To the Graduate Council:

I am submitting herewith a dissertation written by Sabina Mbuso Silaula entitled "Stability of High Oleic Acid Sunflower Oil, Regular Sunflower Oils and a Sunflower-Corn Oil Blend During Frying of a Plain Yeast-Raised Doughnut as a Simulated Model For Swaziland Small Food Vendors and Sensory Evaluation of the Doughnuts". I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the Doctor of Philosophy degree, with a major in Food Science and Technology.

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STABILITY OF HIGH OLEIC ACID SUNFLOWER OIL, REGULAR SUNFLOWER OILS AND A SUNFLOWER-CORN OIL BLEND DURING FRYING OF A PLAIN YEAST-RAISED DOUGHNUT AS A SIMULATED MODEL FOR SWAZILAND SMALL FOOD VENDORS AND SENSORY EVALUATION OF THE DOUGHNUTS

A DISSERTATION

PRESENTED FOR THE

DOCTOR OF PHILOSOPHY DEGREE

THE UNIVERSITY OF TENNESSEE, KNOXVILLE

SABINA MBUSO SILAULA

MAY 1997

AG-VET-MED.
Thesis
97b
.S54

ACKNOWLEDGMENTS

I am thankful to Divine Providence for affording me this opportunity, and for guiding me throughout my program at UTK. I would like to express my heartfelt gratitude to the following people who contributed in various invaluable ways in the pursuit of my studies at UTK and, in the accomplishment of this piece of work:

The W.K. Kellogg Foundation for their generous financial support.

Dr. Sharon L. Melton my major professor, whose council and encouragement was invaluable and helped keep me focused on the objectives of the study. I will forever cherish the professional growth experiences and opportunities you unselfishly afforded me. You did it with great humility! Thank you.

Dr. Marjorie P. Penfield, a member of my committee who helped me greatly in the logistics of the sensory evaluation study.

Dr. Carol Costello, for serving and being a supportive committee member.

Dr. Jim Bailey, for serving and being a supportive committee member and, for the BOOK gift. I will put it to good use!

Dr. John R. Mount, for serving in my committee and being supportive.

Dr. Arnold Saxton, for his assistance with statistics.

All faculty in the Food Science and Technology department, UTK.

The panelists who participated in my sensory evaluation study.

Mr. Rolf Von Ascheredon, Dr. Laurens Du Plessis, Dr. Lipalesa Motjope for being instrumental in securing the research materials from South Africa. Fellow graduate students, support staff and friends around Knoxville. My family, particularly my Mother for being always there for me, and teaching me the value of hard work. And my supportive and loving children (Seni, Nsizwa and Nsika) who gave me the reason and strength to persevere.

ABSTRACT

The stabilities of 4 oils, high oleic sunflower (HOS) and regular sunflower (RCO) oils from the USA and a regular sunflower-corn oil blend (SOS) and regular sunflower (SVS) oil, processed in the Republic of South Africa (RSA) and used in Swaziland, were evaluated during frying. For each oil, 24 batches of 2 plain, yeast-raised doughnuts/batch were fried for 4 hr/day for 5 days. Samples taken from each oil during TIME (fresh, break-in heated and on each of the 5 days) were evaluated by measuring levels of α- and γ-tocopherols, total polar components (TPC), Food Oil Sensor reading (FOS), free fatty acids (FFA), conjugated dienes (DIENES), C18:2/C16:0 ratio, and Hunter color values, *L*, *a*, *b* and ΔE. Crust flavor and color likability, crust color intensity, mouthfeel (greasiness) and overall acceptability of doughnuts fried on days 2 and 4 in each oil were evaluated by a 48-member consumer panel.

When fresh, USA oils contained lower levels of tocopherols and were less yellow than RSA oils; HOS contained the lowest amount of tocopherols of all oils. Levels of each tocopherol decreased while levels of TPC, DIENES, C18:2/C16:0 ratio, *b* and ΔE increased over TIME ($p<0.05$), but the change in any one component differed among the oils. Levels of FFA and *a* increased and *L* decreased ($p<0.05$) across TIME similarly for each oil. Levels of TPC (19.5-20.9%), FOS (1.75-2.13) and FFA (0.058-0.067% oleic acid) on day 5 were the same in all oils and were below recommended levels for oil discard. Although HOS had lowest levels of tocopherols and had a greater ΔE than RCO or SVS, it was comparable in stability with the other oils. None of the sensory scores were affected ($p<0.05$) by type of oil or time. Mean (n=192) crust flavor and color scores were midpoint on 9-point hedonic scales. Overall acceptability was midpoint on an extremely unsacceptable to extremely

acceptable scale. Crust color and mouthfeel scores were midpoint on 9-point scales (light brown and dark brown and not at all greasy - extremely greasy). Results show that HOS is feasible as a frying oil for small food vendors in Swaziland.

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CHAPTER I

INTRODUCTION

Like many developing countries, Swaziland suffers chronic insufficient food supplies for communities mostly in the rural areas. Two factors which exacerbate this problem include high importation tariffs levied on imported processed basic foodstuffs and also financing subsidies to supplement local basic food requirements (Swaziland Government, 1991). Much of the rural population - an estimated 60% of approximately one million people (Swaziland Government, 1993) - depends on seasonal and/or fresh-grown foods which are often in short supply (Sunley, 1995). Commercially processed food items, when available, are usually too costly for people of low income to afford (Downing, 1993; FAO/FNA, 1994). This precipitates a situation where an undesirable vicious cycle of scarcity, unaffordability, insufficient intake of essential nutrients and chronic malnutrition and/or compromised well-being develops (Uauy Dagachy and Olivares, 1994).

Swaziland also has a high population growth rate of 3.2% per annum (UNICEF, 1994). Furthermore, there are no cottage/intermediate food-processing industries that could provide means to ensure that basic food requirements catering to local tastes are met. Additionally, the technology needed to process commonly used foodstuffs for long-term use is insufficient. Together, these factors threaten the health and well being of the Swazi people, particularly the nutritionally vulnerable.

In 1985, approximately one-third of the Swazi children of school age and under five years old were nutritionally stunted (low height for age) and wasted (low weight for height) (Swaziland National Nutrition Council, 1985). High-bulk, low-energy dense weaning and regular diets

and low feeding frequency were cited among the major contributing factors (Swaziland National Nutrition Council, 1985). Earlier, Moolayil (1982) reported that low per capita dietary oil/fat intakes among developing nations (10% of total calories) compared with global (20%) and, USA (36%) (Ganji and Betts, 1995) intakes maybe a possible contributing factor. Consumption of fat of at least 15% for adults and 30-40% for weaning infants has been recommended to ensure sufficient intakes of essential fatty acids (linoleic and arachidonic) and fat soluble vitamins (FAO/FNA, 1994).

Practically all of Swaziland's supply of dietary oil/fat comes from external donors or suppliers. About 2.2 million metric tons of vegetable oil were received during 1988-1990 from the World Food Program (WFP) for distribution among the nutritionally vulnerable. The oil was distributed to some schools for use in school lunch programs, and through Maternal and Child Health (MCH) programs, as an intervention measure for meeting the energy needs of weaning infants and those of pregnant and lactating women (World Food Program, 1992). However, the mainstream oil/fat used for cooking and frying is imported. In 1994, approximately $7,000,000 (U.S.) were spent on edible oil/fat imports mainly from South Africa (Swaziland Government, 1994). On the other hand, South Africa imported 75,000 metric tons of edible oil during 1991-1992, most of that was palm olein from Malaysia (DuPlessis, 1996). Palm olein is added mainly to regular sunflower-corn based frying oils to give thermo-stability and for margarine manufacture. Importation of palm olein was recently reviewed by the South African oilseed board, who concluded other alternatives to importation should be explored. The move was prompted by recent increases in the cost of palm olein concomitant with high importation tariffs (DuPlessis, 1996).

While the South African oil (normally exported for retail in Swazilands markets) may be well suited to high volume, extended frying

operations, the cost at which it is made available to small food vendors is not economically feasible for the type and volume of frying typically practised by small food vendors in Swaziland. Expensive imported, highly refined, and often inaccessible oil may make it difficult for rural populations to consume nutritionally adequate amounts. In addition, the processes for producing such an oil (high technology refining), as is practised in South Africa, may not cater to local tastes and preferences (Downing, 1993; Sunley, 1995). Refinement also strips such oil of needed nutrients (Downing, 1993), particularly carotenoids and tocopherols (FAO/FNA, 1994).

Locally produced and minimally processed oil from regular and/or high oleic sunflower varieties (*Helianthus annus*), alone or in combination with other oils, would conserve tocopherols which protect the oil from premature oxidation. Local oil production may be of sufficient quality to support the frying needs of Swazi families and Swazi small food vendors without compromising the quality of the fried product. Presently, such varieties are grown on a trial basis at Ngculwini, a rural community in Swaziland. Establishment of rural cottage/minimal oil refining industries in Swaziland to process these oil crops could result in an adequate supply of oil with better nutritional value, greater affordability and sustainability, and also generate a positive cash flow for rural areas (Downing, 1993; Otto, 1993).

In the case of South Africa's search for palm olein replacement, high oleic sunflower varieties may provide a solution. The high content of oleic acid (up to 87%) confers thermostability qualities comparable to those obtained with palm olein addition to polyunsaturated oil or partially hydrogenated oil (Fitch, 1994; Noakes et al., 1996). With current health concerns linking palm oil to increased low density lipoprotein (LDL) cholesterol levels and partial hydrogenation to the

trans-fatty acid dilemma, use of high oleic oils would be sound nutritional advice. In addition, the use of oils with a high percentage of cis-monounsaturates in the diet has been reported to lower plasma LDL concentration (Noakes et al., 1996).

Doughnuts (fat-cakes) are a popular fried snack food particularly among school children, construction workers and commercial farm workers in Swaziland. They are also a popular enterprise for small food vendors. Typically, these are prepared by small food vendors at home and sold for consumption the same day. Their high caloric and satiety value per unit serving make them a valuable snack considering energy needs of the population. Locally produced and processed high oleic sunflower oil may make available an inexpensive, high quality, stable frying and cooking oil (an otherwise scarce commodity) (Otto, 1993). Because of the envisaged affordability and accessibility of this oil, a high quality and less expensive doughnut might be produced.

Originally, a plan was devised to obtain minimallly processed sunflower oil from Ngculwini (a community in rural Swaziland that grows and processes regular sunflower oil using a motorized expeller press on a pilot project scale) for use as part of the research material. An alternative plan was to arrange for the growing of high oleic acid sunflower seed in Swaziland and have the seeds shipped to the USA for processing in a way that would closely resemble that being done in Swaziland. Either of these arrangements would have been ideal since the results of this study are, in large part, intended for application to Swaziland. However, both these arrangements met with problems for use in research, that is, wide variability in the oil and possible quality/safety concerns in the case of the former plan and government regulations/international trade of raw agricultural products laws with the latter plan.

The objectives of the study were as follows:

1. To determine the chemical and physical characteristics of high oleic sunflower oil (HOS) as a "test" and/or model oil that might be produced in Swaziland rural areas' cottage industries.

2. To assess the thermostability of high oleic sunflower oil, regular sunflower oil and two commonly available oils imported from South Africa (by Swaziland), using a yeast-raised doughnut as a fried food model system, and deep-fat frying conditions similar to those of a typical small food vendor in Swaziland.

3. To determine the sensory qualities namely; color intensity and mouthfeel (greasiness), color and crust flavor likability, and overall acceptability of yeast raised doughnuts fried in high oleic sunflower oil, regular sunflower oil, and two South African oils that are commercially available in Swaziland.

CHAPTER II

LITERATURE REVIEW

CHARACTERISTICS OF SUNFLOWER OILS

The technology and resources currently available to edible oil/fat processing industries have produced a high quality product in terms of thermostability, but have failed to produce commercial frying oils/fats with a good health image (FAO/FNA, 1994; Downing, 1993). Recently developed high oleic acid sunflower varieties (*Helianthus annuus L.*), show promise both in terms of oil/fat fry-life stability and without the undesirable health problems attributed to saturated fatty acids and trans fatty acids (Dobarganes et al., 1993; DuPlessis, 1995; Fitch, 1994; Noakes et al., 1996). The development of trans-isomers, caused by the partial hydrogenation of frying fats, has spurred concern and debate among health professionals, who regard them as agents that promote atherogenesis and coronary heart disease (AOCS, 1994; Dobarganes et al., 1993; Fitch, 1994; Noakes et al., 1996; Vessby, 1994). Of similar concern is the use of palm olein by oil processors in South Africa. Palm olein is used as an additive to impart fry-life stability to unsaturated oils. Palm olein contains large amounts of LDL-cholesterol-elevating lauric, myristic and palmitic fatty acids. Unhydrogenated polyunsaturated-rich or untreated vegetable oils, like regular sunflower or corn oils, are not stable under thermo-oxidative conditions (Dobarganes et al., 1993; Fitch, 1994) because of their high degree of unsaturation. They are, however, valuable in supplying the essential fatty acid, linoleic. In addition, when oxidized during frying, the

resulting flavor volatiles have been reported desirable to fried food (Fitch, 1994).

Several studies have shown that high oleic sunflower (HOS) or blends thereof, exhibit excellent stability under various conditions of thermal exposure and fried food systems (DuPlessis, 1995; Fitch, 1994; Noakes et al., 1996; Romeo et al., 1995). This desirable trait is attributed to its high proportion (up to 87%) of cis-monounsaturated oleic acid (Fitch, 1994). The high percentage of oleic acid in high oleic sunflower varieties confers properties that make its thermostability comparable to that of hydrogenated oils/fats (Fitch, 1994; Romeo et al., 1995) without the negative connotation now associated with hydrogenation. High oleic sunflower has been shown to exert a significant plasma LDL-lowering effect (Noakes et al., 1996; Vessby, 1994). The properties of high oleic sunflower oil are appealing to manufacturers and health professionals. Furthermore, once the "specialty commodity status" of HOS disappears and its production commercialized, the current premium price and cost of HOS will decrease (Fitch, 1994; Noakes et al., 1996). Notwithstanding its present and promised advantages, the ultimate success of high oleic sunflower oil may lie in optimizing blend formulations with linoleic providing oils to satisfy sensory preferences (Fitch, 1994).

Linoleic containing dietary oils/fats must be supplied by the diet in adequate amounts to satisfy linoleic acid requirements. Linoleic acid is an essential fatty acid required for normal growth and brain development, proper membrane function and as a precursor of eicosanoids. Eicosanoids have been associated with decreased cardiovascular aberrations and reduced platelet aggregation and formation (AOCS, 1994; Fitch, 1994; Vessby, 1994). Sunflower oil is also particularly high (up to 700 ppm) in tocopherols, with over 90% being in alpha tocopherol, the most biologically active form (Fitch,

1994; Yodice, 1990). The potentially high tocopherol content and increased saturation (compared with polyunsatutated oils) make high oleic sunflower oil a suitable option as a cooking oil for most developing countries who do not have the technology for commercial refining. It also might be an appropriate cooking and frying oil to segments of the population in those countries who are unable to afford highly refined and expensive imported oils (Downing, 1993).

Generally, sunflower oils are also good sources of fat soluble vitamins (A, D, E and K) and may be the major sources of these nutrients for most population groups in developing countries (Downing, 1993). Their high caloric density (9 Kcal/g) have made them invaluable in combating energy deficiency seen among the nutritionally marginalized and vulnerable, particularly during and post weaning periods (FAO/FNA, 1994). The fact that most developing nations consume lower dietary oil/fat intake, 10% of the dietary calories for adults (Moolayil, 1982) and less than 15% for children (FAO/FNA, 1994), which is much less than the recommended intake of 15 and 30%, respectively, is cause for concern. High oleic acid sunflower varieties also are hardy crops and well suited to the climatic conditions of southern Africa. In fact, temperate and tropical semi-arid conditions tend to favor an increase in oleic acid concentration (hence, greater yield of oleic acid per unit area) (Fitch, 1994; Patterson, 1989).

THE FRYING MECHANISM

Throughout the world, deep-frying is a popular method used in the production of snacks and fast foods (Perkins, 1992; Stier and

Blumenthal, 1990). Deep-frying, whether carried out on a large or small scale (Brooks, 1991) is a rather complex process involving not only considerations of oil composition and quality, but also the food being fried, the equipment used and the total management of the operation (Blumenthal, 1991; Blumenthal and Stier, 1991; Brooks, 1991; Melton et al., 1994; Pinthus and Saguy, 1994). Understanding the thermo-physico and chemical properties and dynamics of the frying process (oil/fat) and the changes that frying oil undergoes throughout the frying process (Blumenthal and Stier, 1994) can help one optimize the quality of the fried product, the process itself (Pinthus and Saguy, 1994; Stier and Blumenthal, 1993), and ultimately its profitability.

Several researchers, (Blumenthal, 1994; Melton et al., 1994; Romeo et al., 1995) have explained deep-frying as a boiling-distillation-dehydration and browning action, resulting from the intimate contact between the food surface and the hot oil. Upon contact with the surface of the food, heat is transferred conductively by the food's aqueous phase throughout the food matrix. Subsequently, the steam escaping from within the food produces a boiling action at the oil-food interface. The escaping steam strips and distills out the oil volatile decomposition products (VDP), which also are deposited en-route on the surface of the food. These (VDP) are, by and large responsible for the characteristic flavor notes typical of fried foods (Melton et al., 1994; White, 1991).

Starting with a high quality fresh oil, degradation begins when the oil is heated without the food and proceeds along a well defined pattern with periods described as break-in, fresh oil, optimum, breakdown and runaway oils (Blumenthal, 1991; Blumenthal and Stier, 1994; Melton, 1994). These stages correspond to definite quality parameters (Table 1) for both the oil and food (Blumenthal, 1994; Blumenthal and Stier, 1991). During frying, the oil progressively

Table 1—A generalized oil degradation model showing a relationship of an oil's fry-life cycle periods and corresponding quality attributes[a]

Period	TG[b] (%)	TPC[b] (%)	Polymers (%)	FFA[c] (%)	Food quality attribute model food, potato strips
New oil	>96	<4	0.5	0.02	
Break-in	90	10	2.0	0.50	white, not crisp, raw center
Fresh	85	15	5.0	1.0	slight surface browning
Optimum	80	20	12	3.0	golden brown, rich odor/flavor, crisping
Degrading	75	25	17	5.0	excessive darkening and oil pick-up, raw center.
Runaway	65	35	25	8.0	Very dark product, case hardening, raw center.

[a] Source: Blumenthal (1994).
[b] TG=triglyceride and TPC=total polar components (%TG + %TPC = 100).
[c] FFA=free fatty acids.

undergoes degradative physico-chemical changes and/or modifications induced by the food, food substance fall-out, heat, moisture and oxygen content in the oil or food (Blumenthal, 1992; DuPlessis, 1996; White and Wang, 1986). Replenishment with fresh oil and filtering periodically extends the fry-life of the oil (Melton, 1994; Romeo et al., 1995; Stier and Blumenthal, 1991). The break-in stage, achieved by heating the oil alone at a pre-selected frying temperature (170-195°C) (Brekke, 1990) for about 3-4 hr (Blumenthal, 1991) reduces the interfacial tension. A certain degree of surfactancy (lower interfacial tension) is essential and desirable for efficient heat transfer. However, beyond a certain point, typically past the optimum stage, increased surfactancy leads to excessive oil absorption by the food (Stier and Blumenthal, 1990; Blumenthal and Stier, 1994).

Throughout the frying process many low and high molecular products referred to, respectively, as volatile decomposition products (VDP) and primary and secondary non volatile decomposition products (NVDP), are formed (Melton et al., 1994). The NVDP, namely: polar compounds, conjugated dienoic acids, some free fatty acids, polymers, dimers, and trimers, are formed (Fig. 1) in varying amounts, and as such, provide an index for determining the extent of oil degradation (Melton et al., 1994; White, 1991). The rate and extent to which these are formed impact on oil fry-life stability, thermal capacity (Blumenthal, 1991; DuPlessis, 1996, Melton et al., 1994; White, 1991; Singh, 1994), interfacial tension of the system (Pinthus and Saguy, 1994; Singh, 1994) and performance, all of which are in turn dependent on the stress capacity of the type of oil.

Yeast-raised doughnuts provide a rather simple fried food model system that allows the study of oil/fat performance and stability with minimum interference from food particles and/or surfactant, conditioning, stabilizing and leavening ingredients - items that may

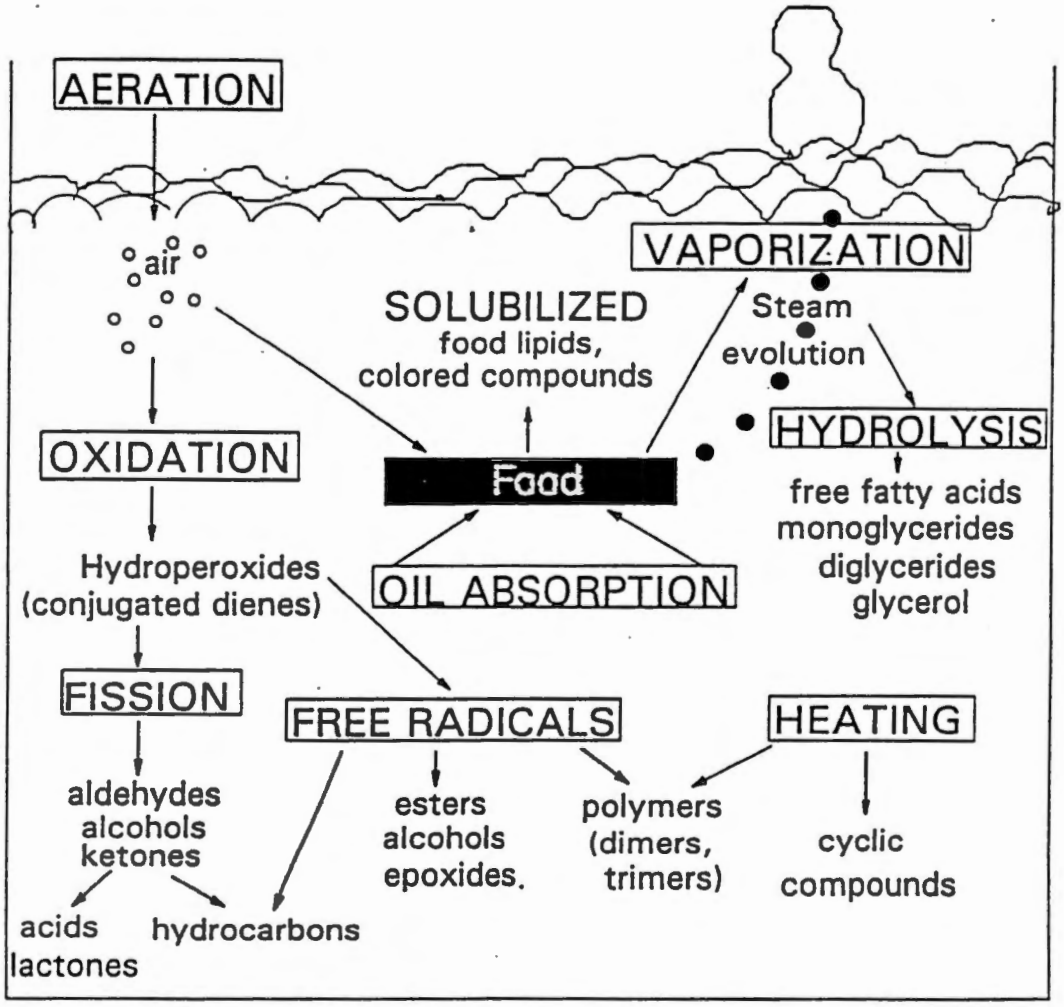

Fig. 1—Reactions occurring in deep fat frying (Fritsch, 1981).

induce premature oil/fat deterioration (Stier and Blumenthal, 1990). Doughnut preparation and selling is one of the most popular and common ways of generating income for most low-income women in several developing countries (Downing, 1993, DuPlessis, 1996). In Swaziland doughnuts also happen to be a very well liked and easily available fried snack food among school children, construction workers, and commercial plantation workers (Personal observation). In addition, doughnuts are more energy-dense and have higher satiety value per unit volume than other snacks of equal cost (Collins and Abdul-Aziz, 1982; Swaziland Nutrition Council, 1985). The processing of high oleic sunflower oil by rural-based cottage/intermediate industries in Swaziland could ensure an inexpensive production of a high quality doughnut and an adequate supply of dietary oil/fat.

FRYING OIL QUALITY MEASUREMENT

The goal of deep-fat frying is the production of high quality food that is wholesome, flavorful and safe while optimizing the fry-life of the frying oil (Blumenthal, 1994; Stier and Blumenthal, 1990). During deep-fat frying of snack foods like doughnuts, the oil is oxidized, hydrolyzed and thermally abused. As a consequence, the oil, which is initially more than 96% triglyceride, is gradually degraded via the formation of primary NVDP namely, hydroperoxides, free fatty acids, monoglycerides, and diglycerides. These are further transformed into secondary products both VDP (aldehydes, ketones, hydrocarbons, short chain fatty acids) and more complex NVDP (dimers, trimers, polar compounds, and higher polymers) via fission, cyclization, polymerization and oxidation with extended and repeated frying (Cuesta et al., 1993; Hansen et al., 1994; Melton et al., 1994; Tyagi and

Vasishtha, 1996). Because of their higher molecular weight and lower volatility than that of VDP, NVDP remain and accumulate in the frying oil. The rate and magnitude at which they are formed differs depending on oil composition, food fried and frying practices of the operator.

The presence of decomposition compounds in the frying oil forms the basis of frying oil quality monitoring as they impact profoundly on its chemical and physical properties (Blumenthal, 1992). Altogether, these processes and compounds are degradative to the oil to such a point where excessive amounts can be deleterious to health (Cuesta et al., 1993; Tyagi and Vasishtha, 1996).

Fried food quality also differs. Excessive oil degradation results in increased oil uptake by the food, excessive browning, burnt flavor, and an undercooked product, all which result mainly from the loss of heat transfer capacity of the oil (Blumenthal, 1991; Melton et al., 1994; Stier and Blumenthal, 1993). In addition, Tyagi and Vasishtha (1996), suggested that excessive frying oil degradation may produce a nutritionally impoverished oil due to the loss of polyunsaturated fatty acids (PUFA's) and tocopherol.

While standards that have been advanced as criteria for determining the discard point of frying oils/fats may not be universally applicable or acceptable (Firestone, 1993), they are still powerful quality monitoring tools (Melton et al., 1994; Perkins, 1992; White and Wang, 1986). Moreover, they can be used to determine objectively the point at which the oil has become a health risk factor (Cuesta et al., 1993; Tyagi and Vasishtha, 1996; Smith et al., 1986). In developing countries where fast foods are becoming popular, and the price of the frying oil is high, frying oil may be a silent health hazard because of absence of standards from authorities like FAO/WHO and government regulation.

CHEMICAL ANALYSES

Tocopherols

Chemically, tocopherols (commonly known as Vitamin E) are a group of biologically active polyisoprenoid derivatives consisting of a saturated side chain and variable methyl groups (Labuza, 1985; Tannenbaum et al., 1985). The number and location of the methyl substituents on the isoprenoid unit determines the type of tocopherol isomer namely: alpha (α-), beta (β-), gamma (γ-) and delta (δ-) (Fig. 2), and hence its chemical properties (Dionisi et al., 1995; Labuza, 1985). Because these isomers are present in different proportions in the various vegetable oils, it has been suggested that perhaps tocopherol assessment could be used to detect oil adulteration (Dionisi et al., 1995). Vegetable oils, particularly sunflower oils, are naturally rich in tocopherols and therefore are excellent sources of Vitamin E (Labuza, 1985; Miyagawa et al., 1991; Tannenbaum et al., 1985).

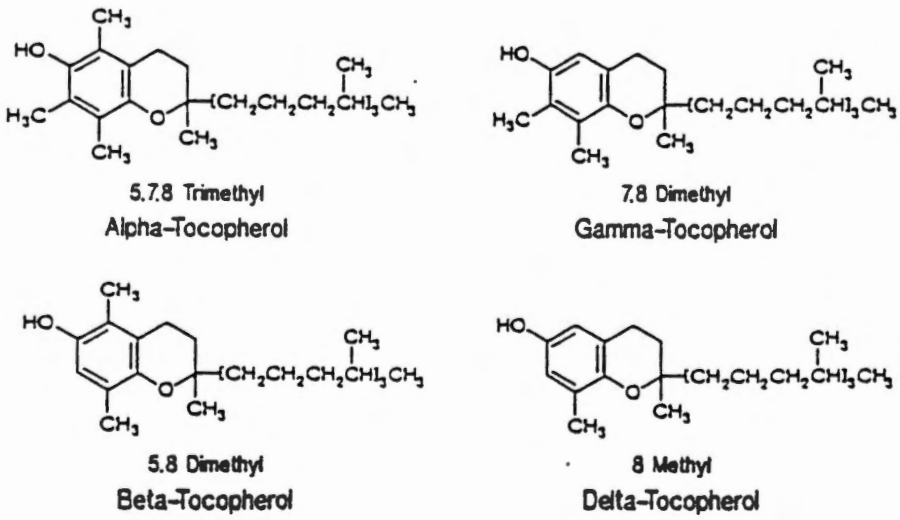

Fig. 2—Chemical structures of alpha-, beta-, gamma- and delta-tocopherol (Warner and Mounts, 1990).

In humans, Vitamin E is an essential fat soluble vitamin and serves vital physiological functions (Dionisi et al., 1995). In food systems, tocopherols serve as antioxidants, hindering oxidation of unsaturated fatty acids (Carpenter, 1979; Dionisi et al., 1995; Huang et al., 1994). During frying, they minimize the formation and decomposition of hydroperoxides (Huang et al., 1994) and hinder the formation of compounds that are deleterious and undesirable to food quality and health (Yodice, 1990). However, Madhari et al.(1996) reported that although all tocopherols exhibit antioxidant and vitamin E activity, their peak activity depended on temperature. They indicated that at 37°C the activity was in the order of $\alpha > \beta > \gamma > \delta$, whereas the order was reversed at higher temperatures (50-100°C).

Tocopherols are generally heat, light and air sensitive, with α-tocopherol showing more sensitivity than γ-tocopherol (Huang et al., 1994). Alkali refining, bleaching and deodorization were found to cause significant losses of tocopherols in finished oil (Sherwin, 1976). During extended frying operations, they oxidize and decompose at different rates and via different mechanisms (Huang et al., 1994; Miyagawa et al., 1991). Gamma-tocopherol is typically oxidized into diphenyl ether dimer and biphenyl dimers, products that were found to be still effective antioxidants. The oxidation products of alpha-tocopherol, alpha-tocopherylquinone (red pigmented products) and small amounts of dimers, however, did not exhibit antioxidant activity (Huang et al., 1994). In view of these observations, perhaps more attention should be given to gamma-tocopherol as potentially more protective to oil during frying than alpha-tocopherol. The destruction of vitamin E in frying oils during frying has also been reported to be accompanied by an exponential increase in the fluorescence intensity of the oil (Miyagawa et al., 1991).

Vitamin E destruction in frying oils can provide a good index for

gauging the extent of frying oil abuse (Dionisi et al., 1995; Huang et al., 1994). Therefore, its analysis and quantification by High Performance Liquid Chromatography (HPLC) has been preferred and used, and different detector systems, columns, mobile phase solvent systems and chromatographic conditions tried. Because of the phenol ring structure, tocopherols exhibit fluorescence and hence detection by a fluorescence detector is recommended (Van Niekirk, 1988). Tocopherol esters on the other hand, are best detected by an ultra violet (UV) detector, as they do not fluoresce. The electrochemical detector has also been used and was found to be 20 times more sensitive than a fluorescence detector (Van Niekirk, 1988). Ultimately, the optimum chromatographic conditions, techniques and detectors for tocopherol analysis must be assessed in light of their sensitivity to the food system being analyzed, and possible interfering compounds within the food (Van Niekirk, 1988).

HPLC normal phase separation and quantification has been preferred over spectrophotometric methods because each tocopherol isomer is measured rather than the amount of total tocopherols. Individual tocopherol quantification aids in determining the lability of each isomer and/or that which exhibits better antioxidant activity throughout much of the frying process.

Several researchers (Carpenter, 1979; Dionisi et al., 1995; Warner and Mounts, 1990) have reported different HPLC conditions for the separation of tocopherol isomers. Carpenter (1979) used a silica (10 μm) column and 1.5% isopropanol (IPA) in hexane as a mobile phase solvent at a flow rate of 2.0 mL/min to measure different tocopherol isomers in vegetable oils. However, later researchers found that solvents containing less than 1.5% IPA in hexane and a lower flow rate produced better resolution between β- and γ-tocopherol isomers using a similar type of column (Dionisi et al., 1995; Warner and Mounts,

1990).

Generally, α-tocopherol was more effective than γ-tocopherol at lower levels (100 ppm) in minimizing hydroperoxide formation. However, at higher levels (250-500 ppm), γ-tocopherol was more effective in controlling both formation and decomposition of hydroperoxides. At 250-500 ppm, α-tocopherol actually acted as a prooxidant by increasing hydroperoxide formation; however, it hindered hydroperoxide decomposition (Huang et al., 1994). In fresh oils, amounts ranging from 0.5 to 10 mg/100 g oil were effective in prolonging the storage life (up to 2 years) of some oils (Van Niekirk, 1988). This is seen as an advantage in ensuring a high quality oil for rural communities who do not have the technology of adding other antioxidants like TBHQ.

Minimal refining of sunflower oils, as suggested for most developing countries (Downing, 1993), will minimize excessive losses of vitamin E that are normally encountered (due to exposure to high temperatures) during commercial oil processing and thereby enable rural communities to have access to frying/cooking oil that is more heat stable and of better quality. In addition, controlling the amount of air and light entering cottage industry processed oil will minimize tocopherols destruction in oils.

Total Polar Components

Total polar compounds (TPC) are the sum total non-triglyceride materials in an oil namely: triglyceride dimers, oxidized triglycerides, diglycerides and free fatty acids (Cuesta et al., 1993). These components form and accumulate in the oil as a result of the thermal oxidation of the fatty acids in the triglyceride and its primary breakdown products (Hansen et al., 1994; Melton et al., 1994; Perkins, 1992; Stier and Blumenthal, 1993). Total polar component measurement using column chromatography provides the best single overall indicator

of total triglyceride alteration and/or degree of breakdown of oil during frying (Cuesta et al., 1993; Firestone et al., 1991; Jacobson, 1991; Melton et al., 1994; Stier and Blumenthal, 1993). It is, however, not specific and is limited in terms of predicting food quality and/or safety from hazardous degradative compounds (Melton et al., 1994; White and Wang, 1986).

Various levels of TPC for different fresh frying oils have been reported; 5.5% for corn oil (Augustin et al., 1987); 3.5% (Dobarganes et al., 1993) and 3.6% (Romeo et al., 1995) for high oleic sunflower oils; 5.1% for conventional sunflower oil (Dobarganes et al., 1993); 2.8% for soybean oil and 3.7% for hydrogenated vegetable shortening (Fritsch et al., 1979). Under typical frying conditions with frequent fresh oil replenishment, TPC increased throughout the break-in stage and up to the optimum stage, where they tended to reach a near steady state (Cuesta et al., 1993). The chemical changes that contribute to this observation have not been established. It could be a combination of factors one of which is fresh oil replenishment. Under thermo-oxidative conditions, however, TPC in conventional sunflower oil were significantly ($p<0.01$) higher (24.2%) than in high oleic sunflower (11.2%) after 5 hr of heating (Dobarganes et al., 1993). This observation suggests that high oleic sunflower oil has a higher degree of resistance to thermo-oxidation than regular sunflower oil. Levels of TPC recovered from the crust of the food and found in the oil, however, were not significantly different (Dobarganes et al., 1993).

Although there is a strong inclination among certain countries including South Africa (DuPlessis and Marais, 1995), to adopt the proposed 25-27% TPC as the criteria for discarding frying oils, further validation of this parameter as it relates to food quality and safety is needed (Melton et al., 1994; White and Wang, 1986). Perhaps specific polar materials rather than total polar components should be used as

markers and/or monitored.

Dielectric Constant

The dielectric constant measured by the Food Oil Sensor (FOS) represents the net balance between the polar and non polar components present in thermally abused oils/fats (Paradis and Nawar, 1981). It is a quick and convenient method to estimate overall frying oil degradation in process (Smith et al., 1986; White and Wang, 1986). The measurement of the dielectric constant is based on the principle that, as frying oil/fat is thermally oxidized, it gradually loses its insulating capability due to the development of polar components which are positively charged groups (Graziano, 1979). The accuracy of the dielectric constant as an oil quality measurement tool, has been validated by correlating with other reliable methods of measuring frying oil degradation.

Augustin and co-workers (1987), reported that the dielectric constant was highly correlated ($r \geq 0.99$) with both iodine value and polyunsaturated to saturated (C18:2/C16:0) ratio ($p<0.001$) of frying oil. Al-Kahtani (1991) found a correlation coefficient (r) of 0.93 between the dielectric constant and TPC of a frying oil. In another frying study, Smith et al.(1986) found $r=0.95$ between the dielectric constant and TPC of the oil.

There is no general consensus on the value of a FOS reading (dielectric constant) at which to discard degraded frying oils. In a study by Fritsch et al.(1979), FOS readings increased from 1.0 to 5.3 for fresh soybean oil, from 1 to 3.7 for hydrogenated vegetable shortening and from 1.0 to 1.8 for an animal-vegetable blend shortening during a 24-hr frying period. In some European countries, fats with an FOS reading of 4.0 are still considered acceptable for commercial use (Smith et al., 1986) even though a value of 3.7 has been reported

to correspond to 27% TPC (Al-Kahtani, 1991). A FOS reading of 4.0 has been proposed as the limit (White, 1991). In developing countries like Swaziland where the more sophisticated methods would be expensive and inaccessible for most fast food chains or groups of street food vendors, the FOS may be the best option. However, the initial cost of the FOS instrument (approximately $1000.00) would limit its usability by single food vendors. The use of a FOS, even if available within a reasonable radius, would improve the chances for the production of a high quality and safe doughnut or product.

Conjugated Dienoic Acids

When polyunsaturated fatty acids (PUFA) are oxidized during frying, a shift in one of the double bonds occurs producing conjugated diene compounds. These oxidation products absorb ultraviolet and visible light (UV-Vis) and can be quantitated by absorbance at UV 232 nm (Fritsch, 1981; White, 1991; Yoon et al., 1985); 230 and 375 nm (Gray, 1978); or 234 nm wavelengths (Perkins, 1992; White and Wang, 1986). The American Oil Chemists Society (AOCS) Official Method Ta 1a-64 (AOCS, 1993) suggests testing of conjugated diene species at 233 nm. Selection of a specific wavelength within the range depends on its sensitivity to detection of analyte (conjugated diene) from the food system (White and Wang, 1986).

Conjugated dienoic acids and their breakdown products have been implicated in carcinogenesis and in a variety of inflammatory processes (Yodice, 1990). Other researchers (Yurawecz et al., 1993), however, reported that conjugated dienoic acids have been shown to have anticarcinogenic and antioxidant properties. As illustrated by these reports, the information on conjugated dienes in frying oil/fats with regard to health is contradictory. In food systems, however, the amount of conjugated dienes has been associated with the degree of oxidation of

the oil, (particularly oils high in PUFA) and hence, its quality (Fritsch et al., 1979; Gray, 1978; Huang et al., 1994; Tyagi and Vasishtha, 1996; White, 1991). Although the amount of conjugated dienes in any given oil is not definitive of degree of deterioration, increase in their concentration provide a reliable predictive measure of extent of oxidation (Gray, 1978; Miller and White, 1988). The amount of conjugated dienes, as reflected by UV absorbance values, increases with an increase in heat abuse of the oil (Miller and White, 1988; Tyagi and Vasishtha, 1996; Yoon et al., 1985). In the early stages of frying, the increase in conjugated dienes is typically linear with a tendency to plateau at later stages. This plateau is the point at which the rate of formation of conjugated dienes is at equilibrium with the rate of polymer formation (Al-Kahtani, 1991; White, 1991; Yoon et al., 1985).

Other variables, which impact on the amount and rate of formation of conjugated dienes, are oil type (Fritsch et al., 1979; Miller and White, 1988; Tyagi and Vasishtha, 1996); variety within each oil type (Miller and White, 1988); and presence of antioxidants (Tyagi and Vasishtha, 1996). Conjugated diene measurement as a method for measuring oxidation of oils high in PUFA seems limited due to the large number of variables which influence diene formation (White, 1991). Treatment of soybean oil with antioxidants produced significantly ($p<0.01$) lower levels of conjugated dienes (Huang et al., 1994; Tyagi and Vasishtha, 1996) after frying for 70 hr at 170, 180 and 190°C than in soybean oil and vanaspati oil devoid of antioxidant (Tyagi and Vasishtha, 1996). Although conjugated diene measurement has been found to be a useful method for measuring oxidation of oils high in PUFA, it is limited for testing oil oxidation in less unsaturated oils (White, 1991) such as high oleic or saturated oils/fats.

Free Fatty Acids

Free fatty acids (expressed as percentage acid value in most countries outside North America) in heated frying oils/fats, are the net titratable fatty acids hydrolyzed off the triglyceride molecule (Stier and Blumenthal, 1993) and those produced by thermal oxidation (Melton et al., 1994). They are used a lot in the food industry in most countries for routine quality monitoring of frying fats (Best, 1987; DuPlessis and Marais, 1995). The recommended point of discard of frying oils in the USA is when free fatty acid (FFA) value exceeds 1.0% (Smith et al., 1986). Other countries however have recommended a value of more than 2.5% FFA as the criteria for when to discard frying oils/fats (Du Plessis and Marais, 1995).

The use of FFA alone to monitor the extent of frying oil degradation seems limited and has been criticized (Stevenson et al., 1984b; Stier and Blumenthal, 1993; White, 1991). Their transient nature, volatility and proneness to further secondary oxidation during frying, underscore the criticism of using FFA concentration as an index for discarding cooking oil (Blumenthal, 1992; Hansen et al., 1994; Stier and Blumenthal, 1993). In contrast, a 3% level of FFA was reported much earlier in a more stable fat system than a less stable one (Jacobson, 1991). Generally, an increase in FFA has been reported to increase with an increase in the fry life of the oil/fat (Fritsch et al., 1979; Stier and Blumenthal, 1993). Despite the claimed limitations, free fatty acid measurement is still applicable and useful particularly in situations where chromatographic resources are not accessible or sufficiently available (Jacobson, 1991; Melton, 1994).

As is the case with other methods, the meaning of FFA levels in a used frying oil and extent to which they can be relied upon, must be viewed in totality of confounding factors (such as type of oil/fat used or frying practices) and interpreted in the context of other oil quality

measurement results (Melton et al., 1994).

Fatty Acid Composition

The fatty acid profiles of different brands of fresh (unused) high oleic and conventional sunflower oils are shown in Table 2. As a measurement of oil degradation of various frying oils/fats the polyunsaturated fatty acid to saturated fatty acid ratio ($C_{18:2}/C_{16:0}$) has been used (Al-Kahtani, 1991; Augustin et al., 1987; Perkins, 1992; Smith et al., 1986). This ratio refers to the proportion of polyunsaturated to saturated fatty acids that are triglyceride bound and have not been altered or lost thermo-oxidatively (Augustin et al.,1987; Sebedio et al., 1986) during frying. Determination of the fatty acid compositions of unused and used frying oils by gas-liquid chromatography (GLC) provides an indication of degree of fatty acid alteration occurring to a particular oil/fat, and consequently, its quality (Tyagi and Vasishtha, 1996). The polyunsaturated to saturated ratio is a fairly reliable yardstick for testing the quality of frying oils (Al-Kahtani, 1991) and has been shown to correlate (r=0.99) with each of several other measurement techniques like FOS reading, TPC, conjugated diene or iodine value (Augustin et al., 1987).

The magnitude and rate of change of polyunsaturated to saturated fatty acid ratio is dependent on initial linoleic acid content of the oil/fat (Al-Kahtani, 1991; Cuesta et al., 1991; Tyagi and Vasishtha, 1996); oil type (Cuesta et al., 1991; Tyagi and Vasishtha, 1996); temperature and duration of frying (Miller and White, 1988; Perez-Camino et al., 1991; Sebedio et al., 1986; Tyagi and Vasishtha, 1996) and the food being fried (Al-Kahtani, 1991; Smith et al., 1986). The leaching of linoleic acid from linoleic acid rich foods like chicken, however, tends to distort the picture by increasing the $C_{18:2}/C_{16:0}$ ratio (Al-

Table 2—Fatty acid composition of some brands of high oleic acid sunflower oil and a regular sunflower brand

Fatty Acid (%)	TRISUN®[a]	SUNOLA®[b]	VIPA®[c]	Regular sunflower[d]
C16:0	4.0	3.0	4.4	6.0
C18:0	4.0	2.8	4.2	5.0
C18:1	80.0	89.0	78.3	16.0 - 19.0
C18:2	10.0	3.5	10.9	68.0 - 72.0
C18:3	0.3	0.2	NR	NR
C20:0	NR[e]	0.2	0.3	NR
C20:1	NR	0.3	0.2	NR
C22:0	NR	0.6	1.0	NR
C24:0	NR	NR	0.4	NR

[a] USA, high oleic acid oil sunflower brand (Yodice, 1990).
[b] Australia, high oleic acid oil sunflower brand (Noakes et al., 1996).
[c] Spain, high oleic acid sunflower oil brand (Romeo et al., 1995).
[d] USA, regular sunflower oil brand (Fitch, 1994).
[e] not reported.

Kahtani, 1991). Decrease in the $C_{18:2}/C_{16:0}$ ratio was more pronounced in linoleic rich oils than in monoene rich oils (Tyagi and Vasishtha, 1996). This is an indication that this test is also more suited to the measurement of polyunsaturated fatty acid-rich oils/fats.

COLOR AND COLOR CHANGE IN FRYING OILS

Color measurement in frying oils is typically quantified by measuring the change (ΔE) in the spectral distribution of the color tristimulus values (*L*, *a* and *b*) (Escolor et al., 1994; Francis and Clydesdale, 1975) using spectrophotometric procedures, the Hunter Lab system or Minolta systems. The *L*, *a* and *b* values describe the spectra of oil as it relates to its lightness or luminosity, redness or greenness, and yellowness or blueness, respectively, under standard observer conditions (Illuminant C and 10^0) (Collins, 1995). Color measurement of frying oils is more a routine quality check measurement than an index to determine the extent of frying oil deterioration or predict fried food quality (Blumenthal, 1992; Fritsch, 1981). However, over the years color of a used frying oil has been used by many fast food operators as a yardstick for determining if the oil has outlived its usefulness (Firestone, 1993; Stevenson et al., 1984b; Stier and Blumenthal, 1993). This practice however, has been viewed by many as being subjective. They assert that its accuracy is dependent largely on the experience of the operator, the type of oil and knowledge of how long the oil had been used. Palm oil for example, is known to darken more quickly than other oils without necessarily meaning poor quality (Al-Kahtani, 1991).

Instrumental analysis of frying oil color does provide useful information about the degree of pigmentation from chlorophyll or carotenoids in fresh unused oil. These pigments are known to act as

prooxidants, and hence are likely to induce premature oxidation if not sufficiently removed (Brekke, 1990). In used frying oil systems, color measurement can provide information about the rate, magnitude and type of color change. This can provide an indication as to what type of abuse may be occurring to the oil during frying. Generally, the red color normally observed in filtered oil, correlates to combined oxidized fatty acids and pyrolytic condensation. The yellow color usually relates to the combined peroxides and aldehydes (Totox value) in the oil. The blue color is related to the haze created by water and fine particulates suspended/emulsified in the oil (Stevenson et al., 1984b; Stier and Blumenthal, 1993).

Change in the color spectrum of frying oils is brought about by many interacting factors during frying. The very nature of frying conditions induce color changes due to the decomposition of degradation products and polymer formation (Graziano, 1979). Many foods contain particulate ingredients and/or substances that leach out, or are solubilized into the oil during frying. These substances react with breakdown products from the oil causing darkening (or loss of luminosity) in the oil (Al-Kahtani, 1991; Augustin et al., 1987; Fritsch, 1981; Lawson, 1985; Melton, 1994). The rate of color change was also reported to be accelerated by higher frying temperatures and longer frying duration (Tyagi and Vasishtha, 1996); breaded, or coated products, or food with a high concentration of pigments (Miyagawa et al., 1991), and infrequent oil turnover rate and/or filtration (Melton et al., 1994). Other factors like phenolic antioxidants (such as TBHQ) and their breakdown products, have also been shown to cause undesirable darkening of oil and fat containing foods (Augustin et al., 1987; Brekke, 1990).

In places where frying oil color is judged by visual examination as part of a quality control strategy, the evaluation should be done by

an experienced and skilled person. Premature discarding of oil results in too great of an economic loss, but using frying oil past the point it should be discarded may result in customer dissatisfaction (Handel and Guerrieri, 1990).

FACTORS AFFECTING FOOD QUALITY ATTRIBUTES

The ultimate goal of monitoring frying oil quality is to ensure/optimize the production of a high quality fried food product, that is wholesome, flavorful, appetizing and nutritionally safe (Firestone, 1993; Blumenthal, 1992; Jacobson, 1991). These parameters are the ultimate criteria for determining the point at which frying oils/fats should be discarded (Melton, 1994). In Germany and the Netherlands, sensory evaluation of fried food and frying oil is stated in regulations used to determine when to throw away a frying oil/fat (Firestone, 1993). At each stage of the degrading oil's/fat's fry-life cycle, the products, which are evolved and/or decomposed, directly affect, and alter the chemical profile and thermodynamics of the frying oil/fat. These changes impact positively and/or negatively on the sensory qualities of the food being fried (Melton, 1994; Pokorny, 1989; Stier and Blumenthal, 1993). Consequently, sensory evaluation is used to discern the extent of quality loss.

The attributes which constitute fried food quality, and which must be optimized during frying are: flavor, color and appearance, mouthfeel (greasiness or mouth-coating properties), and texture (Stevenson et al. 1984b, Stier and Blumenthal, 1993). The fried food must have a pleasant fried flavor/odor, moderate oil pick-up, well gelatinized starch and cooked interior, and crisp and golden brown crust/surface and be free of toxic substances (Blumenthal, 1991).

Unfortunately, the latter attribute is not discernible by sensory evaluation. Acceptability is a subjective composite parameter that panelists use to rate a product's overall eating quality.

The factors that interact to produce a particular fried food quality are: the composition of the food being fried; the composition and chemical tendencies of the oil/fat under stressful thermo-oxidative conditions; the nature and concentration of degradative products from the oil and those leached out/solubilized from the food being fried. Additionally the skill and ability of the operator to control the level of surfactants (soaps) in the frying oil, and to relate the chemistry of the degrading oil to its thermodynamics properties and to food quality are also critical factors (Blumenthal, 1991; Pokorny, 1989; Stier and Blumenthal, 1990, 1993).

Flavor

The flavor of fried food is influenced by several interacting factors such as the oil VDP and the concentration of carbonyl-amine browning reaction products present in the food being fried (Jacobson, 1991; Stevenson et al., 1984b), as well as the flavor volatiles of the constituent ingredients/substances (Jacobson, 1991; Melton, 1994; Pokorny, 1989). For example, yeast-raised doughnuts have been reported to have significantly ($p<0.05$) higher levels of aldehydes than cake doughnuts. This was probably attributable to yeast respiration by-products that evolved in the yeast doughnuts during proofing (Lane and Smathers, 1991). In french fried potatoes, however, pyrazines seemed to dominate and contribute the desirable flavor (Stevenson et al., 1984a).

Different frying oils/fats also impact the flavor of fried food differently. Monoenoic fatty acid oils generally are described as imparting good but less intensive fried flavor than polyunsaturated fatty acid containing oils. Linoleic acid rich oils impart full, rich

and intensive fried flavors. Oils containing high levels of saturated fatty acids, and those which are hydrogenated, result in even less intensive, rich or full fried flavor (Pokorny, 1989). During frying, fatty acids oxidize and react with other substances in the hot oil, generating many VDP and NVDP with specific flavor notes depending on oil/fat composition (Melton, 1994). Some of the products generated such as hexanal and pentanal, impart off or objectionable flavor notes to fried food. Other oxidation products, like decadienal isomers and gamma lactones (which are products of linoleic acid oxidation), were reported to be responsible for the pleasant deep-fried flavor (Melton, 1994; Melton et al., 1994; Snyder and Mounts, 1990). Snyder and Mounts (1990) reported a lower t,t-2,4-decadienal concentration in foods fried in high oleic sunflower oil than in those fried in conventional sunflower oil. The low concentrations of decadienal isomers in food fried in oils with 80% or more oleic acid undoubtedly contribute to their less preferred flavor compared with food fried in linoleic acid-rich oils (Fitch, 1994; Snyder and Mounts, 1990). This fact is still viewed as the major drawback to adopting HOS on full-scale commercial production of snack food in the USA. Other countries like Australia and Spain, that have used HOS oil types for commercial production of snack foods have not reported this problem yet. It may be more a matter of preferences of taste/flavor in the USA than a universal problem. A blend of HOS with other oils that would optimize all the desirable frying attributes of an HOS frying oil is needed (Fitch, 1994).

Color and Appearance

The appearance of fried food is desirable/appetizing when its color is golden brown and the surface moderately glossy and firm (Blumenthal, 1991). Color development in fried foods has been attributed more to the level of surfactants and temperature control than

oil composition (Blumenthal, 1991, 1992). With low levels of surfactants, the oil behaves like an insulator and as such transfers insufficient heat to the surface of the food to activate carbonyl-amine browning reactions (Blumenthal, 1991). On the other hand, excessive levels of surfactants as is characteristic of degrading and runaway oils, will also reduce the heat transfer capacity of the system. This results in food being kept in the fryer longer to adequately cook the inside, and hence increases the chance of surface charring and darkening. The basic principle that underlies this occurrence is that heat conductance within the food is a constant and cannot be speeded up by increasing the temperature of the oil (Blumenthal, 1991; 1992).

Texture and Mouthfeel

The surfactant theory has also been used to explain changes in textural qualities of fried food. Excessive surfactants in the oil result in longer food-oil contact times, and therefore, an opportunity for excessive oil pick up by the food, producing a limp and greasy product (Stevenson et al., 1984b). In addition, longer residence times in a surfactant laden oil produce case hardening from deposits of polymerized dimers and cyclic compounds (Stevenson et al., 1984b; Stier and Blumenthal, 1990). In cases where expensive imported oils are the only available oils to low income fast food vendors like in Swaziland, the tendency may be to overstretch the oil into the degrading stage, thereby comprising fried food sensory characteristics and safety.

CHAPTER III

MATERIALS AND METHODS

FRYING STUDY

Materials for Frying Study

Refined regular sunflower (RCO), TEM-TEX®, and refined high oleic sunflower oil (HOS), SUN-HO®, were obtained from an oil processor (confidential source) in Tennessee, USA. Refined sunflower oil (SVS), SUNVALLEY®, and refined sunflower oil (SOS), SUNOL®, were obtained from NOLA FOODCORP, Randfontein, Republic of South Africa (RSA). The oils from RSA were shipped via air to Knoxville, TN, in sealed, nitrogen flushed, 20-L yellow polyethylene containers. The oils from the USA were shipped in similar containers by truck to Knoxville from within the USA. On arrival all oils were stored at 23-27°C for no longer than 2 months until they were used in this study.

Frozen and pre-cut commercially prepared, yeast-raised potato flour doughnut dough (Appendix A) was obtained from Robert Orr Sysco (Knoxville, TN). Average size (n=5) of each doughnut before frying was 38.5 ± 2.4 g, 2.1 ± 0.1 cm high and 7.9 ± 0.3 cm wide. Prior to frying, doughnuts were removed from freezer storage and thawed overnight at 18°C on baking sheets in a walk-in cooler. The following morning, the doughnuts were removed from walk-in cooler and allowed to stand at room temperature for 20-25 min before proofing. The doughnuts were then put in a proofing cabinet (EPCO Rack and Cabinet Co., Murfreesboro, TN) set at 30-31°C, and allowed to proof for 25-30 min. After proofing, doughnuts were let dry 15 min at room temperature before frying.

Chemicals and solvents were obtained from Fisher Scientific Co.,

Atlanta, GA, unless otherwise noted, and suppliers of other materials and instruments are identified when mentioned in this section.

Experimental Design

The design of the experiment was a randomized block design split-plot factorial (4 X 7 X 2). There were four blocks with each block being a different type of oil or treatment, and each block was split into seven sampling times of oil use (fresh, break-in heated and on days 1 through 5 of consecutive frying). A replication consisted of the four oil treatments (OILTYPE), namely RCO, HOS, SVS and SOS, and the seven sampling times (TIME) for each oil. Two replications (WEEK 1 and 2) were run. Each of the oil treatments was randomly assigned to one of four 3.8-L electric fryers (Model DCP-6, DAZEY products Co. Industrial Airport, KS) for the first WEEK and reassigned for the second WEEK as shown in Table 3.

Frying Study

Prior to each WEEK, each 3.8-L fryer was thoroughly cleaned of all gums from previous use by using a boil-out solution, (Robert Orr Sysco, Knoxville, TN), followed by water rinses, a vinegar rinse and then two deionized water rinses before being dried. At the beginning of each WEEK, each fryer was filled with 3180 ± 50 g of the assigned fresh oil (Table 3) prior to heating and frying. The frying study was conducted under obscured day light (to minimize photooxidation) in Room 208, McLeod Hall, The University of Tennessee, Knoxville, TN, USA. Each oil was heated at 190 ± 3°C for 4 hr to break-in the oil and then sampled (Time 1). After break-in, the first day (Time 2) consisted of frying 24 batches of doughnuts of two doughnuts per batch in each oil at 190 ± 3°C for a total of 2 min per batch. The lapse period between batches was 7 min. This permitted the temperature of the oils to return to frying

Table 3—Assignment of OILTYPE to fryer for each replication (WEEK)

	Fryer			
WEEK	A	B	C	D
1	SVS	RCO	SOS	HOS
2	RCO	SVS	HOS	SVS

temperature (190°C). Cooked doughnuts were placed on an absorbent paper towel and cooled. Except on days 2 and 4, the cooled doughnuts were sealed in 3.8-L polethylene freezer bags and stored at -18°C for further analysis if necessary. On days 2 and 4, the cooled doughnuts were used for sensory evaluation as described later.

At the end of each frying day, each oil was covered and allowed to cool, and filtered using an ALTRA PURE filter (ALTRA Filters Inc., Lincoln Park, NJ). After filtration, oil samples (250 g) were placed in 500-mL glass jars, flushed with nitrogen, sealed, placed in cardboard boxes and stored at 20-23°C in a dark room for no longer than 2 mo until analyzed. Each fryer was cleaned by wiping the pot with lint free absorbent paper.

Prior to the beginning of day 1 of frying and on subsequent frying days, fresh oil of the same type as the used oil, was added (ca 265 g) to each fryer to replenish the oil, which was absorbed by the doughnuts and lost to sampling/filtering, to return it to the original weight (3180 ± 50 g). The oil in each fryer was heated to 190°C (1 hr) prior to the start of frying doughnuts. Doughnuts were fried in each fryer and treated in the same way as described for day 1 and on subsequent days of frying through day 5. Oils were treated and sampled in the same

way as on break-in, with oil samples stored in the same manner, and the fryers were cleaned in the same way daily.

CHEMICAL ANALYSES

The oil samples from the frying study were analyzed for the following chemical and physical characteristics: α- and γ-tocopherol contents, levels of total polar components (TPC), dielectric constant (FOS reading), conjugated dienes ($Abs_{233\ nm}$), free fatty acids (FFA), and fatty acid composition and C18:2/C16:0 ratio. All of these measurements were made within a 2-mo period from the end of the frying study in the teaching and research laboratories of the Department of Food Science and Technology at The University of Tennessee, Knoxville, by the following methods.

Tocopherols

Analyses of the tocopherols were performed on a Water's high performance liquid chromatograph (Water's Associates, Inc., Milford, CT) equipped with a U6K injector, a Model 510 pump, a Shimadzu Model RF-530 fluorescence detector and a Shimadzu Model C-R6A Chromatopac data processor. Shimadzu instruments were purchased from Shimadzu Scientific Instrument, Inc.(Columbia, MD). The method of tocopherol analysis used was a modified procedure of Carpenter (1979). The tocopherols were detected by fluorescence (290 nm excitation; 330 nm emission) instead of ultraviolet absorption, a 300 X 3.90 mm BondClone 10 C18 HPLC silica column (Phenomenex, Torrance, CA) was substituted for the μPorasil column and the flow rate of the solvent, 1.5% isopropanol (IPA) in hexane, was 1.6 mL/min instead of 20 mL/min. Portions (5.0 ± 0.1 g) of each oil (RCO, HOS, SVS and SOS) sample were dissolved in 1.5% IPA in

hexane at different ratios (w/v) of 1:2, 1:10 or 1:20 depending upon the tocopherol content. Actual ratios were determined in preliminary investigation. Standard solutions of α- and γ-tocopherols (Sigma Chemical Company, St. Louis, MO) were prepared containing 0.01 mg/mL of α-tocopherol and 0.05 mg/mL of γ-tocopherol, respectively. Both samples and standard solutions were filtered using a 0.45μ filter to remove particulate matter. Filtered samples were stored under nitrogen in sealed amber glass vials at 5-6°C no longer than 24 hr until analyzed. For determination of calibration curves, aliquots containing 0.05, 0.10, 0.15, 0.20 and 0.25 μg α-tocopherol and 0.025, 0.05, 0.075, 0.100, 0.125 μg γ-tocopherol were analyzed in triplicate by HPLC. The equation for each calibration curve was obtained by linear regression, and average retention times for tocopherols were calculated. For each tocopherol isomer, the amount in individual oil samples analyzed was calculated by the following equations:

$$\alpha\text{-}tocopherol\ (\mu g) = [\frac{Peak\ area - 42183.4}{17974.3}]$$

$$\gamma\text{-}tocopherol\ (\mu g) = [\frac{Peak\ area + 100.6}{7293.7}]$$

The concentration of each tocopherol in (μg/mg oil) was determined in each oil sample by the following formula:

$$\frac{\mu g}{mg\ oil} = [\frac{ng}{X\mu L}][\frac{10^3\mu L}{mL}][\frac{\mu g}{10^3 ng}][\frac{Y\ mL}{g\ sample}][\frac{g}{10^3 mg}]$$

where x μL = volume of oil sample injected into HPLC and Y mL = volume of oil solution, and g sample = weight (g) of oil dissolved in Y mL solution.

Total Polar Components

Total polar components (TPC) were determined by column chromatography and checked for efficiency of separation by thin layer chromatography (TLC) following the AOCS Official Method Cd 20-91 (AOCS, 1993). Silica gel (70-250 mesh) (Sigma Chemical Co., St. Louis, MO) was adjusted to a 5% water content to achieve the correct polarity. Conditioned silica gel (25 g) was slurried with 87:13 (v/v) petroleum ether/diethyl ether (PE/EE) and poured into a 2.1-cm i.d. x 45-cm glass column. Excess solvent was drained to 2.5 cm from the top of the silica gel and about 4 g of clean sea sand were added on top of the silica gel column. A 2.5 ± 0.1 g portion of a frying oil sample was dissolved in 87:13 PE:EE and diluted to 50.0 mL volume. A 20.0-mL aliquot of the sample solution was pipetted into the prepared column and allowed to drain slowly to about 1.0 mm below the surface of the sand layer. Non-polar components (mostly unaltered triglycerides) were eluted slowly (60-70 min) from the column with 150 mL of 87:13 PE:EE into a dried 250- or 500-mL round bottom flask of known weight. The polar components were eluted in a similar fashion with 150-mL diethyl ether. Solvent was removed from both fractions by a Buchner rotary evaporator set at 60°C, under a positive flow of nitrogen. The weight of the non-polar fraction was obtained, and TPC calculated by difference from the following equation:

$$TPC\ (\%) = \frac{(Wt.\ sample\ loaded) - (Wt.\ nonpolar\ fraction)}{(Wt.\ sample\ loaded)} X\ 100$$

Dielectric Constant

The Food Oil Sensor (FOS) (Model No. NI-20, Northern Instrument Corp., Lino Lakes, MN) was used to measure the dielectric constant (DE) of all oil samples. To calibrate the FOS for the measurement of changes in DE for each frying oil, a fresh unused sample was used to set the FOS

of all oil samples. To calibrate the FOS for the measurement of changes in DE for each frying oil, a fresh unused sample was used to set the FOS meter to 0. The fresh sample was placed in the oil sensor cup, and the calibration knob adjusted until the meter reading was zero. The calibration oil was wiped from the sensor cup. The DE of a used frying oil sample was then measured by placing a few drops of used oil in the FOS cup. The change in DE was determined by the difference (FOS reading) required to renull/re-zero the meter dial. DE reflects the degree of oxidation in used frying oil.

Conjugated Dienoic Acids

The determination of conjugated dienoic acids in each oil sample was performed according to AOCS Official Method Ti 1a-64 (AOCS, 1993). Approximately 0.1 ± 0.02 g of sample was diluted with 100 mL 2,2,4-trimethylpentane (isooctane). Samples were further diluted until a final concentration of 0.01 g/L was reached. Samples were placed in quartz cuvettes with a 1.000-cm path length. The spectrophotometer was calibrated by measuring the absorbance of 2,2,4-trimethylpentane against distilled water at 233 nm. Subsequently, an absorbance reading of 0.0296 (n=3) was obtained. Analysis of conjugated dienoic acids in the different oil samples was performed on a Shimadzu UV-VIS scanning spectrophotometer (Model UV-2101) at a wavelength of 233 nm and interfaced with an IBM personal computer, which was equipped with Color Analysis Software Version 2.0 (Shimadzu Scientific, Columbia, MD). Conjugated dienoic acid contents were reported as absorbance at 233 nm (A_{233}).

Free Fatty Acids

The free fatty acid (FFA) level (expressed as % oleic acid) of each sample taken in the frying study was determined according to the

AOCS Official Method Ca 51-40 (AOCS, 1993).

Fatty Acid Analysis

Preparation of fatty acid methyl esters. Fatty acid methyl esters (FAME) were prepared according to AOCS Official Method Ce 2-66 (AOCS, 1993). All oil samples collected during the experiment were analyzed. Each oil sample was hydrolyzed and converted to methyl esters in the following steps. To the approximately 0.1 g lipid residue in the 125-mL Erlenmeyer reaction flask were added 4 mL of 0.5N sodium hydroxide in methanol and a few glass boiling beads. The flasks were attached to condensers, and the contents allowed to boil under reflux for 10 min. Five milliliters of boron trifluoride (14%) in methanol solution (Supelco, Inc., Bellefonte, PA) were added to the contents of each flask and allowed to react for 2 min. The flasks were then cooled, and 7 mL of pentane were added to each flask through the condenser. The flask contents were boiled under reflux for 1 min; before being removed from the condensers. The pentane layer containing the FAME was brought into the neck of the flask by adding a saturated sodium chloride solution to the contents of the reaction flask. The FAME layer was removed into a vial, and a small amount of sodium sulfate was added to the vial in order to absorb the residual water in FAME solution. The vial was flushed with nitrogen, sealed, and stored at -18°C until analysis by gas chromatography (GC).

Chromatographic analysis of FAME. FAME were analyzed by a Shimadzu Model GC-9AM gas chromatograph equipped with an automatic injection system Model AOC-0 (Shimadzu Scientific Instrument, Inc., Columbia, MD). An 0.25 mm i.d. x 30 m long fused silica SP2330 column (Supelco, Inc., Bellefonte, PA) was used to separate the methyl esters, which were detected with a flame ionization detector (FID). The injection temperature was 250°C and the temperature of the column was

programmed from 130° to 220°C at 2°C/min. Helium was the carrier gas with a flow rate set at 50 mL/min, using a split ratio of 1:30. The areas of the peaks corresponding to individual FAME and their relative concentrations were recorded using a Shimadzu data processor, Chromatopac, Model CR-501 interfaced with an IBM personal computer. All chromatograms were stored using the Chromatopac Data Archive Utility version 3.1 software (Shimadzu Scientific Instruments, Inc., Columbia, MD). Fatty acid methyl esters standards (Supelco, Inc., Bellefonte, PA) were injected into the column under the same conditions as the sample methyl esters to determine the retention times of individual FAME. Identification of sample methyl esters was achieved by matching the retention times of sample peaks with those of standard peaks. Quantitative analysis of the sample FAME was done as follows. Standards containing known percentages of individual FAME present in levels similar to those in the samples were analyzed by GC and correction factors for each FAME relative to the palmitic acid (16:0) FAME was determined according to AOCS (1993). The concentration of each fatty acid in each sample was calculated as weight percentage of total FAME present.

C18:2/C16:0 ratio. The concentration ratio of linoleic (C18:2) to palmitic (C16:0) was calculated for every frying oil sample by dividing the percentage of C18:2 by percentage of C16:0.

COLOR MEASUREMENT

Oil samples from each oil from the frying study were analyzed for Hunter color *L*, *a* and *b* values and change in color (ΔE) was calculated for each oil.

Color analysis in each oil sample taken in the frying study was

performed on the Shimadzu UV-VIS scanning spectrophotometer (Model UV-2101)(Shimadzu Scientific Instruments, Inc., Columbia, MD). The spectra of each treatment combination was obtained in the visible range from 400 nm (lowest) to 800 nm (highest), with the equipment set on transmission mode at Illuminant C and 2° observer angle. The spectrum of the oil was further analyzed using UV-2101/3101PC Optical Color Analysis Software Version 2.0 (Shimadzu, Scientific Instrument, Inc., 1994) to express the results of color measurement in the Hunter color values, *L*, *a* and *b* of each oil and the color differences (ΔE) between the fresh and used samples of each oil. The method used was AOCS Official Method Cc 13c-50 (AOCS, 1993). Samples were refiltered before being analyzed using an ALTRA PURE filter (ALTRA Filters, Inc., Lincoln, N.J.). The change (ΔE) in color of samples as a function of frying time were determined from the following equation:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)]^{1/2}$$

where ΔE reflects the difference in *L* values between a fresh and used sample of the same oil; Δ*a*, the difference in *a* values between the fresh and used oil same samples; and Δ*b*, the difference in *b* values between the fresh and used oil samples.

STATISTICAL ANALYSES OF OIL CHARACTERISTICS

All chemical (tocopherol contents, TPC, FOS/dielectric constant, conjugated dienes, FFA, fatty acid composition and C18:2/C16:0 ratio) and physical (Hunter color values *L*, *a* and *b* and ΔE) characteristics were analyzed statistically as a function of WEEK (replication), OILTYPE, TIME (sampling time), and OILTYPE x TIME effects using the following model:

$$Y_{ijk} = \mu + W_i + O_{ij} + T_k + O*T_{ik} + e_{ijk}$$

where Y_{ijk} = dependent variable

μ = overall mean

W_i = week

O_{ij} = oiltype

T_k = sampling time

$O*T_{Ik}$= oiltype*time

e_{ijk} = error total

The analysis of variance for each dependent variable is shown in Table 4. Analyses of variance were run using General Linear Models (PROC GLM) of SAS Institute, Inc. (1985). Significant differences ($p<0.05$) among least-squares means of the main effects (OILTYPE AND TIME) were identified by the PDIFF option in SAS. When significant OILTYPE X TIME interactions were found ($p<0.05$), the significant differences among oils for each sampling time and among sampling times for each oil were determined by the PDIFF option also. Pearson correlation coefficients were determined using PROC CORR to determine relationships among selected chemical measurements (levels of α- and γ-tocopherols, total polar components, Food Oil Sensor reading, conjugated diene concentrations and free fatty acid levels).

Table 4—Analysis of variance for chemical and physical characteristics of frying oils during frying of doughnuts

Source	Degrees of freedom	Error term
WEEK (W)	1	
OILTYPE (O)	3	
O x W	3	Error term for Oiltype (subplot)
Time (T)	6	
O x T	18	
Residual	24	Error Term for whole plot
Total	55	

SENSORY EVALUATION STUDIES

Experimental Design and Statistical Analysis

The experimental design shown by the following model

$$Y_{ijkl} = \mu + W_i + O_j + O*W_{ij} + T_k + Pan(T)_l + O*T_{ik} + W*O*T + e_{ijkl}$$

where:

Y_{ijkl}	= dependent variable
μ	= overall mean
W_i	= week
O_j	= oiltype
$O*W_{ij}$	= oiltype*week
T_k	= sampling time
$Pan(T)_l$	= panelist(time)
$O*T_{ik}$	= oiltype x time interaction
W*O*T	= week x oil x time
e_{ijkl}	= {Pan(W*O*T)} error total

was used for the sensory evaluation study of yeast-raised doughnuts fried in the different oils. It was a randomized block design, with four treatments (OILTYPE), two replications (WEEK), two sampling times (second and fourth day of frying) and 48 panelists nested within day (4 X 2 X 2 X 48). The dependent variables evaluated by a 48-member panel were doughnut crust color and crust flavor likability, and overall acceptability, and doughnuts crust color intensity and mouthfeel (greasiness). Data were analyzed according to analysis of variance table illustrated in Table 5, using RanMix in SAS (SAS Institute Inc., 1996) with guidance from Saxton (1996). The PDIFF option ($p \leq 0.05$) was used to separate significantly different least-squares means.

Table 5—Analysis of variance for sensory evaluation of doughnuts

Source	Degrees of freedom	Error term
OILTYPE	3	
WEEK	1	
OILTYPE X WEEK	3	for OILTYPE
TIME	1	
PAN(TIME)	47	
TIME X OILTYPE	3	
WEEK X OILTYPE X TIME	3	for TIME and TIME X OILTYPE
PAN (TIME X OILTYPE X WEEK)	767	resisual

Sample Preparation and Presentation

Doughnuts for sensory evaluation were taken from the second (earlier) and fourth (later) days of frying in the different oils for each replication. For each replication and day, each of 48 doughnuts fried in each oiltype were cut into one-third equal portion sizes, mixed by type, identified using 3-digit random numbers and presented for evaluation on the same day on which they were fried. Doughnuts were evaluated within 5 hr from the time of preparation.

Each of the 48 panelists received 4 doughnut samples, one from each of the oils. The order of presentation was balanced. Each doughnut sample was evaluated separately from the others on the sensory attributes mentioned above, using the scorecard shown on Appendix B-1. Sensory evaluation was conducted in individual booths under white fluorescent lighting, in the sensory laboratory, Department of Food Science and Technology, at The University of Tennessee, Knoxville. Panelists were asked to rinse with spring water between samples to

minimize taste/flavor carry over.

Panelists rated the crust color, flavor and overall acceptability on a 9-point hedonic scale where 1=extremely dislike/unacceptable and 9=extremely like/acceptable (Appendix B-1). On the same scorecard (Appendix B-1), panelists evaluated the intensity of doughnut crust color and (mouthfeel) greasiness, with 1- and 9- values being light brown and dark brown and not at all greasy and extremely greasy, respectively. On a separate questionnaire, panelists were also asked to indicate how often they consumed yeast-raised doughnuts. In addition, panelists were asked to score the "ideal" doughnut crust color on a 9-point intensity scale where the value of 1 was designated as light brown and 9 as dark brown (Appendix B-2). Panelists also were asked to score their ideal doughnut mouthfeel (greasiness) on a 9-point scale anchored at the value of 1 being "not at all greasy", and 9 being "extremely greasy". Furthermore, panelists were asked to describe the flavor of the samples using their own descriptors. This was optional and open-ended.

CHAPTER IV

RESULTS AND DISCUSSION

QUALITY OF FRESH OILS

Table 6 shows some of the characteristics of the processed fresh frying oils used in this study, as supplied by their processors. High oleic sunflower oil, SUN-HO® (HOS) from the USA, was used in the study because of its possible application to Swaziland's small scale food vendor frying operations. Regular sunflower oil, TEM-TEX® (RCO), also from the USA, was selected because of its similarity (at least in basic composition) to the oil being produced and processed on a pilot scale at Ngculwini (a rural area in Swaziland). Refined sunflower oil, SUNVALLEY® (SVS), from South Africa is a processed regular sunflower oil recommended for household and small-scale frying operations. Refined SUNOL® (SOS), a blend of corn oil and regular sunflower oil, from South Africa, is recommended for deep-frying on a "moderate to large-scale". The latter two oils were selected for the present study because they represent the oils currently available in Swaziland's retail outlets/markets, and those purchased by small and large snack/fast food operators in Swaziland. As can be seen in Table 6, oils processed in South African could be redder and have a higher FFA level and peroxide value than oils processed in the United States.

Table 6—Chemical and physical characteristics of the four fresh, unused oils

	OILTYPE[a]			
Characteristics	SUN-HO® (HOS)	TEM-TEX® (RCO)	SUNOL® (SOS)	SUNVALLEY® (SVS)
Lovibond red	1.50	1.00	4.00[b]	4.00[b]
FFA (% oleic acid)	0.05	0.05	0.10	0.10
Iodine Value	85.00	135.00	128.00[c]	128.00[c]
PV (meq/Kg)	1.00	1.00	2.00	2.00
Fatty Acid Composition (%)[d]				
C16:0	6.60	6.10	6.60	6.50
C18:0	4.00	2.80	5.10	5.50
C18:1	79.20	18.80	22.10	20.90
C18:2	6.70	69.70	64.80	66.00
C18:3	0.20	0.40	0.10	0.10
C20:0	0.10	0.20	0.30	0.30

[a] TEM-TEX®=regular sunflower oil brand from USA; SUNHO®=high oleic acid sunflower oil brand from USA; SUNOL®=blend of sunflower and corn oils from South Africa; SUNVALLEY®=regular sunflower oil brand from South Africa.
[b] Maximum allowable.
[c] Variable depending on varieties used.
[d] Some of the peaks in fatty acid methyl ester chromatograms for each oil were not identified, but were calculated as part of the percentage of fatty acids present.

CHEMICAL COMPONENTS OF OILS

Tocopherols

Analyses of variance for levels of α- and γ-tocopherols for TIME (sampling time), OILTYPE and their interaction are given in Tables 7 and 8, respectively. The main treatment effects (OILTYPE and TIME) and their interaction were significant for the level of each tocopherol measured in this experiment. Least-squares means (LSMEANS) (n=2) of α- and γ-tocopherol concentrations for each oil at each sampling time and across sampling times (n=14) are shown in Tables 9 and 10, respectively.

When averaged across all sampling times, HOS had the lowest contents of both α- and γ-tocopherols of all oils (Tables 9 and 10), while SOS had the highest concentrations. Oils obtained from South Africa had higher levels of γ-tocopherol than oils from the USA (Table 10). Tocopherols are lost through the oil processing steps of refining, bleaching and deodorization (Sherwin, 1976). Most likely, the processing of the oils, in particular, the deodorization step may have been more rigorous for the HOS and RCO oils obtained in the USA than the SOS and SVS oils obtained from South Africa. The significant TIME X OILYTPE interactions for α- and γ-tocopherol (Tables 7 and 8) indicate that during heating of oil and use for frying doughnuts, the concentration levels were affected differently for each oil (Tables 9 and 10).

Tocopherols are heat sensitive (Huang et al., 1994). Heating the oils and frying doughnuts had a profound effect on α- and γ-tocopherol concentrations in all oils, but particularly on the α-isomer in HOS (Table 9). Heating fresh oils reduced α-tocopherol in all oils more than frying doughnuts. Replenishment of used oil with fresh oil, on each frying day, resulted in additional amounts of α-tocopherol (from

Table 7—Mean squares (type III) from the analysis of variance for levels of α-tocopherol (μg/mg) in the four oils[a] sampled when fresh, break-in heated and on each of five consecutive days of frying doughnuts

Source	Df[b]	Mean squares	Type III F-value	Pr>F[c]
WEEK	1	0.0000060		
OILTYPE	3	0.0039577	1319.00	0.0001
OILTYPE X WEEK[d]	3	0.0000030		
TIME	6	0.0004679	311.74	0.0001
OILTYPE x TIME	18	0.0000149	9.82	0.0001
ERROR[e]	24	0.0000015		

[a] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[b] Degrees of freedom.
[c] Probability of greater F-value.
[d] Error term for testing OILTYPE.
[e] Residual error.

Table 8—Mean squares (type III) from the analysis of variance for levels of γ-tocopherol (μg/mg) in the four oils[a] sampled when fresh, break-in heated and on each of five consecutive days of frying doughnuts

Source	Df[b]	Mean squares	Type III F-value	Pr>F[c]
WEEK	1	0.0000033		
OILTYPE	3	0.0011249	535.67	0.0001
OILTYPE X WEEK[d]	3	0.0000021		
TIME	6	0.0000345	11.51	0.0001
OILTYPE x TIME	18	0.0000074	2.49	0.0191
ERROR[e]	24	0.0000030		

[a] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[b] Degrees of freedom.
[c] Probability of greater F-value.
[d] Error term for testing OILTYPE.
[e] Residual error.

Table 9—Least-squares means[a,b,c] of α-tocopherol levels (μg/mg) in each frying oil at each sampling time (fresh, break-in heated and on each of five consecutive days of frying doughnuts)

Oil sampling time	OILTYPE[d]			
	HOS	RCO	SOS	SVS
Fresh	29.35c,x	50.60b,w	56.50a,x	50.20b,w
Break-in	2.73d,y	36.05b,x	40.50a,y	31.00c,z
Frying Day 1	0.24c,yz	33.50b,y	36.85a,z	33.45b,yz
Day 2	0.12c,z	32.10b,yz	37.25a,z	35.90a,xy
Day 3	0.00c,z	31.50b,yz	36.80a,z	34.05a,xy
Day 4	0.00d,z	30.55c,z	40.10a,y	36.20b,x
Day 5	0.36c,yz	33.35b,y	38.25a,yz	35.05b,xy
$\bar{x}$[e]	4.70c	35.40b	40.90a	36.60b

[a] N=2.
[b] LSMEANS within a row followed by unlike letters, a-c, are different ($p<0.05$).
[c] LSMEANS within a column followed by unlike letters, w-z, are different ($p<0.05$).
[d] HOS=high oleic sunflower oil from USA; RCO=regular sunflower oilfrom USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[e] LSMEANS across sampling times (n=14).

Table 10—Least-squares means[a,b,c] of γ-tocopherol levels (μg/mg) in each frying oil at each sampling time (fresh, break-in heated and on each of five consecutive days of frying doughnuts)

Oil sampling time	OILTYPE[d]			
	HOS	RCO	SOS	SVS
Fresh	1.35d,z	5.05c,z	27.45a,w	18.55b,y
Break-in	0.65d,z	4.45c,z	23.65a,x	16.65b,y
Frying Day 1	0.10d,z	3.90c,z	19.85a,y	12.75b,z
Day 2	0.00d,z	3.90c,z	18.40a,yz	12.65b,z
Day 3	0.00d,z	3.60c,z	19.75a,y	11.30b,z
Day 4	0.00d,z	3.45c,z	16.30a,yz	11.30b,z
Day 5	0.00d,z	3.60c,z	14.85a,z	10.50b,z
$\bar{x}$[e]	0.30d	3.99c	20.04a	13.39b

[a] N=2.
[b] LSMEANS within a row followed by unlike letters, a-d, are different ($p<0.05$).
[c] LSMEANS within a column followed by unlike letters, v-z, are different ($p<0.05$).
[d] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[e] LSMEANS across sampling times (n=14).

the fresh oil) that may have helped to maintain the α-tocopherol level in each oil, at a fairly steady level during frying (Table 9). The tendency of α-tocopherol to decrease drastically during the break-in stage, but remain fairly steady during frying, also may have been due to the steam released during frying of doughnuts, acting as a surface protective blanket against air incorporation and light. Alpha-tocopherol levels in HOS were the lowest throughout each sampling period of all oils. At each sampling time, except on days 2 and 3 of frying, SOS had higher α-tocopherol levels than the other oils. RCO, which started off with nearly the same amount of α-tocopherol as SVS, also ended with an equivalent amount. However, at break-in, and on frying days 2, 3 and 4, the α-tocopherol contents in these oils differed significantly (Table 9).

Break-in heating reduced γ-tocopherol levels significantly in HOS, RCO and SOS oils, but not in SVS (Table 10). From the fresh oil stage throughout the heating and doughnut frying, the γ-tocopherol content of each oil differed from each other as follows: HOS < RCO < SVS < SOS. However break-in heating and frying doughnuts did not affect ($p>0.05$) the γ-tocopherol levels in HOS or RCO. Frying doughnuts for one day in SOS and SVS resulted in additional significant decreases in γ-tocopherol contents, but continued frying of doughnuts had no further effect on γ-tocopherol concentration in any oil except SOS (Table 10). The lack of significant decreases in γ-tocopherol levels in HOS or RCO may have been due to relatively lower amounts initially present in these oils and its relative stability to destruction by heat (Huang et al., 1994). The relative steady levels of γ-tocopherol in each oil during frying of doughnuts, most likely, was due to its replenishment by make-up oil. It is possible also that γ-tocopherol oxidation products (diphenyl ether dimer and biphenyl dimers), which are antioxidants themselves (Miyagawa et al., 1991), may have contributed in some way to the maintenance of

existing γ-tocopherol levels during heating and frying.

Other tocopherols, such as δ-tocopherol were not detectable at the oil sample concentrations used to measure the α- and γ- isomers. These results concurred with those of Carpenter (1979), who found only trace amounts (<0.01 μg/mg) of δ-tocopherol in regular sunflower seed oil varieties.

Total Polar Components

The analysis of variance shows that only the TIME main treatment effect and OILTYPE X TIME interaction significantly affected TPC levels in the different oils (Table 11). Least-squares means (n=2) of TPC levels for each oil at each sampling time, and across sampling times (n=14) are shown on Table 12.

Previously, Romeo et al. (1995) reported lower (3.6-3.8%) TPC levels in a fresh high oleic acid oil brand (VIPA®) than the one found in the high oleic oil brand (SUN-HO®) used in this study (Table 12). The differences in content may be due to different sunflower varieties, or differences in processing techniques. TPC levels in HOS, RCO, SOS and SVS were similar at each sampling time (Tables 11 and 12) indicating overall similarity in the degree of stability among the oils. Generally, the break-in heating increased the level of TPC in each oil significantly. Additionally, frying doughnuts on the first day resulted in a significant increase in TPC levels in HOS, RCO and SOS but not in SVS. On days 2 and 3 of frying doughnuts, the TPC levels in HOS, RCO and SOS did not change significantly whereas TPC level continued to increase in SVS. The results on HOS were generally comparable to those of Romeo et al. (1995) who reported a significant increase in TPC levels only between 0 and 8 hr and between 8 and 20 hr of repeated frying of potatoes in a high oleic sunflower brand (VIPA®), but found no significant differences after frying for 20 hr and up to after frying for 75 hr.

Table 11—Mean squares (type III) from the analysis of variance for total polar components levels (%) in the four oils[a] sampled when fresh, break-in heated and on each of five consecutive days of frying doughnuts

Source	Df[b]	Mean squares	Type III F-value	Pr>F[c]
WEEK	1	3.5855		
OILTYPE	3	3.7932	5.27	0.1027
OILTYPE X WEEK[d]	3	0.7194		
TIME	6	214.8008	283.81	0.0001
OILYTPE x TIME	18	1.9828	2.62	0.0143
ERROR[e]	24	0.7568		

[a] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[b] Degrees of freedom.
[c] Probability of a greater F-value at.
[d] Error term for testing OILTYPE.
[e] Residual error.

Table 12—Least-squares means[a,b,c] of total polar components levels (%) in each oil at each sampling time (fresh, break-in heated and on each day of five consecutive days of frying doughnuts)

Oil sampling time	OILTYPE[d]			
	HOS	RCO	SOS	SVS
Fresh	5.41a,z	4.53a,z	5.09a,z	6.50a,z
Break-in	8.28a,y	8.06a,y	9.44a,y	9.12a,y
Frying Day 1	10.26a,x	10.05a,x	11.79a,x	9.70a,y
Day 2	12.11a,w	13.14a,w	15.33a,vw	12.18a,x
Day 3	12.87a,w	14.40a,w	14.64a,w	16.58a,w
Day 4	18.22a,v	18.35a,v	16.86a,v	19.09a,v
Day 5	19.68a,v	19.47a,v	20.02a,u	20.94a,u
$\bar{x}$[e]	12.40a	12.57a	13.31a	13.44a

[a] N=2.
[b] LSMEANS within a row followed by unlike letters, a-d, are different ($p<0.05$).
[c] LSMEANS within a column followed by unlike letters, u-z, are different ($p<0.05$).
[d] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend oil from South Africa; SVS=regular sunflower oil from South Africa.
[e] LSMEANS across sampling times (n=14).

Dobarganes et al. (1993) suggested that the slower rate of TPC formation during frying (as opposed to when oils were heated at frying temperatures without food), may be that the food was protective to the oil. These latter researchers also reported TPC were more a product of oxidized and polymeric compounds (oil abuse from heat) than fatty acids or diglycerides (food related).

The lack of significant increases in TPC levels that emerged between some consecutive sampling times was expected because of the dilution effect of daily replenishment with fresh oil. What was not expected however, was that RCO, with a higher degree of unsaturation (Table 6), did not show higher susceptibility to degradation when TPC concentration was the yardstick for monitoring oil quality. In fact the level of TPC in RCO was the same as that in HOS (the most saturated oil) on each frying day (Table 12). Total polar component levels in any oil in this study did not reach the 25-27% cut-off point that has been suggested as criteria for discarding frying oils (Firestone et al., 1991). All oils exhibited good stability under the conditions (simulated to small fast food operators in Swaziland) used in this study.

Dielectric Constant

The main treatment effects (OILYTPE and TIME) and their interaction (OILTYPE X TIME) affected the dielectric constant or FOS (measured by the Food Oil Sensor) of the oils throughout the sampling time (Table 13). Least-squares means (n=2) showing FOS reading for each oil at each sampling time, and across sampling times (n=14) are shown in Table 14.

On frying days 4 and 5, SVS had the lowest ($p<0.05$) FOS readings of all oils (hence lowest change in dielectric constant) (Table

Table 13—Mean squares (type III) from the analysis of variance for the Food Oil Sensor reading in the four oils[a] sampled when fresh, break-in heated and on each of five consecutive days of frying doughnuts

Source	Df[b]	Mean squares	Type III F-value	Pr>F[c]
WEEK	1	0.01858		
OILTYPE	3	0.24132	19.05	0.0186
OILTYPE X WEEK[d]	3	0.01267		
TIME	6	3.94023	673.95	0.0001
OILTYPE x TIME	18	0.01740	2.98	0.0068
ERROR[e]	24	0.00585		

[a] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS= regular sunflower-corn oil blend from South Africa; SVS= regular sunflower oil from South Africa.
[b] Degrees of freedom.
[c] Probability of a greater F-value.
[d] Error term for testing OILTYPE.
[e] Residual error.

Table 14—Least-squares means[a,b,c] of the Food Oil Sensor reading in each oil at each sampling time (fresh, break-in heated and on each of five consecutive days of frying doughnuts)

Oil sampling time	OILTYPE[d]			
	HOS	RCO	SOS	SVS
Fresh	0.00a,z	0.00a,z	0.00a,z	0.00a,z
Break-in	0.79b,y	0.98a,y	0.85ab,y	0.86ab,y
Frying Day 1	1.35b,x	1.57a,x	1.30bc,x	1.15c,x
Day 2	1.45c,x	1.81a,w	1.65b,w	1.35c,w
Day 3	1.68b,w	1.95a,vw	1.85a,v	1.63b,v
Day 4	1.85b,v	2.10a,uv	2.00ab,v	1.65c,v
Day 5	2.00a,v	2.13a,u	2.00a,v	1.75b,v
$\bar{x}$[e]	1.30bc	1.51a	1.38b	1.19c

[a] N=2.
[b] LSMEANS within a row followed by unlike letters, a-c, are different ($p<0.05$).
[c] LSMEANS within a column followed by unlike letters, u-z, are different ($p<0.05$).
[d] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[e] LSMEANS across sampling times (n=14).

14). The across sampling time least-squares means of FOS reading for each oil show that SVS had the lowest FOS reading among all oils except HOS. The mean FOS readings across sampling time indicate that the stability of oils to degradation were SVS ≥ HOS ≥ SOS > RCO.

FOS readings of 3.7-4.0 reported by Al-Kahtani (1991) and Smith et al. (1986), and of 3.1-3.5 reported by Firestone et al. (1991) were shown to correspond to 25-27% and 27-29% TPC, respectively. As reported previously, TPC levels of 25-27% in frying oils have been recommended as the point at which they should be discarded (Firestone et al., 1991). However, in this study none of the oils used in frying doughnuts for 4 hr, daily over 5 consecutive days had FOS readings that came close to those which correspond to TPC levels recommended for discarding frying oil (Table 14). According to Firestone et al. (1991), this meant that after frying yeast-raised doughnuts for 4 hr daily, over 5 days, HOS, RCO, SOS and SVS were still of suitable quality for continued frying.

The increases in FOS readings were greatest when the fresh oils were break-in heated and also during the first day of doughnut frying (Table 14). After day 1 of frying, the daily increase in FOS reading for SOS and SVS was gradual but significant up to Day 3 of frying, then it leveled off from day 3 to day 5 of frying. FOS reading increased fairly steadily with incrasing days of frying in HOS and RCO, however, some daily increases were not significant.

Conjugated Dienes

The main treatment effects (OILTYPE and TIME) and their interaction (OILTYPE and TIME) significantly affected the level of conjugated dienoic acids in the oils during heating and frying of doughnuts as shown by the analysis of variance in Table 15. Least-squares means (n=2) showing the degree of conjugated diene formation (as

Table 15—Mean squares (type III) from the analysis of variance for conjugated dienes levels in the four oils[a] sampled when fresh, break-in heated and on each of five consecutive days of frying doughnuts

Source	Df[b]	Mean squares	Type III F-value	Pr>F[c]
WEEK	1	0 0072004		
OILTYPE	3	0.0795327	135.02	0.0011
OILTYPE X WEEK[d]	3	0.0005891		
TIME	6	0.0256737	28.82	0.0001
OILTYPE x TIME	18	0.0034962	3.65	0.0018
ERROR[e]	24	0.0009573		

[a] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[b] Degrees of freedom.
[c] Probability of a greater F-value.
[d] Error term for testing OILTYPE.
[e] Residual error.

measured by absorbance at 233 nm) in each oil at each sampling time, and across sampling times (n=14) are presented in Table 16.

Averaged across sampling times, the conjugated dienoic acid level (expressed as absorbance values at 233 nm) for HOS was significantly lower ($p<0.05$) than those in RCO, SOS and SVS (Table 16). Since conjugation of double bonds occurs at higher rates in heated frying oils that have appreciably high amounts of linoleic acid (Gray, 1978; White, 1991), the lower content of conjugated dienes in the high oleic acid oil (HOS) was expected. There was no significant difference in the level of dienes between RCO and SOS at each sampling time. RCO had higher dienes levels on days 2, 4 and 5 than SVS or HOS, while SOS had a higher degree of conjugated dienes than SVS or HOS on day 3 (Table 16). The higher α-tocopherol content (Table 9 and 10) in SOS than in either RCO or SVS did not show any advantage in minimizing conjugated dienoic formation. In fact, conjugated dienes were significantly lower in SVS than in SOS. Perhaps, as suggested by Huang et al. (1995), the higher α-tocopherol content in SOS initially induced prooxidation of the oil, resulting in a situation where the formation of conjugated dienes was more favorable.

All fresh oil samples had similar absorbance values at 233 nm (conjugated dienes). It is surprising that the fresh HOS had as much conjugated dienes as the other oils which were much higher in linoleic acid (Table 6). The levels of conjugated dienes in all frying oils did change significantly during break-in heating indicating a significant oxidation of linoleic acid. Throughout the frying time, however, HOS and SVS showed no change in the absorbance value, indicating no change in the level of conjugated dienoic acids as a result of frying doughnuts. After break-in heating, the level of conjugated dienes in RCO and SOS remained fairly stable, but the level of dienes on day 2 of frying in RCO was higher than in RCO after break-in heating and the diene level in SOS on day 5 was higher than on day 4.

Table 16—Least-squares means[a,b,c] of conjugated diene levels in each oil at each sampling time (fresh, break-in heated and on each of five consecutive days of frying doughnuts)

Oil sampling time	OILTYPE[d]			
	HOS	RCO	SOS	SVS
Fresh	0.202a,z	0.206a,z	0.210a,z	0.205a,z
Break-in	0.268b,y	0.356a,y	0.389a,y	0.354a,y
Frying Day 1	0.233b,yz	0.408a,xy	0.387a,y	0.358a,y
Day 2	0.217c,yz	0.459a,x	0.413ab,xy	0.385b,y
Day 3	0.229c,yz	0.401ab,xy	0.437a,xy	0.350b,y
Day 4	0.229c,yz	0.427a,x	0.388ab,y	0.333b,y
Day 5	0.198c,z	0.452a,x	0.454a,x	0.352b,y
$\bar{x}$[e]	0.225c	0.387a	0.382a	0.334b

[a] N=2.
[b] LSMEANS within a row followed by unlike letters, a-c, are different ($p<0.05$).
[c] LSMEANS within a column followed by unlike letters, x-z, are different ($p<0.05$).
[d] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[e] LSMEANS across sampling times (n=14).

This trend was probably attributable to the addition of fresh oil (replenishment). The levels of tocopherols, mainly α-tocopherol, present in RCO, SOS and SVS (Table 9), also may have hindered conjugated diene formation during frying (Huang et al., 1995). Other factors that could possibly explain the little change that occurred in conjugated diene during frying are that the dienes may have reacted further to produce polymers at the same rate they were formed (Al-Kahtani, 1991; Yoon et al., 1985) and that frying of food was less stressful to the oil than heating alone.

Free Fatty Acids

Free fatty acid (FFA) levels in the oils were significantly affected by only the TIME treatment and not by OILTYPE or the interaction (Table 17). Least-squares means (n=8) of FFA levels averaged across oils and replication for each sampling time appear in Fig. 3. Overall, FFA levels in the oils increased progressively with break-in heating and on each day of frying (Fig. 3).

The biggest increase in FFA content occurred in all oils during the first day of frying doughnuts. This increase, may have been due to the moisture in the doughnuts inducing hydrolysis of the triglyceride molecule in addition to FFA being formed by thermal oxidation (Melton et al., 1994). The FFA levels in this study were, however, very low, well below the 2.5% which is the general recommended cut-off point for a deteriorated oil/fat to be discarded (DuPlessis and Marais, 1995; Firestone, 1993). Averaged across sampling time (n=14), the FFA levels in HOS, RCO, SOS and SVS were 0.066, 0.058, 0.067 and 0.062% oleic acid, respectively.

Table 17—Mean squares (type III) from the analysis of variance for free fatty acids levels as % oleic acid in the four oils[a] sampled when fresh, break-in heated and on each of five consecutive days of frying doughnuts

Source	Df[b]	Mean squares	Type III F-value	Pr>F[c]
WEEK	1	0.0002284		
OILTYPE	3	0.0002594	3.94	0.1447
OILTYPE X WEEK[d]	3	0.0000658		
TIME	6	0.0086748	380.83	0.0001
OILTYPE x TIME	18	0.0000419	1.84	0.0816
ERROR[e]	24	0.0000228		

[a] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[b] Degrees of freedom.
[c] Probability of a greater F-value.
[d] Error term for testing OILTYPE.
[e] Residual error.

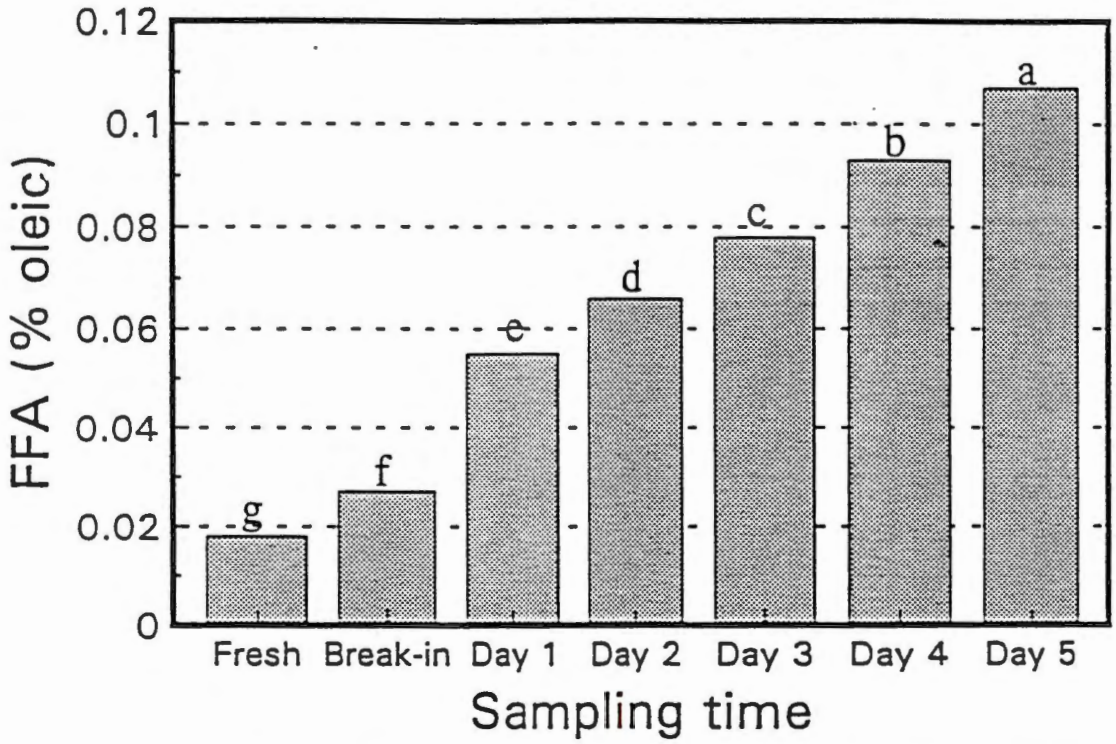

Fig. 3--Least-squares means (n=8) of FFA levels (% oleic acid) averaged across oils for each sampling time (fresh, break-in heated, and each day of five consecutive days of frying doughnuts); bars with unlike letters differ ($p<0.05$).

Fatty Acid Composition and C18:2/C16:0 Ratio

The fatty acid composition of each fresh, unused frying oil is presented in Appendix C. Six fatty acids, palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2), linolenic (C18:3) and arachidic (C20:0) were identified and measured in the different frying oils. HOS contained the highest level of C18:1 as expected, while RCO contained the most C18:2. The most abundant fatty acid in the South African oils, SOS and SVS, was C18:2. Although these latter oils differ in constituent oil source, there was little difference in their fatty acid composition. The fatty acid composition of each oil analyzed in this study was similar to that reported by the respective oil processors (Table 6). The higher levels of C16:0 and C18:1 in the South African oils than in RCO might have been due to addition of small amounts of palm olein (rich in C16:0 and C18:1), to the oils to impart fry life stability (DuPlessis, 1996). However, the differences in fatty acid composition between RCO and the South African SVS oil, may have been also varietal and/or produced by differences in sunflower seed agronomic (mainly climatic) conditions as suggested by Moolayil (1988). The lower levels of saturated fatty acids (C16:0 and C18:0) contents in HOS have been reported by many researchers to be beneficial in combating cardiovascular disease when they are ingested, by lowering serum LDL cholesterol (Best, 1987; Noakes et al., 1996; Yodice, 1990).

The ratio of the weight percentages of C18:2 to C16:0 (C18:2/C16:0 ratio) was calculated for each oil at each sampling time (fresh, break-in heating and on each of five consecutive days of frying doughnuts). The analysis of variance (Table 18), shows that both the main treatment effects (OILTYPE and TIME) and their interaction were significant for the C18:2/C16:0 ratio. The least-squares means for the C18:2/C16:0 ratio in each oil at each sampling time (n=14), and across sampling times (n=14) are presented in Table 19.

Table 18—Mean squares (type III) from the analysis of variance for C18:2/C16:0 ratio in the four oils[a] sampled when fresh, break-in heated and on each of five consecutive days of frying doughnuts

Source	Df[b]	Mean squares	Type III F-value	Pr>F[c]
WEEK	1	0.95944		
OILTYPE	3	221.98973	6021.13	0.0001
OILTYPE X WEEK[d]	3	0.03687		
TIME	6	0.96024	24.24	0.0001
OILTYPE X TIME	18	0.09684	2.44	0.0210
ERROR[e]	24	0.03961		

[a] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[b] Degrees of freedom.
[c] Probability of a greater F-value.
[d] Error term for testing OILTYPE.
[e] Residual error.

Table 19—Least-squares means[a,b,c] of C18:2/C16:0 ratio in each oil at each sampling time (fresh, break-in heatied and at each of five consecutive days of frying doughnuts)

Oil sampling time	OILTYPE[d]			
	HOS	RCO	SOS	SVS
Fresh	2.4c,y	12.2a,w	9.8b,x	10.2b,w
Break-in	2.2c,yz	11.3a,y	9.5b,xy	9.7b,x
Frying Day 1	2.0c,yz	11.3a,y	9.2b,yz	9.5b,xy
Day 2	2.1c,yz	11.0a,xy	9.1b,yz	9.0b,z
Day 3	2.0c,yz	10.6a,z	8.8b,z	9.1b,yz
Day 4	2.4c,y	10.9a,yz	8.9b,z	9.0b,z
Day 5	1.9c,z	10.9a,yz	9.0b,z	9.1b,yz
$\bar{x}$[e]	2.1c	11.2a	9.2b	9.4b

[a] N=2.
[b] LSMEANS within a row followed by unlike letters, a-c, are different ($p<0.05$).
[c] LSMEANS within a column followed by unlike letters, w-z, are different ($p<0.05$).
[d] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[e] LSMEANS across sampling times (n=14).

Throughout sampling and averaged across sampling times, RCO had the highest C18:2/C160:0 ratio of all oils while HOS had the lowest, and the C18:2/C16:0 ratio was not different ($p<0.05$) between SOS and SVS. The SOS and SVS C18:2/C16:0 ratios were closest in value to that of RCO. These results were consistent with the amounts of linoleic acid, respectively, present initially in these oils (HOS, RCO, SOS and SVS) (Table 6).

During break-in heating, the C18:2/C16:0 ratio decreased in RCO and SVS oil but not in HOS or SOS (Table 19). Frying doughnuts in SOS on day 1 decreased the ratio from that in the fresh SOS oil but not in the other oils. Further doughnut frying in SOS on days 2-5 did not affect the C18:2/C16:0 ratio. However, the day 3 oil sample of RCO had a lower C18:2/C16:0 ratio than the day 2 sample but no differences existed among the days 3,4 and 5 RCO samples (Table 19).

With increasing use (heating/frying) of the oils, the C18:2/C16:0 ratio decreased but the amount of decrease was dependent on the oil. These observations concurred with those reported by Miller and White (1988), Sebedio et al. (1986), Cuesta et al. (1991) and Tyagi and Vasishtha (1996) who accordingly reported that the magnitude of change in C18:2/C16:0 ratio was dependent on temperature, duration of frying and type of oil, respectively. The finding of the greatest amount of decrease of the C18:2/C16:0 ratio in RCO and the smallest in HOS agreed with that of Al-Kahtani (1991) and Cuesta et al. (1991) who reported that the magnitude of change in the C18:2/C16:0 ratio was dependent on the initial linoleic acid content of the oil. The leveling-off trend observed with TPC, FOS reading or in conjugated dienes, across frying time also was observed in the C18:2/C16:0 ratio. Again, replenishment with fresh oil may have contributed to this trend by increasing C18:2 content and replenishing the α- and γ-tocopherol content especially in RCO, SOS and SVS oils. The contributing factor to the C18:2/C16:0 ratio

stabilization in HOS more likely was the low degree of polyunsaturation in the oil.

Correlations and Summary of Chemical Measurements

The Pearson correlation coefficients (Table 20) were calculated to determine if there were relationships between some of the chemical measurements used to monitor frying oil quality. Correlation coefficients of ≥0.79 were significant ($p<0.05$). These results show a positive correlation ($r=0.79$) between α- and γ-tocopherol isomers as a consequence of heating/frying in the different oils. Although tocopherols work together to enhance each other's performance (Huang et al., 1995), the correlation coefficient between α- and γ-tocopherols also suggest some differences in their destruction rates with continued heating-frying (Madhari et al., 1996). Gamma-tocopherol was correlated negatively ($p<0.05$) to TPC and FOS but not α-tocopherol. Both α- and γ-tocopherols were negatively correlated ($p<0.05$) to FOS and conjugated dienes, but the correlation coefficient with FOS was greater for γ- than α-tocopherol while the conjugated dienes had a higher correlation coefficient with α- then γ-tocopherol. Generally, this strengthens the argument that all tocopherols are essential for controlling various oxidation and decomposition products and as such ought to be present in adequate amounts relative to each other for optimum antioxidant activity (Huang et al., 1996; Madhari et al., 1996).

FFA correlated strongly with TPC and FOS reading but not with conjugated dienes. Conjugated dienes did not correlate significantly with TPC. However, there was a correlation ($p<0.05$) between conjugated dienes and FOS reading. Conjugated dienes are primary oxidation products of linoleic acid oxidation formed by double bond shifts in the fatty acid. However, conjugated dienes, which are polar material, also

Table 20—Pearson correlation coefficients[a,b] of selected chemical characteristics averaged across OILTYPE

	Tocopherol					
	Alpha	Gamma	TPC[c]	FOS[c]	Conjugated dienes	FFA[c]
Gamma-tocopherol	0.79					
TPC	-0.65	-0.94				
FOS	-0.86	-0.98	0.93			
Conjugated dienes	-0.98	-0.82	0.69	0.88		
FFA	-0.63	-0.96	0.99	0.93	0.66	1.00

[a] Correlation coefficient ≥ 0.79 is significant at $p<0.05$ level.
[b] N=7.
[c] TPC=total polar components, FOS=Food Oil Sensor reading (dielectric constant) and FFA=free fatty acids.

may degrade to other polar secondary oxidation products. Thus, the level of conjugated dienes may decrease while the level of TPC in the oils increase (Tables 12 and 16). Also, during oxidation, high oleic acid oils such as HOS produce smaller amounts of conjugated dienes but higher levels of polymers (polar components) than the high linoleic acid oils (RCO, SOS and SVS) (Melton et al., 1994). This may be another reason for the lack of a significant correlation between conjugated dienes and TPC. The dielectric constant (FOS reading) depends on the polar/non polar material ratio (Al Kahtani, 1991), and has been related significantly to TPC in several studies (Augustin et al., 1987; Melton et al., 1994; Stevenson et al., 1984a,b). On the other hand, the significant correlation of FOS with the congugated diene level indicates that perhaps these latter products contribute more to the dielectric constant of an oil than do some of the secondary oxidized polar products. These correlations, however, do show that FOS, which is related ($p<0.05$) to all chemical characteristics in the present study used to measure oil degradation, may be the best predictor of those characteristics for oil stability.

COLOR MEASUREMENT OF FRYING OILS

The mean squares (type III) from the analyses of variance for Hunter color *L, a, b and ΔE* values are presented in Tables 21, 22, 23 and 24, respectively. OILTYPE treatment effects were not significant for any of the Hunter color values. TIME was significant for all of the color values of the oils. The interaction (OILTYPE X TIME) was significant for only the Hunter *b*- (yellowness) and ΔE values.

While no differences ($p<0.05$) in Hunter *L* (lightness), *a*- (greenness) and ΔE (color difference) were found among the oils when

Table 21—Mean squares (type III) from the analysis of variance for *L*-values (lightness) in the four oils[a] sampled when fresh, break-in heated and on each of five consecutive days of frying doughnuts

Source	Df[b]	Mean squares	Type III F-value	Pr>F[c]
WEEK	1	6.11822		
OILTYPE	3	1.67146	3.36	0.1729
OILTYPE X WEEK[d]	3	0.49702		
TIME	6	35.48060	12.19	0.0001
OILTYPE x TIME	18	3.91178	1.34	0.2462
ERROR[e]	24	2.91133		

[a] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[b] Degrees of freedom.
[c] Probability of a greater F-value.
[d] Error term for testing OILTYPE.
[e] Residual error.

Table 22—Mean squares (type III) from the analysis of variance for Hunter *a*-value (greenness) in the four oils[a] sampled when fresh, break-in heated and on each of five consecutive days of frying doughnuts

Source	Df[b]	Mean squares	Type III F-value	Pr>F[c]
WEEK	1	0.00362		
OILTYPE	3	4.05053	4.77	0.1158
OILTYPE X WEEK[d]	3	0.84847		
TIME	6	29.63228	164.71	0.0001
OILTYPE x TIME	18	0.28397	1.58	0.1467
ERROR[e]	24	0.17991		

[a] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[b] Degrees of freedom.
[c] Probability of a greater F-value.
[d] Error term for testing OILTYPE.
[e] Residual error.

Table 23—Mean squares (type III) from the analysis of variance of Hunter *b*-value (yellowness) in the oils[a] sampled when fresh, break-in heated and on each of five consecutive days of frying doughnuts

Source	Df[b]	Mean squares	Type III F-value	Pr>F[c]
WEEK	1	4.3569		
OILTYPE	3	126.1562	8.55	0.0557
OIL X WEEK[d]	3	14.7549		
TIME	6	456.8535	225.38	0.0001
OILTYPE x TIME	18	5.3522	2.64	0.0137
ERROR[e]	24	2.0270		

[a] HOS=high oleic acid sunflower oil from USA; RCO=regular oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[b] Degrees of freedom.
[c] Probability of a greater F-value.
[d] Error term for testing OILTYPE.
[e] Residual error.

Table 24—Mean squares (type III) from the analyses of variance for ΔE (color difference) in the four oils[a] sampled when fresh, break-in heated and on each of five consecutive days of frying doughnuts

Source	Df[b]	Mean squares	Type III F-value	Pr>F[c]
WEEK	1	8.0524		
OILTYPE	3	94.7568	5.74	0.0925
OILTYPE X WEEK[d]	3	16.5018		
TIME	6	312.8452	120.04	0.0001
OILTYPE X TIME	18	7.2319	2.77	0.0173
ERROR[e]	24	2.6062		

[a] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[b] Degrees of freedom.
[c] Probability of a greater F-value.
[d] Error term for testing OILTYPE.
[e] Residual error.

separated by the PDIFF option (SAS Institute, Inc. 1985), some differences ($p<0.05$) were found in the *b*-values (yellowness) when least-squares means were separated among oils on each sampling time and across sampling times. In the fresh oils, SOS and SVS had a higher *b*-value than did HOS or RCO, and RCO had a lower *b*-value then SOS on days 3, 4 and 5 of sampling and also when averaged across sampling time. The color difference in the fresh oils was expected since the allowable Lovibond red color numbers in the fresh oils (Table 6) were lower in HOS and RCO than they were in either SOS or SVS. Also, fresh SOS and SVS appeared to have darker, more yellow color than HOS or RCO suggesting the possibility of a higher concentration of carotenoid pigments in the South African oils. The significantly lower *b*-values in fresh HOS and RCO versus fresh SOS or SVS (Table 25) may reflect differences in oil processing techniques (particularly the bleaching step) between the USA and South Africa. The bleaching step removes most of the pigments, that is, carotenoids (yellowness), to produce a colorless oil (Brekke, 1990). The *b*-values of HOS and RCO became equal to those of SOS and SVS by the break-in heating period and those of HOS were equivalent to those of SOS and SVS on each subsequent day of frying. The increasing yellow color intensity in the oils with increasing heating/frying is due to the increasing concentrations of oxidized products in the oils. For example, Augustin et al. (1987) reported that darkening (increased color intensity) of oils during heating/frying were related to polymer formation.

Color difference (ΔE) was not significantly different among oils at any sampling time or when averaged across sampling times (Table 26). However, in each oil, the color difference had increased significantly in all oils by break-in heating or by frying day 1. Generally the color difference continued to increase with increasing frying time in each

Table 25—Least-squares means[a,b,c] of Hunter *b*-value of the different oils taken at each sampling time (fresh, break-in heated and on each of five consecutive days of frying doughnuts)

Oil Sampling time	OILTYPE[d]			
	HOS	RCO	SOS	SVS
Fresh	7.1b,z	7.5b,z	14.5a,z	16.2a,z
Break-in	12.8a,y	7.3a,z	13.2a,z	10.9a,y
Frying Day 1	16.3a,x	13.7a,y	19.4a,y	17.7a,y
Day 2	21.6a,w	17.6a,x	24.2a,x	20.9a,x
Day 3	22.9ab,w	21.1b,w	28.3a,w	25.0ab,w
Day 4	27.5ab,v	23.2b,vw	31.3a,v	28.0ab,v
Day 5	30.6ab,u	24.7b,v	34.4a,u	30.5ab,v
$\bar{x}$[e]	19.8ab	16.4b	23.6a	21.3ab

[a] N=2.
[b] LSMEANS within a row followed by an unlike letter, a, are different ($p<0.05$).
[c] LSMEANS within a column followed by unlike letters, u-z, are different ($p<0.05$).
[d] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[e] LSMEANS across sampling time (n=14).

Table 26—Least-squares means[a,b,c] of ΔE (color difference) values of the different oils[c] sampled at each sampling time (fresh, break-in heated and at each of five consecutive days of frying doughnuts)

Oil sampling time	OILTYPE[d]			
	HOS	RCO	SOS	SVS
Break-in	6.2a,z	1.1a,z	1.8a,z	5.8a,z
Frying Day 1	9.9a,y	6.7a,y	5.7a,y	3.3a,z
Day 2	14.5a,x	10.8a,x	10.9a,x	6.4a,z
Day 3	16.7a,x	14.8a,w	14.9a,w	9.8a,y
Day 4	21.8a,w	17.0a,vw	17.9a,vw	12.7a,xy
Day 5	25.0a,w	18.3a,v	20.9a,v	15.2a,x
$\bar{x}$[e]	15.7a	11.5a	12.0a	8.9a

[a] N=2.
[b] LSMEANS within a row followed by unlike letters, a-c, are different ($p<0.05$).
[c] LSMEANS within a column followed by unlike letters, u-z, are different ($p<0.05$).
[d] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower from South Africa.
[e] LSMEANS across sampling times (n=12).

oil (Table 26).

Hunter *L*-value, averaged across all oils, decreased across increasing heating/frying time (Table 27) but not significantly with consecutive sampling times. For example, the *L*-value of oils sampled on day 2 of frying doughnuts was less than that of break-in heated oil but not fresh oil. The *L*-value in oils on day 5 was least among all oil samples. The Hunter *a*-value (greenness) on the other hand increased with each sampling period and then levelled off on frying days 4 and 5.

The ultimate purpose to frying oil quality monitoring using these different tools (chemical and physical tests) is to aid in predicting fried food quality. The underlying principle is that degradation and/or decomposition products and their concentration in the frying oil impact (directly and indirectly) on the quality of the fried product. The economic benefit to fried food vendors is to minimize the risk of customer dissatisfaction that can result from accidentally producing a low quality product. Although at the present time these tests may seem sophisticated for Swaziland, they can inform future choices of intermediate oil processing technologies. Additionally, they can be used to develop a criteria for oil quality standards applicable to Swaziland. In the meantime, sensory evaluation the oil and fried food may be the main test for oil quality as is used currently in many other countries in the world today (Firestone, 1993).

SENSORY EVALUATION STUDIES

The mean squares (type III) from the analysis of fixed treatment effects (OILTYPE and TIME) and their interaction, for doughnut crust color intensity, mouthfeel (greasiness), crust color and flavor

Table 27—Least-squares means[a,b] of Hunter *L* (lightness) and *a*-values (greeness) averaged across oils[c] at each sampling time (fresh, break-in heating and on each of five consecutive days of frying doughnuts)

Sampling time	*L*	*a*
Fresh	96.9wx	-2.9u
Break-in	97.5w	-3.6v
Frying Day 1	96.4wxy	-5.3w
Day 2	94.9xy	-6.3x
Day 3	94.1y	-7.0y
Day 4	93.4y	-7.6z
Day 5	91.6z	-7.8z

[a] N=8.
[b] LSMEANS within a column followed by unlike letters, u-z, are different($p<0.05$).
[c] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.

likability, and overall acceptability, appear in Appendix D. Mean (n=48) intensity and hedonic sensory scores and standard deviations for the "ideal" and actual yeast raised doughnut fried in the different oils are presented in Table 28. A histogram showing the frequency of consumption of yeast-raised doughnuts among panelists is shown in Fig. 4.

Analysis of fixed treatment effects showing type III Mean squares (adjusted by using OILTYPE*WEEK and WEEK*OILTYPE*TIME error terms) are in Appendix E. None of the fixed effects or their interaction were significant for doughnut crust color intensity, mouthfeel (greasiness), crust color and flavor likability, and overall acceptability of plain yeast raised doughnuts.

Flavor Hedonic Scores

Generally, the crust flavor likability scores of doughnuts fried in the different oils were at mid-scale on a 9-point hedonic scale with 1 = dislike extremely and 9 = like extremely (Table 28). Mean crust flavor scores of doughnut samples fried in HOS, RCO, SOS and SVS did not differ from each other. The tendency of the doughnut crust flavor scores to fall on mid scale may have been partially due to the infrequency of yeast-raised doughnut consumption by panelists, as illustrated in Fig. 4. Comments from most panelists also showed that a sweeter doughnut was preferred. The standard deviations among oils were similar, indicating similar variability in crust flavor likability of doughnut samples fried in the different oils.

Favorable comments of the crust flavor of doughnuts cooked in HOS included: better than the others, toasted flavor, nutty, buttery, rich aroma, delightful aroma, flavorful; Negative comments included: rancid, burnt, stronger, raw bean, bitter, metallic flavors. From the positive comments, it seems likely that a better tasting doughnut (fried in HOS), with a higher hedonic rating could be produced by sweetening

Table 28—Least-square means and standard deviations[a] of crust color intensity, crust color and flavor likability, mouthfeel (greasiness) and overall acceptability sensory scores for plain, yeast-raised doughnuts cooked in HOS, RCO, SOS and SVS

	Sensory attributes[b]				
OILTYPE[c]	Crust color intensity	Crust color	Crust flavor	Mouthfeel (greasiness)	Overall acceptability
HOS	4.38 ± 1.85	6.29 ± 1.82	4.61 ± 2.19	5.20 ± 2.04	4.68 ± 2.07
RCO	4.41 ± 2.01	6.12 ± 1.89	5.29 ± 1.97	4.68 ± 1.97	5.38 ± 1.95
SOS	5.15 ± 1.85	6.08 ± 1.88	5.28 ± 1.95	4.97 ± 2.10	5.23 ± 1.95
SVS	4.20 ± 1.83	6.42 ± 1.80	5.47 ± 1.96	4.93 ± 1.93	5.39 ± 1.93
"Ideal doughnut"[d]	3.89 ± 1.6			3.16 ± 1.6	

[a] Means averaged across 48 panelists X 2 days X 2 replications (n=192).
[b] 9-point intensity scale: Crust color intensity (1=light brown and 9=dark brown); Mouthfeel (greasiness) (1=not at all greasy and 9=extremely greasy); and a 9-point hedonic scale for crust color and crust flavor likability: (1=dislike extremely and 9=like extremely); Overall acceptability:(1=extremely unacceptable and 9=extremely acceptable).
[c] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.
[d] Means averaged across 48 panelists X 2 days X 2 replications (n=192).

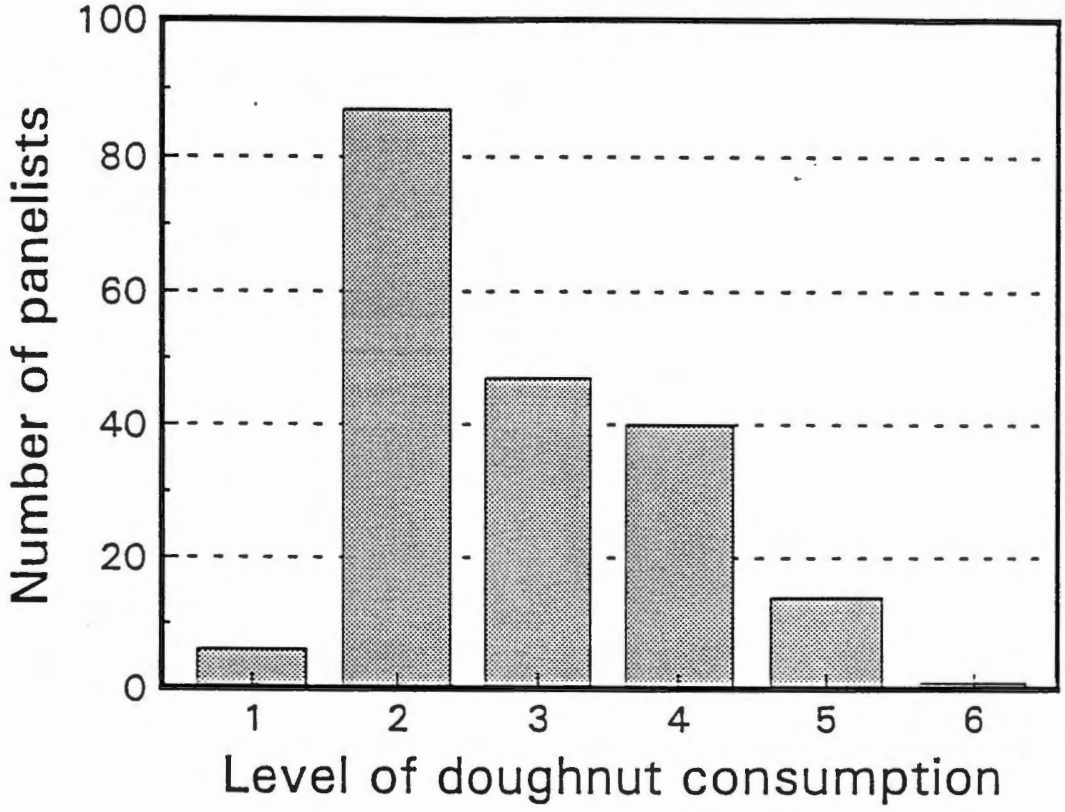

Fig. 4-Histogram showing the relative frequency of consumption of yeast-raised doughnuts among panelists (n=192); with the values of 1=never; 2=less often than once a month; 3=once a month; 4=several times a month; 5=once a week; 6=more than once a week.

the dough or doughnut. Blending HOS with high linoleic acid rich oils such as regular sunflower, has been suggested as a possible technique to improving the flavor profile of foods fried in high oleic acid sunflower oils (Fitch, 1994; Fitch-Haumann, 1996; Frankel and Huang, 1994).

Mouthfeel (greasiness)

The doughnuts fried in any oil seemed to be have a greasier mouthfeel than that considered "ideal" by the panelists (Table 28); however, this is based on comparison of the means and standard deviations only and not on statistical analysis. Doughnut samples fried in HOS, RCO, SOS and SVS were perceived to have the same level of greasiness by panelist. The standard deviations were also similar in this case, indicating similar variability in the perception of greasiness among doughnut samples fried in the different oils. Some panelists described doughnuts cooked in the HOS, as non-greasy, typical, and as having a waxy after eating feeling. This description (waxy), may be explained by the fact that the degree of saturation in HOS was higher than in the other oils; and that doughnut samples were cool when evaluated.

Crust Color of Doughnuts

The doughnuts from the different oils were perceived to have the same crust color intensity (Table 28). These crust color intensity scores (4.20-5.15) corresponded to mean (n=48) crust color likability scores of 6.08-6.42. The panelists liked the crust color of doughnuts fried in the different oils to the same degree.

Overall Acceptability

The mean (n=192) overall acceptability scores of doughnuts fried in the different oil were the same and tended to fall around mid-scale.

The moderate mean ratings on overall acceptability of plain, yeast-raised doughnuts may be attributable to the fact that in general, panelists were used to, and preferred a sweeter tasting doughnut (deduced from written comments). Therefore, from these results we could not say conclusively whether the low acceptability scores could be explained by oil quality/type or by the composition of doughnut system.

Modification in the fatty acid composition of HOS, by blending with linoleic acid rich oils as suggested by Fitch-Haumann (1996) and Frankel and Huang (1994), might enhance its flavor volatile composition and acceptability rating. The volatile oxidation products of linoleic acid, like decadienal isomers and gamma lactones have been reported to impart a desirable fried food flavor (Melton et al., 1994; Snyder and Mounts, 1990). In addition, sweetening the dough might improve the flavor of the doughnuts by producing a sweeter tasting doughnut and/or through an increase in the formation of carbonyl-amine reaction flavor compounds. The apparent lack of differences in all the sensory attributes' ratings for doughnut samples fried on day 2 (earlier) and on day 4 (later), was consistent with:

(1) The levelling-off and/or steady rate of increase that was observed with some chemical indicators (namely: TPC, dielectric constant, conjugated dienes).

(2) The fry-life prolonging effect of oil filtration and daily replenishment with fresh oil.

(3) The fact that, generally, frying oil remains at the optimum stage longer, particularly if it is filtered and frequently replenished with fresh oil.

CHAPTER V

SUMMARY AND IMPLICATIONS

SUMMARY

Deep-fat frying is still the most popular and commonly used method of producing snack and fast foods throughout the world. As much as deep-fat frying and deep-fat fried foods have become equally popular in most developing countries like Swaziland, a disturbing factor is that these countries in most cases, do not produce or process their own frying oils, nor have standards by which to monitor and control frying oil quality. Also, there are no quality standards that specify the critical safety limits of used frying oil. In the rural areas of these countries in particular, where the incomes are substandard, and doughnut vendoring the typical way of generating income, the cost of imported frying oils may be too high to enable the production of high quality, low cost and safe products. There is need to find a frying oil source that can be produced and processed locally, which has a fairly stable fry life. In addition, there is need to develop a better understanding of the frying process (even among small fried food operators in rural Swaziland), in order to optimize the oil's fry life, and also ensure the production of a high quality and safe product.

Regular and high oleic sunflower varieties as sources of frying oil for these communities, show promise because of their high tocopherol content and low unsaturation, respectively - both of which confer stability to frying oils. In fact, the case becomes stronger in the wake of growing health concerns over hydrogenation; and that

hydrogenation technology as well as that of treatment of oil with artificial antioxidants is unavailable in most developing countries like Swaziland. Additionally, the idea that high oleic sunflower oil has been shown to possess properties beneficial to health adds more weight in favor of its adoption as the alternative oil for rural communities.

In our study, it was clear that certain chemical or physical measurements were better predictors of quality for one type of oil compared with another. Conjugated diene level and linoleic acid: palmitic acid (C18:2/C16:0) concentration ratio appeared to be of less value in evaluating the stability (or degradation) of high oleic sunflower oil (HOS) than oils rich in linoleic acid (RCO, SOS and SVS). However, frying yeast-raised doughnuts intermittently in SUN-HO® (HOS) and in the other oils, for 4 hr per day over 5 consecutive days, produced a definite pattern in percentage TPC and in FOS reading. In addition, when used oil was replenished with new oil, TPC and FOS reading seemed to respond, indicating that TPC and FOS reading were sensitive (hence reliable) indicators of change that may be occurring in the oils used in this study. Also, TPC correlated highly with FOS reading.

High oleic sunflower oil (HOS) which together with RCO was less yellow than SOS and SVS when fresh, changed more in ΔE-value than did other oils (except SOS on days 4 and 5), largely due to the changes in the *b*-value (yellowness). The high sensitivity of this parameter (color) to changes occurring to HOS during frying might make it a better predictor of quality in this type of oil, particularly for use by small fried food operators in Swaziland where color adsorbents are not likely to be used due to their cost.

Free fatty acid analysis showed that HOS had similar hydrolytic stability to that of other oils under the frying conditions used in this study. Free fatty acids also had a strong inverse correlation with γ-

tocopherol concentration, indicating a rapid destruction of γ-tocopherol with an increase in FFA level. Also, FFA correlated strongly with FOS reading (r=0.93) and TPC (r=0.99).

The low initial amounts of α- and γ-tocopherol seemed to be insufficient to carry HOS oil throughout the heating/frying periods used in this study. In addition these tocopherols seemed to be destroyed at a faster rate in HOS. These observations may be responsible for the development of deleterious flavor volatiles, perhaps from oleate oxidation products, that have been associated with foods fried in high oleic acid sunflower oils. However, the stability of HOS as a frying medium compared very favorably to either SOS or SVS.

The degree of likability of crust color and crust flavor, mouthfeel (greasiness) and overall acceptability of plain yeast-raised doughnuts fried in HOS was given an equal rating to that of doughnuts fried in the other oils. The overall mediocre acceptability ratings of doughnuts from the oils may have reflected panelists' response to the plain yeast-raised doughnuts rather than the oil per se. In view of the similarity and similar variability in the sensory scores of doughnuts fried in the different oils, it is clear that HOS as an alternative frying oil to SOS or SVS compared very favorably.

IMPLICATIONS

High oleic sunflower oil, as an alternative frying oil (for the production of fried snack foods like doughnuts) for Swaziland appeared competitive (in terms of thermal stability and sensory quality) when compared with counterpart oils, SOS and SVS. In this regard, HOS merits consideration for application as one of the main oils to be produced and processed in Swaziland. However, blending high oleic sunflower oils

with regular sunflower oil will be necessary to achieve an oil with an attractive vitamin E, essential linoleic acid, flavor and health profile.

A major limitation of the study was, not being able to further analyze constituent/individual polar components and polymer content in the respective oils. This analysis would have provided information on the pattern and/or magnitude in which these compounds are formed in the various oils and, hence, serve to further inform the process of blending high oleic acid sunflower oils with other oils with a different fatty acid composition.

Daily replenishment with fresh make-up oil is good for prolonging the fry life of a degrading oil. However, the frequency and/or point at which it should be done must be determined for each oil. This will help minimize unnecessary waste of fresh oil (over replenishment).

Tocopherols are essential and crucial from the point of view of imparting thermo-stability to oil during frying, minimizing excessive oxidation of oleic and linoleic acids to minimize premature and excessive formation of deleterious compounds. Future studies should investigate additional factors that may be responsible for its rapid loss in HOS oils, if indeed that is the case. Different doughnut formulations with differing degrees of sugar and flavoring/flavor ingredients need to be investigated to elucidate the formulation that produces optimum sensory qualities in doughnuts fried in HOS oils.

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APPENDICES

Appendix A

Ingredient list of potato flour yeast-raised doughnut doughs
(Robert Orr Sysco, Knoxville, TN)

Enriched flour (flour, niacin, enzyme, iron as ferrous sulfate, thiamine mononitrate, riboflavin), Water, Corn syrup, Skim milk, Whey, Yeast, partially hydrogenated soybean oil. Contains less than 2% of the following: Dextrose, salt, eggs, leavening (baking soda, sodium acid pyrophosphate, monocalcium phosphate), Mono- and diglycerides, wheat gluten, sodium stearoyl lactylate, potato flour, partially hydrogenated cottonseed oil, ammonium sulfate, calcium sulfate, ascorbic acid, azodicarbonamide, artificial flavor, colored with beta carotene

Appendix B-1

Plain yeast-raised doughnut score card

Judge:____

Rate each of four yeast-raised plain doughnuts by placing an X across the line segment that represents the intensity of the sensory characteristics or best expresses how well you like the sensory characteristics of the sample. Please rinse your mouth between samples.

Sample:_____

1. Crust Color: ___ ___ ___ ___ ___ ___ ___ ___ ___
   Light brown — Dark brown

2. Crust Color: ___ ___ ___ ___ ___ ___ ___ ___ ___
   Dislike extremely — Like extremely

3. Crust Flavor: ___ ___ ___ ___ ___ ___ ___ ___ ___
   Dislike extremely — Like extremely

4. Mouthfeel (greasiness): ___ ___ ___ ___ ___ ___ ___ ___ ___
   Not at all greasy — Extremely greasy

5. Overall Acceptability: ___ ___ ___ ___ ___ ___ ___ ___ ___
   Extremely unacceptable — Extremely acceptable

Please describe the flavor of this sample_____
_____
_____.

Comments:_____
_____
_____.

Appendix B-2

Frequency of doughnut consumption and "ideal" doughnut crust color intensity and mouthfeel (greasiness) questionnaire.

1. Please indicate how often you eat yeast-raised doughnuts

____ Never

____ Less than once a month

____ Once a month

____ Several times a month

____ Once a week

____ More than once a week

2. On the scale provided please indicate by placing an X on the line segment that best describes the "ideal" yeast-raised plain doughnut for each of the characteristics.

Crust color: ___ ___ ___ ___ ___ ___ ___ ___ ___

Light brown — Dark brown

Mouthfeel (greasiness): ___ ___ ___ ___ ___ ___ ___ ___ ___

Not at all greasy — Extremely greasy

Appendix C

Fatty acid composition[a] in fresh unused HOS, RCO, SOS and SVS

	OILTYPE[b]			
Fatty acid (%)	HOS	RCO	SOS	SVS
Unknown < C16:0	6.60	-	-	-
Palmitic	2.80	5.80	6.60	6.50
Stearic	3.00	4.00	5.10	5.50
Oleic	79.20	18.30	22.10	20.90
Linoleic	6.70	70.70	64.80	66.00
Linolenic	0.20	0.10	0.10	0.10
Arachidonic	0.20	0.10	0.30	0.30
Unknown > C20:0	1.10	1.00	1.10	0.80

[a] Analyzed by gas chromatography; average of 2 replications.
[b] HOS=high oleic acid sunflower oil from USA; RCO=regular sunflower oil from USA; SOS=regular sunflower-corn oil blend from South Africa; SVS=regular sunflower oil from South Africa.

Appendix D

Mean squares (type III) from the analysis of FIXED effects for the sensory characteristics of doughnuts fried in the four different oils[b]

Sensory attribute[b]	Source	Df[c]	Mean squares	Type III F-value	Pr>F[d]
Crust color intensity	OILTYPE	3	4.31847	1.52	0.3697
	TIME	1	0.11364	0.04	0.8497
	OIL*TIME	3	1.42055	0.50	0.7000
	ERROR	767	2.84111		
Crust color likability	OILYTPE	3	1.61716	0.55	0.6839
	TIME	1	0.00000	0.00	1.0000
	OIL*TIME	3	1.91120	0.65	0.6211
	ERROR	767	2.94029		
Crust flavor likability	OILTYPE	3	21.61121	5.71	0.0931
	TIME	1	4.20113	1.11	0.3519
	OIL*TIME	3	2.83860	0.75	0.5780
	ERROR	762	3.78480		
Mouthfeel	OILTYPE	3	8.56205	2.48	0.2375
	TIME	1	6.49059	1.88	0.2423
	OIL*TIME	3	2.10599	0.61	0.6417
	ERROR	767	3.45244		
Overall acceptability	OILTYPE	3	20.99923	6.13	0.0853
	TIME	1	4.72740	1.38	0.3058
	OIL*TIME	3	3.52842	1.03	0.4673
	ERROR	766	3.42565		

[a] N=48 (48 panelists, 2 days, 2 replications and 4 oiltypes).
[b] CCI=crust color intensity; CCP=crust color likability; CFP=crust flavor likability; MFP=mouthfeel (greasiness) likability; OAA=Doughnut overall acceptability.
[c] Degrees of freedom.
[d] Probability of a greater F-value at $p<0.05$.

VITA

Sabina Mbuso Silaula was born in Mbabane, Swaziland, on August 12, 1955. She received her elementary and secondary education at Mater Dolorosa School in Mbabane and graduated from Swazi National High School, Kwaluseni Swaziland in 1974. In 1976 she graduated with an associate degree in Home Economics from the University of Botswana Lesotho and Swaziland. Subsequently, she worked as a home economics extension agent in rural Swaziland. In 1978, she joined the University of Botswana and Swaziland (UBS) as a laboratory technician in Foods and Nutrition, Program Planning and Evaluation and Child Development.

In 1979, under an UN/FAO scholarship she studied and graduated in 1981 with a Bachelors of Science degree in Family Resources with a major in Human Nutrition from West Virginia University USA. She returned to Swaziland to assume an assistant instructor position at UBS. In 1982, she returned to the USA under a USAID scholarship to pursue a Master of Science degree in Foods and Nutrition at Michigan State University. After she graduated in 1985, she returned to the University of Swaziland (UNISWA) to assume a lecturer position in Foods and Nutrition. In 1986, she served as chairperson of the department of Home Economics in addition to her teaching responsibilities, and served in this capacity until 1992. December, 1992, she returned to the USA under the W.K. Kellogg Foundation fellowship, to pursue a doctoral program in Food Science and Technology at The University of Tennessee Knoxville, Tennessee.

In 1990 she was nominated a W.K. Kellogg Foundation Fellow in a Kellogg International Leadership Program (KILP). The author is also a member of the Gamma Sigma Delta and Phi Kappa Phi Honor societies, Swaziland Nutrition Council, Swaziland Home Economics Association, Africa Home Economics Association, American Oil Chemists Society and Institute of Food Technologists.

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