replications in this investigation.

Frozen french fried potatoes and frozen codfish patties used in this study were obtained from J. T. Hackney Wholesale Co., Knoxville, TN. The french fried potatoes were 3/8 inch straight cut potatoes which were partially fried and frozen. The fish patties were 10 cm by 5 cm by 1 cm in size, breaded and frozen. Each patty weighed approximately 112 g. Separate batches of french fries and fish patties were shipped to the Department of Food Technology, The University of Tennessee, Knoxville, for each

replication. The french fries and fish patties were kept frozen at -20 C until used for frying.

The deep-fat fryers used were each a 0.9 liter capacity portable electric "Fry Daddy" manufactured by National Presto Industries, Inc. The frying temperatures were controlled by the use of thermostats, and the temperatures of the oils were monitored by the use of cooking thermometers.

Analysis of 0-Day Frying Oil Samples

Samples of each type of oil were taken from the homogeneous lots at the beginning, middle and end of this frying study. These three samples of oil were analyzed for dielectric constant, conjugated dienoic acid content, free fatty acid levels, smoke point, total polar materials content and fatty acid composition.

Analysis of Frozen Food Samples

Samples of french fried potatoes and fish were taken from the representative lots at the beginning of each replication. The potato and fish samples were analyzed for moisture and fat content and the results obtained were the average percent fat and moisture present in the samples before frying.

B. FRYING PROCEDURE AND SAMPLING

Frying was conducted in the Food Technology and Science laboratory. Adequate ventilation was provided during the course of the frying experiment. Eight hundred seventy-five grams of fresh

oil were placed in the deep-fat fryer, and the oil was allowed to heat up to a frying temperature of $180\text{ C} \pm 5\text{ C}$. One hour after the heat was turned on, a frozen fish patty or a batch of approximately 112 g of frozen french fried potatoes were fried in the hot oil. The fish patty was deep-fried for 2 minutes on each side for a total of 4 minutes, and the french fried potatoes were deep-fried for 7 minutes. At the end of the frying time, the food was lifted from the hot oil, and as much oil as possible was allowed to drain from the food back into the fryer. The temperature of the oil in the deep-fat fryer which dropped slightly during frying was then allowed to return to 180 C and maintained at that temperature until the next frying. In each fryer, one fish patty or one batch of french fried potatoes was fried every 2 hours for 8 hours each day. Before the heat was turned off at the end of each day, foam and dielectric constant tests were performed on the oil. After the heat was turned off and the oil allowed to cool, the oil was filtered through four thicknesses of cheese cloth to remove any food debris present. All four fryers were cleaned daily. Frying was conducted for five consecutive days.

At the end of the second and fourth day of frying, the oil that had been cooled and filtered was returned to the fryer and left covered overnight. At the end of the first, third and fifth days of frying, after the oil had been cooled and filtered, 135 grams of oil were removed for analytical tests. Also, the last food samples fried at 1, 3 and 5 days were saved for chemical analyses.

The oil samples were placed in 250-ml Erlenmeyer flasks, flushed with nitrogen, sealed and stored at -18 C for further evaluation. The fried samples were also stored at -18 C in nitrogen flushed, sealed Whirlpak plastic bags for chemical analyses.

At the end of the first and third days, fresh oil was added to the filtered oil to return the total weight to 875 grams, and this oil was returned to the fryer for subsequent frying the next day.

C. PHYSICAL MEASUREMENTS

Foam Height

Foam height was determined according to the procedure by Fritsch et al. (1979). This test was performed daily on the hot oil just before the heat was turned off at the end of the day. A 250-ml graduated cylinder with 35 mm internal diameter was cut at the bottom to form a hollow cylinder. The cylinder was clamped to a retort stand and lowered into the hot oil so that the cylinder almost touched the bottom of the fryer. The reading on the surface level of the oil was recorded. A raw potato was cut with a vegetable cutter to obtain rectangular cubes 3.1 cm by 1 cm by 1 cm in dimension. A potato cube was dropped through the cylinder into the hot oil. The maximum foam height was observed. The foam height in cm was equal to the final reading minus the initial reading.

Dielectric Constant

The dielectric constant of the oil was measured on a Food Oil Sensor, Model NI-20 according to the method by Fritsch et al. (1979). This test was performed daily on the 180 C oil just before the heat was turned off at the end of the day. The Food Oil Sensor was turned on at least one hour prior to the measurement. The instrument was calibrated to a zero reading with the fresh oil of the sample to be tested. Once calibrated, a small quantity of the hot oil was taken from the fryer and the dielectric constant of the oil sample was determined.

Smoke Point

The smoke point of the oil was determined according to the A.O.C.S. (1983) Official Method 9a-48. The test was performed using a smoke point cabinet constructed according to the A.O.C.S. specification. The oil sample was placed in an open flash cup supported on a heating plate and a ring stand. A thermometer was suspended vertically into the center of the cup with the end of the bulb close to the bottom of the cup. The oil sample was heated rapidly with a gas burner to within 41.7 C of the smoke point. Thereafter, the heat was regulated so that the temperature of the oil increased at a rate of 5 C to 6.1 C per minute. The smoke point was the temperature indicated by the thermometer when the sample gave off a thin, continuous stream of bluish smoke.

D. CHEMICAL MEASUREMENTS

Conjugated Dienoic Acid

The diene conjugation of unsaturated linkages present in the oil was determined according to the A.O.C.S. (1983) Official Method Ti 1a-64. This analysis was performed on oil samples at 1, 3 and 5 days. A designated amount of the oil sample was dissolved in A.C.S. reagent grade isooctane (2,2,4-trimethyl pentane) and the volume made up to 100 milliliters. Absorbance readings were obtained using a spectrophotometer equipped with a UV light source and 1.00 cm quartz cells. The spectrophotometer was calibrated using 1.00 cm quartz cells containing pure isooctane. The absorbancy of the solution was measured at 233 nm against a pure isooctane blank. The solution was diluted with isooctane, if necessary, to obtain absorbance readings between 0.2 and 0.8. Percentage of conjugated dienoic acid was calculated from the absorbance value.

Free Fatty Acid

Free fatty acid determination was performed according to the A.O.C.S. (1983) Official Method Ca-5a40. Oil samples at 1, 3 and 5 days were analyzed for free fatty acids. A specified amount of the oil sample was mixed with neutralized 95 percent ethyl alcohol and phenolphthalein indicator. The mixture was titrated with 0.1 N sodium hydroxide solution until a light pink color appeared and the volume of sodium hydroxide solution required to reach this point was recorded. The percentage of free fatty acids in the oil was calculated as percentage oleic acid.

Total Polar Materials

The amount of total polar materials in the oil was determined using column chromatography according to the procedure proposed by Waliking and Wessels (1981). This analysis was performed on oil samples at 1, 3 and 5 days. The polar fraction of the oil was separated from the non-polar fraction (unaltered triglycerides) on a silica gel (70-230 mesh) column by elution with a 87:13 v/v mixture of petroleum-ethyl ether. The non-polar fraction was eluted in 60-70 minutes, followed by evaporation of the solvent using a rotary evaporator. From the amount of non-polar fraction obtained, the percentage polar materials was calculated by subtraction.

Fatty Acid Composition

For each fresh oil sample and used frying fat sample, the fatty acid concentration was determined by converting the triglycerides to methyl esters of their fatty acids by Method Ce 2-6 (A.O.C.S., 1983). The relative percentage of each fatty acid was determined on a 30-m x 0.25 mm fused silica capillary column coated with SP2330 (Supelco, Bellefonte, PA) in a Shimadzu 6AM gas chromatograph (GC) equipped with a flame ionization detector, a 30:1 capillary splitter and a Shimadzu C-E1B electronic integrator and data processor. Conditions for the GC analysis were:

Helium flow rate	40 ml/min
Hydrogen flow rate	20 ml/min
Air flow rate	200 ml/min
Injector temperature	250 C

Detector temperature	250 C
Initial oven temperature	150 C
Final oven temperature	250 C
Temperature program rate	2 C/min

In the chromatogram of each sample, each peak was assigned either to a known fatty acid or an unknown compound based on retention time. The relative percentage of each fatty acid was determined according to the method of A.O.C.S. (1983). A standard containing known concentrations of the fatty acids 14:0, 16:0, 16:1, 18:0, 18:1 ω 9, 18:2 ω 6, 18:3 ω 3 similar to the concentrations present in frying fats was prepared and analyzed by the GC method. Correction factors for the fatty acids in this standard were determined as described by A.O.C.S. (1983) to be as follows: 1.4885 for 14:0, 1.0000 for 16:0, 1.3323 for 16:1, 1.1543 for 18:0, 1.0142 for 18:1 ω 9, 1.2425 for 18:2 ω 6 and 1.2771 for 18:3 ω 3. The correction factor for all other known and unknown acids was assumed to be 1.00

Concentrations of the fatty acids: 12:0, 14:0, 15:0, 16:0, 16:1, 18:0, 18:1 ω 9, 18:1 isomer1, 18:1 isomer2, 18:2 isomer1, 18:2 ω 6, 18:2 isomer2, 18:2 isomer3, 20:0, 18:3 ω 3, 20:1 ω 9, 18:2 ω 7 (diene), 20:2 ω 6, 22:1, 24:0 and unknown acids in each fresh oil and each used frying fat samples were determined. The concentration of the unknown acids consisted of the sum of percentages of 13 GC peak that could not be identified even tentatively by the GC-mass spectrometer in the chromatograms of the methyl esters of the fatty acids of the fresh and used frying fats.

Representative samples of the fresh oils and used frying fats were converted to their methyl esters and analyzed on the same capillary column and under the same conditions as previously reported except a Shimadzu 9AM GC interfaced with a Shimadzu QP-1000 mass spectrometer was used for the analysis. Mass spectra were obtained of each GC peak in the EI mode at 70 ev. Positive identification of the compounds responsible for each peak was made by matching sample peak spectra and retention times with corresponding spectra and retention times of known compounds analyzed in the same way as the samples. Identification of peaks were made by matching sample spectrum with those in the literature or based on their retention time in relation to other methyl esters of fatty acids and the molecular weight obtained from their mass spectra.

E. ANALYSES OF RAW AND FRIED FOOD SAMPLES

Each food sample was converted into powder in liquid nitrogen in a Waring blender using a 0.9 liter stainless steel jar to obtain a homogeneous sample. Percentage of fat in the food was determined by extracting fat from 4 g powdered sample in extraction thimbles for 24 hours with ethyl ether (A.O.A.C., 1980). Percentages of moisture in the food sample was determined by drying 2 g of the powdered sample in a vacuum oven at 100 C for 6 hours according to A.O.A.C. (1980).

V. STATISTICS

Experimental Design

The experimental design of this study was a 4 x 4 Latin Square with a split in each square (Sanders, 1985). The 4 x 4 design was represented by four replications and four deep fryers. The split was the sampling times from each fryer. The four fryers used were labeled F1, F2, F3 and F4, respectively. The frying procedure was replicated four times such that each treatment (A, B, C, D) occurred only once in each replication and fryer as shown in Table 1.

TABLE 1
EXPERIMENTAL DESIGN

Replication	Deep Fryer			
	F1	F2	F3	F4
	Treatment ^a			
1	A	B	C	D
2	B	A	D	C
3	C	D	A	B
4	D	C	B	A

^aA = potato in palm oil olein.

B = fish in palm oil olein.

C = potato in soybean oil.

D = fish in soybean oil.

One replication was conducted simultaneously in respect to fryers and treatments. Sampling of oil and fried foods was conducted

during a 5-day frying period. Samples were obtained daily from 1 day to 5 days for the dielectric constant and foam height tests and on days 1, 3 and 5 days for the smoke point, conjugated dienoic acid, free fatty acids, total polar materials, and fatty acid composition.

Statistical Analysis

Characteristics and fatty acid composition of used frying oils were statistically analyzed as a function of Fryer (F), Replication (R), Treatment (T), Day of Frying (D), and specific interactions, FxD, RxD, TxD, FxRxT and FxRxTxD using the General Linear Model in Statistical Analysis System (Barr et al. 1979). Significant treatment effects were separated by orthogonal contrasts shown in Table 2.

TABLE 2
ORTHOGONAL CONTRASTS FOR TREATMENT EFFECTS

Contrast	Treatments			
	1	2	3	4
1	-1	-1	+1	+1
2	-1	+1	-1	+1
3	-1	+1	+1	-1

NOTE: Contrast 1 compared the two oils, contrast 2 compared the two products and contrast 3 compared the oilxproduct interaction.

Significant differences among days of frying were separated by orthogonal polynomials across treatments in the absence of a significant TxD interaction and for each treatment in the presence of a significant TxD interaction. Significant fryer effect and fryer interaction with treatment and day were not analyzed further.

CHAPTER IV

RESULTS AND DISCUSSION

Analysis of variance for the effects of treatment, fryer and day of frying on dielectric constant and foam height is shown in Table 3. The 4 by 4 Latin Square design with a split allowed the experimenter to choose the sources of variation of interest for further analysis. While the effects of treatment and day of frying are considered to be the most relevant to the purpose of this investigation, sources of variation due to fryer and replication are also presented for statistical justification.

As shown in Table 3, there were significant differences in the dielectric constant and foam height values among the four treatments. The measured values were also found to be affected significantly by day and day by treatment interaction effect. Orthogonal comparisons of the treatment effects showed that the dielectric constant was significantly affected by the product fried in the oil, while foam height was significantly affected by the type of frying oil used as well as the product fried.

Analyses of variance for the effects of treatment, fryer and day of frying on dienoic acid content, percentage free fatty acids, percentage polar materials and smoke point are presented in Table 4. There were significant differences in the conjugated dienoic acid and free fatty acid contents and also the smoke point of the oils among the four treatments. Dienoic acid and free fatty acid contents

TABLE 3

ANALYSIS OF VARIANCE FOR THE EFFECTS OF TREATMENT, FRYER AND DAYS
OF FRYING ON DIELECTRIC CONSTANT AND FOAM HEIGHT

Source	DF	Sum of Squares	
		Dielectric Constant	Foam Height
Fryer (F)	3	2.84	4.78
Replicate (R)	3	20.06 ^a	128.29 ^a
Treatment (T)	3	11.66 ^a	151.33 ^a
Oil (O)	1	0.25	61.01 ^a
Product (P)	1	11.41 ^a	90.30 ^a
O X P	1	0.01	0.03
Error A [R(FxT)]	6	7.59	25.56
Day (D)	4	172.74 ^a	480.28 ^a
D X F	12	2.32	8.98
D X R	12	8.64	37.53
D X T	12	3.86 ^a	104.71 ^a
Error B [R(DxFxT)]	24	2.01	22.15
Total	47		

^aSignificant at the $P < 0.05$ level.

TABLE 4

ANALYSIS OF VARIANCE FOR THE EFFECTS OF TREATMENT, FRYER AND DAYS OF FRYING ON DIENE CONTENT,
FREE FATTY ACIDS, POLAR MATERIALS AND SMOKE POINT

Source	DF	% Dienoic Acid	Sum of Squares		
			% Free Fatty Acid	% Polar Materials	Smoke Point
Fryer (F)	3	0.1330	0.0408	144.251	24.4167
Replicate (R)	3	0.3742	0.0646	116.3679	648.4167
Treatment (T)	3	5.2102 ^a	1.097 ^a	105.5258	2669.5833 ^a
Oil (O)	1	4.8375 ^a	0.9381 ^a	1.9494	2380.083 ^a
Product (P)	1	0.3712 ^a	0.1544 ^a	39.0915	270.7500 ^a
O X P	1	0.0014	0.0047	64.4848	18.7500
Error A [R(FxT)]	6	0.0655	0.0376	400.8431	117.500
Day (D)	2	0.9910 ^a	2.3130 ^a	6483.0559 ^a	5991.5417 ^a
D X R	6	0.0826	0.0341	321.0412	121.4583
D X F	6	0.0541	0.0173	196.2266	150.9583
D X T	6	0.1341 ^a	0.1716 ^a	177.6954	75.7917
Error B [R(DxFxT)]	12	0.0625	0.0215	391.0149	120.2500
Total	47				

^aSignificant at the P<0.05 level.

were both significantly affected by days of frying and had a significant day by treatment interaction while percentage of polar materials and smoke point were significantly affected only by days of frying. Orthogonal comparisons of the treatment effects showed that diene content, free fatty acids and smoke point were significantly affected by both the type of frying oil used and the product fried in the oil. No significant difference among treatments was observed for percentage of polar materials. The partitioning of the sum of squares for days of frying effect across treatment for percentage polar materials and smoke point as well as the days of frying effect for each treatment on levels of dienes and free fatty acids are shown in Appendix Tables A-4, A-5 and A-6, respectively.

Mean values for dielectric constant for each treatment during the 5-day frying period are presented in Table 5. Polynomial equations for describing the relationship between dielectric constant (Y) and days of frying (X) for each treatment are also shown in Table 5 (see Appendix Table A-2 for the partitioning of the sum of squares for days of frying effect for each treatment on dielectric constant). There was a quartic relationship between dielectric constant and length of frying for each of the four treatments. Generally, the mean values for the dielectric constant increased steadily from the first day until the third day of frying but decreased slightly on the fourth day. The dielectric constant values rose again rapidly by the fifth day (Table 5). The dielectric

TABLE 5
MEAN VALUES FOR DIELECTRIC CONSTANT FOR EACH TREATMENT
DURING 5-DAY FRYING PERIOD

Treatments	Day of Frying (X)				
	1	2	3	4	5
1 ^b	2.02	2.71	3.81	3.55	4.63
2 ^c	2.20	3.10	4.34	4.24	5.63
3 ^d	2.00	3.00	3.90	3.70	4.70
4 ^e	2.14	3.24	4.40	4.43	5.61

^a1 = Potato in Palm Oil; 2 = Fish in Palm Oil; 3 = Potato in Soybean Oil; 4 = Fish in Soybean Oil.

^bSignificantly affected by days frying (X) where $Y = 8.0 - 12.49 X + 8.50 X^2 - 2.16 X^3 + 0.186X^4$.

^cSignificantly affected by days frying (X) where $Y = 7.57 - 11.74 X + 8.27 X^2 - 2.13 X^3 + 0.19 X^4$.

^dSignificantly affected by days frying (X) where $Y = 4.9 - 7.04 X + 5.46 X^2 - 1.47 X^3 + 0.13 X^4$.

^eSignificantly affected by days frying (X) where $Y = 5.55 - 8.00 X + 6.03 X^2 - 1.58 X^3 + 0.14 X^4$.

constant was significantly higher when fish was fried in the oils (treatment 2 and 4) than when potatoes were fried in the oils (treatment 1 and 3).

The gradual increase in dielectric constant from the first day of frying to the third day of frying indicated the accumulation of polar components in the frying oil. As the oil breaks down thermally and oxidatively, peroxides and other radicals are formed on the triglycerides that cause it to become polar, thus contributing to the increase in the dielectric constant of the oil (Graziano, 1979).

Addition of fresh oil to the used oil at the end of the third day diluted the amount of polar compounds in the frying oil as shown by the lower mean values for the dielectric of the oils on the fourth day of frying compared with that on the third day of frying. However, addition of fresh oil to the frying oil at the end of the first day of frying did not result in a decrease in the dielectric constant of the oils from the first to the second day.

In the study of Fritsch et al. (1979), the dielectric constant of a soybean oil, a hydrogenated vegetable shortening and a hydrogenated animal-vegetable shortening was found to increase linearly with hours of frying. However, the frying fats used in their study were not replenished with fresh fat. The increase in the dielectric constant of the frying oil with frying time also agreed with the results obtained by Paradis and Nawar (1981).

Table 6 shows the mean values for the measured parameters averaged across product fried and day of frying for each frying oil. Table 7 shows the mean values for the same parameters averaged across frying fat and days of frying for each fried product. These tables will be referred to in the subsequent discussion of each measured parameter.

There was no significant difference in the dielectric constant between palm oil and soybean oil (Table 6). The dielectric constant was, however, significantly affected by the product fried in the oil with fish causing the oil to have a higher dielectric constant than potato (Table 7).

Mean values for the foam height of frying oils for each treatment during the 5-day frying period are shown in Table 8. Except for treatment 1 where there was a significant linear relationship between foam height and days of frying, all other treatments had a significant quartic relationship between foam height (Y) and days of frying (X). (See Appendix Table A-3 for partitioning of days of frying effect for each treatment on foam height.)

As was found with the dielectric constant, the addition of fresh oil at the end of the third day of frying diluted the frying oil in all treatments such that foam height on the fourth day of frying was lower than that on the third day of frying (Table 8).

Soybean oil as a frying oil had a significantly higher foam height than palm oil olein (Table 6) and frying fish compared with frying potatoes resulted in a higher foam height in both frying oils

TABLE 6
 MEAN VALUES FOR MEASURED CHARACTERISTICS OF EACH
 FRYING OIL AVERAGED ACROSS PRODUCT AND
 FRYING TIME

Characteristic	Palm Oil	Soybean Oil
Dielectric Constant	3.62	3.70
Foam Height, cm	3.42 ^a	4.65 ^b
Dienoic Acid, %	1.00 ^a	1.44 ^b
Polar Material, %	27.80	28.10
Free Fatty Acid, %	0.46 ^a	0.27 ^b
Smoke Point, °C	206 ^a	220 ^b

^{ab}Means in a row bearing unlike superscripts are significantly different ($p < 0.05$).

TABLE 7

MEAN VALUES FOR MEASURED CHARACTERISTICS ACROSS FRYING OIL
AND FRYING TIME FOR EACH PRODUCT FRIED

Characteristic	Potatoes	Fish
Dielectric Constant	3.39 ^a	3.92 ^b
Foam Height, cm	3.28 ^a	4.78 ^b
Dienoic Acids, %	1.16 ^a	1.28 ^b
Free Fatty Acids, %	0.33 ^a	0.41 ^b
Polar Material, %	27.30	28.60
Smoke Point, °C	215 ^a	211 ^b

^{ab} Means in a row bearing unlike superscripts are significantly different ($p < 0.05$).

TABLE 8
MEAN VALUES FOR FOAM HEIGHT (cm) OF FRYING OILS FOR EACH
TREATMENT DURING 5-DAY FRYING PERIOD

Treatment ^a	Day of Frying (X)				
	1	2	3	4	5
1 ^b	2.0	2.2	2.8	2.6	3.8
2 ^c	1.8	2.3	4.5	4.5	7.6
3 ^d	1.7	2.5	4.8	4.3	6.1
4 ^e	1.9	2.7	6.5	6.8	9.3

^aSee Table 5 footnote.

^bSignificantly affected by days frying (X) where $Y = 1.46 + 0.492 X$.

^cSignificantly affected by days frying (X) where $Y = 15.9 - 27.79 X + 17.73 X^2 - 4.36 X^3 + 0.04 X^4$.

^dSignificantly affected by days frying (X) where $Y = 16.33 - 29.40 X + 19.11 X^2 - 4.73 X^3 + 0.04 X^4$.

^eSignificantly affected by days frying (X) where $Y = 22.9 - 41.22 X + 25.88 X^2 - 6.19 X^3 + 0.51 X^4$.

(Table 7). These significant differences are also reflected in Table 8 in Treatments 1 and 2 versus 3 and 4 and in Treatments 1 and 3 versus 2 and 4, respectively. These results indicate that the frying of fish resulted in quicker and more extensive deterioration of the frying oil than the frying of potatoes, and that the soybean oil used in this study foamed more during frying than palm oil olein.

Foaming in frying oils is caused by an increase in viscosity which in turn is caused by a buildup of polymers (Weiss, 1983). Soybean oil did not foam more than palm oil olein at the end of one day of frying; however, as the time of frying increased the difference in foam height between palm oil olein and soybean oil became increasingly greater (Table 8). This indicated that soybean oil probably had a greater polymer content than palm oil olein from 2 to 5 days of frying.

The breaded fish compared with potatoes would be expected to cause faster deterioration of a frying oil for two reasons. A breaded product loses part of the breading during frying, and the breading burns in the frying oil resulting in a faster breakdown of the oil (Robertson, 1967; Stevenson et al., 1984b). Also, fish compared with potato has a greater content of polyunsaturated fatty acids, and as a result fish oil oxidizes faster than fat from potatoes (DeMan, 1980). Unrefined fats from foods are leached into the frying medium during frying (McGill, 1980), and since the fish contains these polyunsaturated fatty acids, fish would be expected

to contribute to the faster breakdown of the frying oils than potatoes.

Mean values for percentage dienoic acid for each treatment during the 5-day frying period are given in Table 9 to explain significant day of frying by treatment interaction found from statistical analysis (Table 4, page 40). Overall, soybean oil used for frying for 5 days had higher percentage dienoic acids than palm oil olein used for frying the same length of time (Table 6, page 45), and fish fried in either oil resulted in higher levels of dienoic acids than did potatoes (Table 7, page 46). In addition, in each oil, the percentage dienoic acids increased from day 1 of frying through day 3 of frying and either leveled off or decreased from day 3 to day 5 of frying (Table 9). There was a significant quadratic relationship between the level of dienoic acids and days of frying for each treatment (Table 9). The significant interaction may be explained by using these equations to calculate the level of dienoic acids in fresh or 0-day frying oil and by observing what happened to the dienoic acid percentages from 0 to 1 day frying in each treatment. The calculated percentages for 0-day oil for treatment 1 is 0.69; treatment 2, 0.55; treatment 3, 1.13 and treatment 4, 1.08. In treatment 1, levels of dienoic acids increased from 0.69 to 0.83 percent while in treatment 2, the levels of dienoic acid increased from 0.55 to 0.86 percent or crossed the curve for treatment 1. This is the reason for the significant interaction. In treatment 3, during the first day of frying the

TABLE 9
MEAN VALUES FOR PERCENTAGE OF DIENOIC ACIDS FOR EACH
TREATMENT DURING 5-DAY FRYING PERIOD

Treatment	Day of Frying (X)		
	1	3	5
1 ^b	0.83	0.98	0.98
2 ^c	0.86	1.19	1.13
3 ^d	1.30	1.46	1.40
4 ^e	1.32	1.59	1.60

^aSee Table 5 footnote.

^bSignificantly affected by days frying (X) where $Y = 0.69 + 0.15 X - 0.02 X^2$.

^cSignificantly affected by days frying (X) where $Y = 0.55 + 0.36 X - 0.05 X^2$.

^dSignificantly affected by days frying (X) where $Y = 1.13 + 0.02 X - 0.03 X^2$.

^eSignificantly affected by days frying (X) where $Y = 1.08 + 0.27 X - 0.03 X^2$.

percentage dienoic acids increased from 1.13 to 1.3 percent, while in treatment 4, the dienoic acid content increased from 1.08 to 1.32 percent. The curve for treatment 4 crossed the curve for treatment 3 from 0 to 1 day of frying, also causing another significant interaction.

The levels of dienoic acids in fresh palm oil and fresh soybean oil are given in Appendix Table A-1. Palm oil olein had 0.07 percent dienoic acids while soybean oil had 0.99 percent. The calculated values for 0-day or fresh palm oil olein were excessively higher than the actual value, however, the calculated values for 0-day or fresh soybean oil were fairly close to the actual level. The values for the fresh oils were not used to obtain the equations showing the behavior of levels of dienoic acids in oils during 5-days frying. This is the reason for the difference between the calculated dienoic acids content and the actual content in fresh palm oil olein.

The levels of dienoic acids in both oils increased greatly from the initially low levels before frying to the end of the first day of frying. This is especially true for palm oil olein in which the dienoic acid level increased approximately 5-fold after 8 hours heating and frying. The dienoic acid level increased only slightly after 1 day of frying for both oils.

Augustin and Berry (1983) reported similar increases in the diene content of palm olein that was continuously heated at 180 C or used for frying potato chips for 4 hours a day for two consecutive days. { The investigators suggested that the small increases in diene content at the later stages of frying were due to the attainment

of equilibrium between the rate of formation of conjugated dienes and the rate of formation of polymers. Fritsch et al. (1979) also found similar increases in the diene content with increased frying time for the three different frying fats used in their study.

Palm oil olein used for frying across 5 days had a higher percentage of free fatty acids than did soybean oil used for the same frying period (Table 6, page 45). Also, the frying of fish in either oil for 5 days resulted in a higher percentage of free fatty acids than did frying potato (0.41 versus 0.33 percent, Table 7, page 46). The levels of free fatty acids in all treatments increased at a decreasing rate from the first day of frying through the fifth day of frying as shown in Table 10. Significant treatment by day interactions did exist as shown in Table 4, page 40. The equations (Table 10) showing the effect of day 1 to day 5 of frying on free fatty acid content resulted in interactions among treatments from 0 to 1 day of frying. However, since data for 0-day or fresh oils were not used to obtain these equations, the interactions were not important. Free fatty acid contents in the fresh oils were 0.03 percent for palm oil and 0.1 percent for soybean oil (Appendix Table A-1), and these values were considerably lower than the levels of free fatty acids in any of the oils after 1 day of frying (Table 10).

Increases in the free fatty acid content of frying oils with frying time have been observed in other studies involving deep-fat frying of foods (Bracco et al., 1981; Fritsch et al., 1979; Handel

TABLE 10
MEAN VALUES FOR PERCENTAGE OF FREE FATTY ACIDS FOR EACH
TREATMENT DURING 5-DAY FRYING PERIOD

Treatment ^a	Day of Frying (X)		
	1	3	5
1 ^b	0.20	0.48	0.62
2 ^c	0.22	0.55	0.72
3 ^d	0.09	0.25	0.32
4 ^e	0.13	0.34	0.47

^aSee Table 5 footnote.

^bSignificantly affected by days frying (X) where $Y = 0.01 + 0.21 X - 0.02 X^2$.

^cSignificantly affected by days frying (X) where $Y = 0.00 + 0.24 X - 0.02 X^2$.

^dSignificantly affected by days frying (X) where $Y = -0.02 + 0.13 X - 0.01 X^2$.

^eSignificantly affected by days frying (X) where $Y = -0.02 + 0.16 X - 0.01 X^2$.

et al., 1984; Meltzer et al., 1981; Morrison et al., 1973; Peers and Swoboda, 1982; Robertson et al., 1978; Stevenson et al., 1984a; Thompson and Aust, 1983). Bracco et al. (1981) found that the free fatty acids produced during the deep-fat frying of potato slices in either palm oil liquid fraction or peanut oil increased linearly with time. In the present study, however, the free fatty acid level (Y) increased with frying time (X) in a quadratic fashion.

The increased production of free fatty acids associated with the frying of fish could probably be caused by "leaching out" of raw fat from the fish and of other soluble materials present in the breaching. The leaching of these materials into the frying oil tend to promote hydrolysis, thus contributing to the increased free fatty acid level (Roth and Rock, 1972b). The higher free fatty acid level observed in the used palm oil might have been due to the higher initial free fatty acid level of the palm oil compared to that of soybean oil. A higher initial level of free fatty acids catalyzes the formation of additional acids (Baeuerlen et al., 1968; Fritsch, 1981).

Mean values for polar materials were not significantly different between palm oil olein and soybean oil used for frying for 5 days or affected significantly by the product fried in those oils (Tables 4 and 5, pages 40 and 42, respectively). However, the amount of polar materials in the oil was significantly affected by frying time in a quadratic pattern (Tables 4 and 11).

The oil might be considered as deteriorated by the third day of frying since the amount of polar materials present in the oil at

TABLE 11

MEAN VALUES FOR CHARACTERISTICS OF FRYING OILS ACROSS
TREATMENTS FOR DAYS OF FRYING TIME

Characteristics	Day of Frying (X)		
	1	3	5
Polar Material, % ^a	16.79	30.67	36.36
Smoke Point, °C ^b	227	212	200

^aSignificantly affected by days of frying (X) where $Y = 6.77 + 11.04 X - 1.03 X^2$.

^bSignificantly affected by days frying time (X) where $Y = 237 - 10.09 X + 0.55 X^2$.

this point exceeded the 27 percent cut-off level recommended as the rejection point of a frying fat (Billek et al., 1978).

In the study of Fritsch et al. (1979), soybean oil required 32 hours of cooking two 100-g batches of potatoes per hour in 2500 g oil at 190 C, 8 hours a day, and turning the heat off at night followed by an additional 8 hour heating period (IV = 122) to reach a total polar material concentration of 27 percent. In a hydrogenated vegetable shortening (IV = 70), following the same treatment, however, the total polar materials was only 8.5 percent. Differences in the frying oil, food product and frying conditions could account for the more rapid deterioration of the frying oils in the present study compared to the results obtained by Fritsch et al. (1979) and Stevenson et al. (1984a).

A significant difference in the smoke point of the frying oils existed between palm oil olein and soybean oil (Table 6, page 45) and between frying fish and potato (Table 7, page 46). The used palm oil smoked at a lower temperature than did the used soybean oil (206 versus 220 C, Table 6). On the average, the frying of fish resulted in a lower smoke point (211 C) than did the frying of potatoes (215 C, Table 7). The smoke point of the frying oils increased curvilinearly with increasing frying time (Table 11).

The smoke point of frying oil is inversely related to the amount of free fatty acids present (McGill, 1980; Roth and Rock, 1972b). The increasing concentration of free fatty acids with increased frying time (Table 10) corresponds with the decreasing

trend in the smoke point of the frying oil with increasing frying time (Table 11). The higher concentration of free fatty acids in used palm oil olein compared with that in used soybean oil most likely is the cause of used palm oil olein having a lower smoke point than that of the used soybean oil. The fact that the frying of fish also caused a greater increase in free fatty acid content compared with frying potatoes could also be the reason that frying fish resulted in a lower smoke point than did frying potatoes.

The results obtained for smoke point decreasing with increasing frying time in the present study agreed with the findings of Bracco et al. (1981) who found that for peanut oil and palm oil liquid fraction, the smoke point decreased with hours of frying potato slices at 180 C. Stevenson et al. (1984a), who analyzed the effects of extended deep-fat frying of french fries in canola and soybeans fats, also demonstrated negative correlations between smoke point and frying time.

The fatty acid composition of fresh palm oil olein and fresh soybean oil is presented in Appendix Table A-7. Comparisons of the fatty acid composition of used palm oil olein and used soybean oil (Table 12) with their corresponding fresh oils indicate possibly greater percentages of all saturated fatty acids except 20:0 for both of the used oils. The used oils also contained larger concentrations of the longer chain fatty acids (20:1 ω 9, 20:4 ω 6, 22:1 or 23:0 and 24:0) and the unknown acids. Used palm oil olein had

TABLE 12
FATTY ACID COMPOSITION OF USED FRYING OILS
ACROSS DAYS OF FRYING

Fatty Acid	Palm Oil	Soybean Oil
	-----%	-----
12:0 ^a	0.556 ^b	0.068 ^c
14:0	1.134 ^b	0.128 ^c
15:0 ^a	0.650 ^b	0.014 ^c
16:0	40.882 ^b	12.549 ^c
16:1	0.164 ^b	0.073 ^c
18:0	5.312 ^b	4.859 ^c
18:1 ω 9	41.497 ^b	55.970 ^c
18:1 ω 5 ^a	0.013 ^b	6.243 ^c
18:1 isomer ^{ad}	0.035 ^b	1.027 ^c
18:1 isomer ^{ad}	0.081 ^b	2.712 ^c
18:2 isomer ^{ad}	0.180 ^b	1.455 ^c
18:2 ω 6	7.837 ^b	11.452 ^c
18:2 isomer ^{ad}	0.000 ^b	0.679 ^c
18:2 isomer ^{ad}	0.013 ^b	0.085 ^c
20:0 ^a	0.274	0.290
18:3 ω 3	0.356	0.392
20:1 ω 9 ^a	0.162 ^b	0.381 ^c
18:2 ω 7 (diene) ^{ae}	0.086	0.161
20:4 ω 6 ^a	0.381	0.325
22:1 or 23:0 ^a	0.044 ^b	0.316 ^c
24:0	0.010	0.014
Unknown acids	0.755	0.691

^aTentatively identified.

^{bc}Means in a row followed by different superscript letters are significantly different ($P < 0.05$).

^dPositional isomers.

^eDouble bonds are conjugated.

slightly higher percentages of 18:1 ω 5 and 18:2 ω 7 (diene) than fresh palm oil olein, while used soybean oil appeared to have greater levels of 18:1 ω 9 and 18:3 ω 3 acids and lower levels of 18:1 ω 5 and 18:2 isomers than fresh soybean oil. Lower concentrations of 18:1 ω 9, 18:2 ω 6, 18:1 isomers and 18:2 isomers were generally observed in both used oils compared with the fresh oils (Table 12).

The used palm oil olein contained significantly higher concentrations of 12:0 (lauric acid), 14:0 (myristic acid), 16:0 (palmitic acid), 16:1 (palmitoleic acid) and 18:0 (stearic acid) than did the used soybean oil. On the other hand, the used soybean oil contained significantly higher concentrations of oleic acid (18:1 ω 9) and its isomers and linoleic acid (18:2 ω 6) and its isomers (Table 12).

The analysis of variance for percentage fatty acids affected by product or days of frying is given in Appendix Table A-8. Linoleic (18:2 ω 6), linolenic (18:3 ω 3) and arachidic (20:0) acids were all affected significantly by the product fried. The frying of fish resulted in higher concentrations of all three fatty acids in the frying oils than did the frying of potatoes (Table 13). However, a significant oil by product interaction was found for 18:3 ω 3 and 20:0. The frying of fish in palm oil olein resulted in a lower percentage of 18:3 ω 3 than did frying potatoes (Table 14). The reverse of this was found in used soybean oil; the frying of fish resulted in a higher percentage of 18:3 ω 3 than did the frying of potatoes. Arachidic acid (20:0) percentage was higher in palm

TABLE 13

MEAN PERCENTAGES OF FATTY ACIDS IN FRYING OILS AFFECTED
SIGNIFICANTLY BY PRODUCT FRIED

Fatty Acid	Product Fried	
	Potato	Fish
18:2 ω 6	8.818 ^a	10.527 ^b
18:3 ω 3	0.350 ^a	0.399 ^b
20:0	0.235 ^a	0.330 ^b

^{ab}Means in a row bearing unlike superscripts are significantly different ($p < 0.05$).

TABLE 14
 MEAN VALUES FOR PERCENTAGE FATTY ACIDS AFFECTED
 SIGNIFICANTLY BY OIL x PRODUCT INTERACTION

Fatty Acid ^a	Palm Oil		Soybean Oil	
	Potatoes	Fish	Potatoes	Fish
18:3 ω 3	0.372	0.340	0.328	0.456
20:0	0.172	0.381	0.299	0.282

^aA significant interaction (oil x product) among treatments was found for these acids.

oil olein when fish was fried in it than when potatoes were fried. In soybean oil, however, the frying of fish compared to the frying of potato resulted in a lower percentage of 20:0 acid. These observations explain the significant interaction.

Changes in fatty acid composition of frying fats are due to degradation of the fatty acids during frying and to food fats leaching into the frying fat during frying. Aust and Thompson (1981) compared the fatty acid composition of a partially hydrogenated soybean oil with the fatty acid composition of french fries before and after frying in the oil and found that the fatty acid composition of the finished fried potatoes resembled that of the oil in which they were fried more than the composition of the partially fried potatoes. The authors suggested that an exchange of lipid between the precooked potatoes and the frying oil along with a net uptake of oil resulted in this closer resemblance to the frying oil. Robertson (1967) suggested that an exchange of lipid occurs during frying when the voids created in the outer zone of the fried foods caused by moisture release and lipid loss are filled up by the frying fat.

The higher concentration of the polyenoic acids, 18:2 ω 6 and 18:3 ω 3, in the frying oils due to the frying of fish probably resulted from "leaching out" of fish lipids into the frying oil. According to DeMan (1980), the lipid composition of cod fish consists predominantly of polyenoic acids. The significance of the potatoes in affecting the concentrations of these acids might have been due

also to the leaching out of the soybean oil that was used for partial frying of the precooked fries. The increase in the linolenic acid concentration of the used oils compared with the 0-day oils also suggests that frying caused the diffusion of linolenic acid in the fish lipid and in the partially fried potatoes.

The mean percentages of the fatty acids of the frying fats significantly affected by frying time are given in Table 15, and the equations showing those significant effects are given in Table 16. In Table 15, the mean concentrations of 18:0, 18:1 isomer, 18:2 isomer and 20:4 ω 6 showed an increasing trend as frying time progressed, while those of 18:2 ω 6, 18:3 ω 3, 20:1 ω 9, 18:2 ω 7 (diene) and 24:0 decreased ($P < 0.05$). The oxidation of the polyunsaturated fatty acids into shorter chained acids might account for the decrease in the concentration of the polyunsaturates and the resulting increase in 18:0 and 18:1 isomer. Isomerization of 18:2 ω 6 and other polyunsaturated fatty acids might also explain the increase in the isomers. The increasing trend of 20:4 ω 6 concentration, might be explained by the leaching of the codfish fat into the frying oil during frying.

The analysis of variance for the effects of fryer, treatment and days of frying on percentage moisture and percentage fat (wet basis) of fried products are presented in Table 17. There were significant differences in the moisture and fat contents of the fried products among the four treatments. Orthogonal comparisons of the treatment effects showed that both moisture and fat contents

TABLE 15
MEAN PERCENTAGES OF FATTY ACIDS OF FRYING OILS
AFFECTED BY DAYS OF FRYING FISH AND POTATO

Acid	Days of Frying		
	1	3	5
18:0 ^a	4.822	5.158	5.275
18:1 isomer ^{ab}	0.341	0.567	0.706
18:2 isomer ^{ab}	0.666	0.849	0.962
18:2 ω 6 ^a	10.509	9.415	9.047
18:3 ω 3 ^a	0.438	0.376	0.308
20:1 ω 9 ^{ab}	0.367	0.246	0.202
18:2 ω 7 (diene) ^{ab}	0.160	0.121	0.091
20:4 ω 6 ^{ab}	0.181	0.473	0.407
24:0 ^{ab}	0.030	0.007	0.000

^aThe concentrations of these acids were significantly affected by days of frying.

^bTentatively identified.

TABLE 16

EQUATIONS FOR THE EFFECT OF DAYS OF FRYING FISH AND POTATO ON
FATTY ACID CONCENTRATIONS OF FRYING OILS

Acid	R ²	Equation
18:0	0.26	$Y = 4.774 + 0.1136 X$
18:1 isomer	0.16	$Y = 0.264 + 0.0915 X$
18:2 isomer	0.11	$Y = 0.603 + 0.0743 X$
18:2 ω 6	0.22	$Y = 10.755 - 0.3664 X$
18:3 ω 3	0.10	$Y = 0.471 - 0.0324 X$
20:1 ω 9	0.20	$Y = 0.395 - 0.0413 X$
18:2 ω 7 (diene)	0.14	$Y = 0.176 - 0.0171 X$
20:4 ω 6	0.38	$Y = -0.0997 + 0.325 X - 0.0447 X^2$
24:0	0.17	$Y = 0.034 - 0.0074 X$

^aY = percentage fatty acid and X = days of frying.

TABLE 17

ANALYSIS OF VARIANCE OF THE EFFECTS OF FRYER, TREATMENT
AND DAYS OF FRYING ON THE MOISTURE AND FAT CONTENTS
OF FRIED FISH AND POTATO

Source	DF	Variables	
		Moisture	Fat
Fryer (F)	3	210.0	42.6
Replication (R)	3	539.5	184.5
Treatment (T)	3	1419.4 ^a	637.1 ^a
Oil (O)	1	0.1	0.3
Product (P)	1	1371.5 ^a	599.6 ^a
O X P	1	47.8	47.2
Error A [R(FxT)]	6	522.8	96.5
Day (D)	2	22.8	19.9
D X R	6	184.6	122.4
D X F	6	207.2	136.3
D X T	6	107.3	103.4
Error B [R(DxFxT)]	12	420.1	175.7
Total	47		

^aSignificant at the $P < 0.05$ level.

were significantly different between the fried potatoes and fried fish. Fried fish had a higher moisture content than fried potatoes. The fried potatoes, however, had a higher percentage of fat than the fried fish (Table 18).

As shown in Table 19, the potatoes before frying contained significantly higher moisture content than the uncooked fish. After frying, however, the fried potatoes contained significantly lower moisture content than the fried fish. The fish contained a significantly higher fat content than the potatoes before frying. After frying, the potatoes contained significantly higher fat content than the fish. The results indicate that the greater loss of moisture from the potatoes during frying resulted in a greater absorption of oil in the voids created by moisture loss. Since the moisture lost from fish during frying was significantly lower, only a limited amount of fat could be absorbed by the fried fish.

Simple correlation coefficients among all measurements of frying oils are given for palm oil olein and soybean oil in Tables 20 and 21, respectively. Significant correlation coefficients were found among most measurements. Correlation between total polar materials and other analyses of the individual frying oils showed that free fatty acids had the highest correlation ($r = 0.86$) followed by dielectric constant ($r = 0.83$) and smoke point ($r = -0.76$) for palm oil olein, while the dielectric constant showed the highest correlation ($r = 0.96$), followed by free fatty acids ($r = 0.93$) and foam height ($r = 0.92$) for soybean oil. The correlations between total polar materials and the other analyses were much higher

TABLE 18
MEAN VALUES FOR PERCENTAGE MOISTURE AND FAT IN FRIED
FISH AND POTATO FOR EACH TREATMENT

Variable	Treatment ^a			
	1	2	3	4
Moisture, %	47.88	56.86	49.36	55.50
Fat, %	14.90	8.54	13.61	10.05

^a1 = potatoes fried in palm oil olen;
 2 = fish fried in palm oil olein;
 3 = potatoes fried in soybean oil;
 4 - fish fried in soybean oil.

TABLE 19
MEANS FOR PERCENTAGE MOISTURE AND PERCENTAGE FAT IN
PRODUCTS BEFORE AND AFTER FRYING

Variable	Before Frying		After Frying	
	Potato	Fish	Potato	Fish
Moisture, %	73.72 ^a	61.29 ^b	48.62 ^c	56.18 ^d
Fat, % Wet Basis	3.32 ^a	5.24 ^b	14.25 ^c	9.30 ^d

^{ab}For before frying means in a row bearing unlike superscripts are significantly different ($P < 0.05$).

^{cd}For after frying, means in a row bearing unlike superscripts are significantly different ($P < 0.05$).

TABLE 20
CORRELATION COEFFICIENTS^a AMONG MEASUREMENTS FOR
PALM OIL USED FOR FRYING (N=24)

	Polar	DC	Foam	Diene	FFA	Smoke
Polar	1.00					
DC	0.83	1.00				
Foam	0.69	0.89	1.00			
Diene	0.40	0.67	0.61	1.00		
FFA	0.86	0.97	0.83	0.63	1.00	
Smoke	-0.76	-0.77	-0.64	-0.49	-0.84	1.00

^a $r = \pm 0.40$; $P < 0.05$.

TABLE 21
CORRELATION COEFFICIENTS^a AMONG MEASUREMENTS FOR
SOYBEAN OIL USED FOR FRYING (N=24)

	Polar	DC	Foam	Diene	FFA	Smoke
Polar	1.00					
DC	0.96	1.00				
Foam	0.92	0.94	1.00			
Diene	0.68	0.66	0.68	1.00		
FFA	0.93	0.95	0.95	0.70	1.00	
Smoke	-0.80	-0.76	-0.71	-0.43	-0.82	1.00

^a $r = \pm 0.40$; $P < 0.05$.

for soybean oil than for palm oil olein (Tables 20 and 21). In Table 22, the correlation between total polar materials and other analyses of the combined data of the two oils showed that dielectric constant yielded the best correlation ($r = 0.90$), followed by foam height ($r = 0.80$), and free fatty acid ($r = 0.74$). Fritsch et al. (1979) reported correlations between dielectric constant and free fatty acids ($r = 0.569$) for the combined data of three different shortenings. The results of our study, however, showed a higher correlation ($r = 0.82$) between dielectric constant and free fatty acids across frying oils. The high correlations between the quick tests (dielectric constant and foam height) and total polar materials suggest that these tests can be used as rapid and reliable methods for measuring frying oil deterioration.

TABLE 22
SIMPLE CORRELATION COEFFICIENTS^a AMONG MEASUREMENTS
OF FRYING OIL ACROSS OIL SOURCES (N=48)

	Polar	DC	Foam	Diene	FFA	Smoke
Polar	1.00					
DC	0.90	1.00				
Foam	0.80	0.89	1.00			
Diene	0.33	0.40	0.46	1.00		
FFA	0.74	0.82	0.59	-0.06	1.00	
Smoke	-0.66	-0.66	-0.46	0.15	-0.58	1.00

^a $r = \pm 0.29$; $P < 0.05$.

CHAPTER V

SUMMARY

The deterioration of partially hydrogenated soybean oil (PHSO) and palm oil olein (POO) during the frying of fish and potatoes was compared. The rapid analytical tests: measurements of dielectric constant and foam height; changes in the fatty acid composition and levels of free fatty acids, dienoic acids and total polar material were used to measure the deterioration of the two frying oils past the point where the frying oils should be discarded. Correlations among these measurements were also obtained. This study consisted of four treatments: frying potatoes in POO (Treatment 1), frying fish in POO (Treatment 2), frying potatoes in PHSO (Treatment 3), and frying fish in PHSO (Treatment 4).

The statistical design of this experiment was a 4 x 4 Latin Square with a split in each square. The 4 x 4 design was represented by four replications and four fryers. The split was sampling time from each fryer. The products were fried every 2 hours in each oil beginning 1 hour after the frying oils were heated to 180 C and continuing up to 7 hours. The frying oils were heated at 180 C for an additional hour after the last batch of food was fried. Frying was continued for 5 consecutive days. Fresh oil was added to the frying oils to replace the fat lost during sampling, filtering and uptake by the fried foods at the end of the first, third and fifth days of frying time. Dielectric constant and foam height were

measured on the frying oils at the end of each day of frying. Levels of free fatty acids, total polar material and dienoic acids, the fatty acid composition, and the smoke point of the frying oils were determined after 1, 3 and 5 days of frying time. These measurements were also made on the fresh frying oil sampled at three times during the experiment. Fat and moisture contents of the last samples of the products fried each day were also determined at 1, 3 and 5 days of frying. Dependent variables were analyzed as a function of fryer, replication, treatment, days of frying time and appropriate interactions.

Across the 5 days of frying, PHSO had a greater foam height and a higher smoke point and level of dienoic acids than P00. P00, however, had a higher concentration of free fatty acids and a lower smoke point than PHSO. No significant differences were found between the frying oils for the concentration of total polar material or the dielectric constant.

Frying fish had a greater effect on the deterioration of frying oils than did frying potatoes. Frying fish compared with frying potatoes resulted in the oils having a higher dielectric constant, a lower smoke point, a greater foam height and increased levels of dienoic acids and free fatty acids. The type of product fried did not significantly affect the level of polar material in the frying oils.

In general, the dielectric constant and foam height increased from the first through the third day of frying and decreased

slightly on the fourth day of frying before increasing again on the fifth day of frying. The most likely reason for the decrease observed on the fourth day of frying was the dilution of the frying oils with new oil.

The levels of the other chemical components of the frying oils: dienoic acids, free fatty acids and total polar material, increased at a decreasing rate with increasing days of frying. The smoke point, however, decreased at a decreasing rate across days of frying time. The level of total polar material increased from 16.79 percent at the end of the first day of frying time to 30.7 percent by the third day of frying in both frying oils, and this concentration is greater than the 27 percent level that indicates a deteriorated frying fat should be discarded.

Fatty acid composition differed significantly among the frying oils, was affected significantly by the type of product fried, and changed across days of frying time. Used P00 contained significantly higher concentrations of saturated fatty acids (12:0, 14:0, 16:0 and 18:0) and 16:1 and lower concentrations of the unsaturated fatty acids (18:1 ω 9, 18:1 isomers, 18:2 ω 6 and 18:2 isomers) than the used PHS0. The frying of fish resulted in significantly higher concentrations of 18:2 ω 6, 18:3 ω 3 and 20:0 in the frying oils than the frying of potatoes. However, a significant frying oil x product interaction was found for 18:3 ω 3 and 20:0. The frying of fish in P00 resulted in a lower percentage of 18:3 ω 3 and a higher percentage of 20:0 than did the frying of potatoes; in the

PHS0, the reverse of this was true. The average percentage of 18:0, one of the 18:1 isomers, an 18:2 isomer, and 20:2 ω 6 in the frying oils increased significantly across frying time, while the average percentage of 18:2 ω 6, 18:3 ω 3, 20:1 ω 9, 18:2 ω 7 (diene) and 24:0 decreased.

Significant differences between fish and potatoes were found in their fat and moisture levels. Fried fish had a higher level of moisture and a lower level of fat than the fried potatoes. Frying of either product resulted in a decrease in the moisture content and an increase in the fat content.

Simple correlation coefficients among the measurements of frying oil deterioration were obtained. Some of the highest significant correlation coefficients were found between the level of total polar material and other measurements. For P00, the highest correlation coefficients were found with level of free fatty acids ($r = 0.86$) followed by the dielectric constant ($r = 0.83$) and smoke point ($r = -0.76$). For PHS0, the highest correlation coefficients were found with the dielectric constant ($r = 0.96$), followed by free fatty acid content ($r = 0.93$) and foam height ($r = 0.92$). Across both frying oils, the highest correlation coefficients between total polar content and other measurements were with the dielectric constant ($r = 0.90$) followed by foam height ($r = 0.80$) and free fatty acid ($r = 0.74$).

To summarize, measurements of deterioration showed that the frying oils differed in how they reacted during heating and frying.

P00 developed higher levels of free fatty acids and a lower smoke point during frying than did the PHSO but the PHSO had a higher foam height and a higher dienoic acid content. In most commercial frying operations, the fat that has the highest free fatty acid content would be considered the most deteriorated. Changes in fatty acid composition of the frying oils across frying time, the increase in saturated fatty acid content and decreases in polyunsaturated fatty acid levels, agreed with results of previously reported experiments.

However, all of the measurements of frying oil deterioration except the total polar material concentration were affected by the type of product fried and by type of frying oil used. Therefore, concentration of total polar material is a good measurement to determine the point at which a used frying oil should be discarded. However, it is not possible to have a single value of any of the other measurements, including the "fast" tests that would indicate when a deteriorated oil should be discarded for all situations.

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LITERATURE CITED

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APPENDIX

EQUATIONS FOR CALCULATING PERCENTAGE VALUES OF
DIENOIC ACID AND FREE FATTY ACIDS (AS PERCENT
OLEIC) IN FRYING OILS

1. Percent Conjugated Dienoic Acid = $0.84 \left(\frac{A_s}{bc} - k_o \right)$

where

k_o = absorptivity by acids = 0.03

A_s = observed absorbancy at 233 m μ

b = cell length in centimeters

c = concentration of sample in grams per liter of final
dilution used for the absorption measurement.

2. Percent Oleic Acids = $\frac{\text{ml of Alkali} \times \text{Normality} \times 28.2}{\text{Weight of Sample}}$

TABLE A-1
MEANS FOR THE CHARACTERISTICS OF FRESH PALM OIL
OLEIN AND SOYBEAN OIL

Characteristic	Palm Oil Olein	Soybean Oil
Dienoic acids, %	0.17	0.99
Polar material, %	7.07	3.86
Free fatty acids, %	0.03	0.01
Smoke point, °C	234.0	245.0

TABLE A-2

PARTITIONING OF THE DIELECTRIC CONSTANT SUM OF SQUARES FOR
DAYS OF FRYING AND EACH TREATMENT

Source	DF	Sum of Squares
<u>TREATMENT 1</u>		
Day	1	29.2094 ^a
Day x Day	1	0.2006
Day x Day x Day	1	0.6882 ^a
Day x Day x Day x Day	1	2.2861 ^a
<u>TREATMENT 2</u>		
Day	1	52.4880 ^a
Day x Day	1	0.1157
Day x Day x Day	1	1.1640 ^a
Day x Day x Day x Day	1	2.2695 ^a
<u>TREATMENT 3</u>		
Day	1	29.2215 ^a
Day x Day	1	0.7973 ^a
Day x Day x Day	1	1.3261 ^a
Day x Day x Day x Day	1	1.1340 ^a
<u>TREATMENT 4</u>		
Day	1	52.9751 ^a
Day x Day	1	0.4758
Day x Day x Day	1	0.9680 ^a
Day x Day x Day x Day	1	1.2826 ^a

^aSignificant at the $P < 0.05$ level.

TABLE A-3
PARTITIONING OF THE FOAM HEIGHT SUM OF SQUARES FOR DAYS
OF FRYING FOR EACH TREATMENT

Source	DF	Sum of Squares
<u>TREATMENT 1</u>		
Day	1	12.9605 ^a
Day x Day	1	0.8229
Day x Day x Day	1	1.0351
Day x Day x Day x Day	1	1.3900
<u>TREATMENT 2</u>		
Day	1	150.4261 ^a
Day x Day	1	5.4472 ^a
Day x Day x Day	1	1.2751
Day x Day x Day x Day	1	9.1290 ^a
<u>TREATMENT 3</u>		
Day	1	88.2000
Day x Day	1	0.4889
Day x Day x Day	1	0.6125
Day x Day x Day x Day	1	10.5326 ^a
<u>TREATMENT 4</u>		
Day	1	285.0125 ^a
Day x Day	1	0.0003
Day x Day x Day	1	0.5281
Day x Day x Day x Day	1	17.1150 ^a

^aSignificant at the $P < 0.05$ level.

TABLE A-4

PARTITIONING OF THE SUM SQUARES FOR DAYS OF FRYING EFFECT
ACROSS TREATMENT FOR PERCENTAGE TOTAL POLAR MATERIALS
AND SMOKE POINT

Source	DF	Sum of Squares
<u>Total Polar Materials, %</u>		
Day	1	6123.6494 ^a
Day x Day	1	359.4064
<u>Smoke Point</u>		
Day	1	5940.5000 ^a
Day x Day	1	51.0417 ^a

^aSignificant at the $P < 0.05$ level.

TABLE A-5

PARTITIONING OF THE PERCENTAGE OF DIENOIC ACIDS SUM OF
SQUARES FOR DAYS OF FRYING FOR EACH TREATMENT

Source	DF	Sum of Squares
<u>TREATMENT 1</u>		
Day	1	0.0961 ^a
Day x Day	1	0.0310 ^a
<u>TREATMENT 2</u>		
Day	1	0.2809 ^a
Day x Day	1	0.2107 ^a
<u>TREATMENT 3</u>		
Day	1	0.0361 ^a
Day x Day	1	0.0705 ^a
<u>TREATMENT 4</u>		
Day	1	0.3053 ^a
Day x Day	1	0.0945 ^a

^aSignificant at the $P < 0.05$ level.

TABLE A-6

PARTITIONING OF THE PERCENTAGE OF FREE FATTY ACIDS SUM OF
SQUARES FOR DAYS OF FRYING FOR EACH TREATMENT

Source	DF	Sum of Squares
<u>TREATMENT 1</u>		
Day	1	0.7098 ^a
Day x Day	1	0.0248 ^a
<u>TREATMENT 2</u>		
Day	1	1.0151 ^a
Day x Day	1	0.0305 ^a
<u>TREATMENT 3</u>		
Day	1	0.2025 ^a
Day x Day	1	0.0114 ^a
<u>TREATMENT 4</u>		
Day	1	0.4796 ^a
Day x Day	1	0.0111 ^a

^aSignificant at the $P < 0.05$ level.

TABLE A-7
MEAN PERCENTAGE OF FATTY ACIDS IN 0-DAY FRYING OILS

Acid	Palm Oil	Soybean Oil
	-----%-----	
12:0	0.436	0.042
14:0	1.009	0.080
15:0	0.030	0.000
16:0	38.787	11.935
16:1	0.147	0.050
18:0	4.800	4.243
18:1 ω 9	43.807	52.121
18:1 ω 5 ^a	0.000	9.711
18:1 isomer a ^{ab}	0.096	1.271
18:1 isomer b ^{ab}	0.123	2.921
18:2 isomer a ^{ab}	0.371	2.272
18:2 ω 6 ^a	9.432	12.591
18:2 isomer b ^a	0.000	0.596
18:2 isomer c ^{ab}	0.0583	0.132
20:0 ^a	0.456	0.414
18:3 ω 3 ^a	0.173	0.292
20:1 ^a	9.151	0.338
18:2 ω 7 (diene) ^{ac}	0.000	0.312
20:4 ω 6 ^a	0.000	0.000
24:0	0.000	0.000
Unknown acids		

^aTentatively identified.

^bPositional isomers.

^cDouble bonds are conjugated.

TABLE A-8
ANALYSIS OF VARIANCE FOR PERCENTAGE FATTY ACIDS IN USED FRYING OILS
AFFECTED SIGNIFICANTLY BY PRODUCT OR DAYS OF FRYING

Source	DF	Sum of Squares								
		18:0	18:1 Isomer	18:2 Isomer	18:2ω6	18:2ω7 (diene)	18:3ω3	20:0	20:1ω9	20:2ω6
Fryer (F)	3	0.7026	1.2282	3.4691	14.1276	0.0583	0.0975	0.0316	0.1359	0.2095
Replication (R)	3	3.3074	2.5314	2.2469	10.4021	0.0089	1.6127	0.9904	0.4935	2.2339
Treatment (T)	3	7.3603 ^a	21.5559 ^a	36.3938 ^a	521.8904 ^a	0.1194	0.3278 ^a	0.4593	1.0814	0.2706
oil (O)	1	6.5339 ^a	21.5088 ^a	35.4067 ^a	428.9982		0.0366	0.0052		
Product (P)	1	0.8167	0.0164	0.0451	90.2267 ^a		0.0754 ^a	0.1942 ^a		
O X P	1	0.0006	0.0635	0.9253	1.2876		0.2101 ^a	0.2848 ^a		
Error A [(R(FxT))]	6	1.0248	1.2957	1.7714	6.7982	0.3139	0.0667	0.0501	0.6427	0.4515
Day (D)	2	4.6279 ^a	1.8209 ^a	1.1916 ^a	52.0901 ^a	0.0637 ^a	0.3793 ^a	0.1561	0.4310 ^a	1.3579 ^a
D X F	6	0.1485	3.4452	4.6476	11.4646	0.1025	0.1457	0.2081	0.5021	1.2352
D X R	6	2.008	1.9956	2.9696	39.4539	0.0290	1.1788	0.0964	0.2245	0.1611
D X T	6	2.0702	2.4082	1.6569	12.9603	0.2461	0.2024	0.2819	0.5338	0.5302
Error B [(R(DxFT))]	12	2.8968	3.2039	2.1650	40.6319	0.0863	0.7653	0.5612	0.4062	0.6723
Total	47									

^aSignificant at P<0.05 level.

VITA

The author was born July 11, 1961, in the state of Selangor, West Malaysia. She attended primary school at her hometown in Rawang, Selangor. She completed her secondary education in the same city. In January of 1980, she came to the United States and was enrolled in the University of Wisconsin, Green Bay, where she completed her freshman year. The following year, she attended The University of Tennessee, Knoxville. In December 1983 she received her Bachelor of Science degree, majoring in Food Technology and Science. She enrolled in the graduate program in Food Technology and Science the following year. She received a Master of Science degree, majoring in Food Technology and Science, in August 1986. She is a member of the American Oil Chemists Society and the Institute of Food Technologists Society.