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Jose Arnaldo Gerde
Iowa State University

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Frying performance of soybean oils with reduced linolenate content and methods to monitor deteriorative changes

by

Jose Arnaldo Gerde

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Program of Study Committee:
Pamela White, Major Professor
Lawrence Johnson
Linda Pollak

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ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
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To my father, my mother, and my brother

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Abstract

The performance during frying of three expeller-pressed physically refined soybean oils with different contents of linolenic acid (ULL, 1.5%; LL, 2.6%; control, 5.2%) was tested. French fries were fried in a commercial-like setting for 6 hr/day during 23 consecutive days. There were no significant differences in color or in polar material content. The amount of conjugated dienoic acids was higher in the control than in both ULL and LL oils throughout the frying process. Free fatty acid levels were not different among the oils until day 14, after which ULL was higher than the control for the remainder of frying. There were no differences in painty, buttery, and potato flavors, but the control had higher sensory scores for rancid flavor. NIR spectroscopy calibrations were developed to determine free fatty acids, conjugated dienes and total polar materials as methods to reduce time and chemical waste in frying oil quality determinations.

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General Introduction

Frying is one of the most important processes in the food industry because it has several advantages over other cooking methods. Food is cooked quickly and the flavor and other sensory attributes developed during this process give the food unique characteristics. These characteristics not only depend on the product that is being fried but on the oil that is used as the frying medium. Oils are subjected to aggressive conditions during the frying process because of the high temperature, and the presence of oxygen, water and other compounds from the food that promote oil degradation. The presence of unsaturated fatty acids increases the breakdown susceptibility of oils.

For many years, hydrogenation seemed to be the solution to the instability problem in polyunsaturated oils such as soybean oil. During this process, *trans* fatty acids isomers are formed. These *trans* fats have recently been found to be associated with health problems including increased risk of coronary heart disease and increased cholesterol levels in human blood serum. Based on these issues, the Food and Drug Administration passed a rule that starting on January 1, 2006 manufacturers had to declare in their product labels the content of *trans* fat. Because of these health concerns the food industry is trying to find healthier alternatives to partially hydrogenated oils. Breeding oil crops with altered fatty acid compositions and implementing oil extraction methods that improve oil stability seem to be the most viable solutions to replacing partially hydrogenated oils in frying operations.

The general objectives of this study were to evaluate the performance of the oils from two soybean cultivars with reduced linolenic acid content during frying, and to use the data from this study to explore and develop a calibration procedure to determine the degree of oil degradation by near-infrared spectroscopy. To achieve these objectives three different expeller-pressed soybean oils, two with reduced linolenic acid content and one commodity oil, were evaluated during the frying of French fries in a commercial-like setting. Aliquots of the oils were taken and analyzed to determine the degree of degradation, and sensory evaluation of the fries was performed by a trained panel. Oil aliquots also were scanned with a near-infrared spectrometer to develop a calibration to determine free fatty acids, total polar material, and conjugated dienoic fatty acid contents.

LITERATURE REVIEW

Lipid Degradation During Frying

Deep-fat frying is one of the most important cooking processes used in the food industry, not only because of the fast cooking process that allows the availability of fresh and ready-to-eat food in just minutes, but also for the desirable flavor and texture characteristics developed during this process. These flavor attributes are the result of the chemical and physical interactions between the food and the frying media (hot oil).

Oxidation is one of the most important deteriorative changes that occur in frying oils. In oils that are being heated this phenomenon comprises five main stages (Fig. 1).

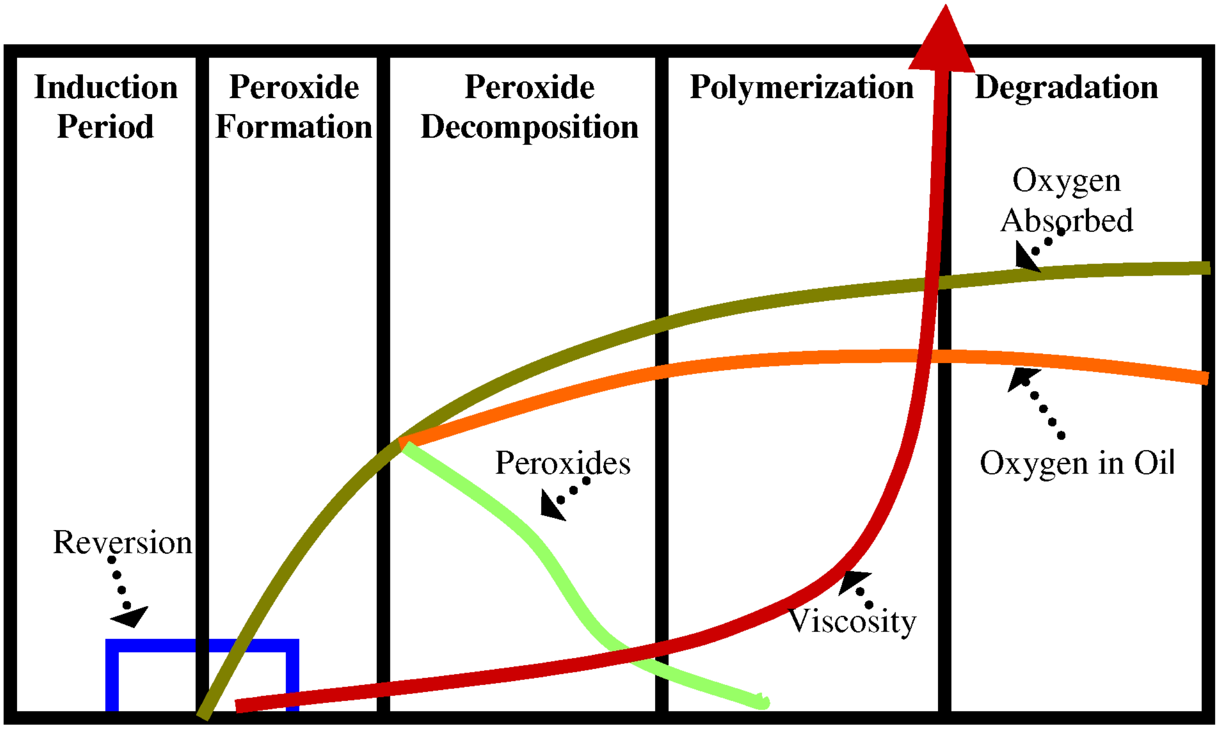


Fig.1. Stages of oil degradation stages during heating (Adapted from Perkins, 1967 (1)).

The first stage of oxidation is the induction period. During this phase, the changes in the quality of the oil are hard to quantify and the only phenomenon that is significant is oil reversion where refined oils re-acquire the flavor of crude oils (typical of oils containing linolenic acid such as soybean, linseed, and rapeseed oils). It is also in this stage that the free radical mechanism of the oil oxidation is triggered (Initiation).

Initiation:

$$RH \longrightarrow R + H\bullet \qquad \text{Eq. 1}$$

Oil reversion can occur under non-oxidative conditions producing some obnoxious flavors (2). The second stage is signaled by the formation of peroxides through the reaction of the oxygen present in the system and the fatty acids.

Propagation:

$$R\bullet + O_2 \longrightarrow ROO\bullet \qquad \text{Eq. 2}$$

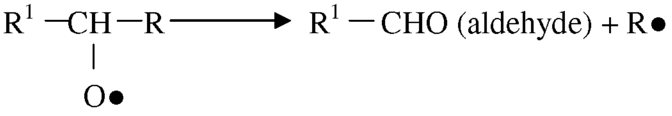
$$ROO\bullet + RH \longrightarrow ROOH + R\bullet \qquad \text{Eq. 3}$$

These peroxides will further degrade in other products that are responsible for the odor and flavor development (peroxide decomposition).

Decomposition:

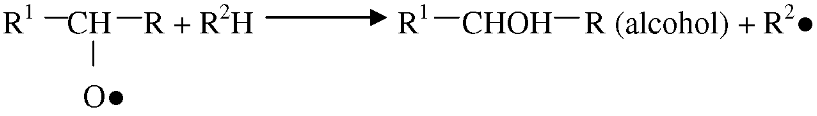
$$ROOH \longrightarrow RO\bullet + OH\bullet \qquad \text{Eq.4}$$

Dismutation:



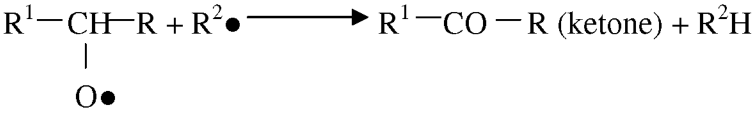
$$R^1-\underset{\underset{O\bullet}{|}}{CH}-R \longrightarrow R^1-CHO\ (\text{aldehyde}) + R\bullet$$

Eq.5



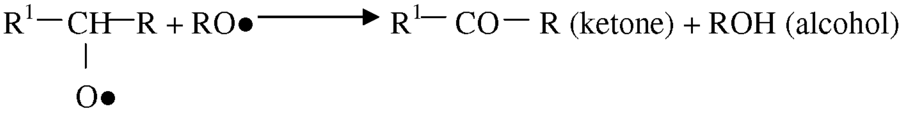
$$R^1-\underset{\underset{O\bullet}{|}}{CH}-R + R^2H \longrightarrow R^1-CHOH-R\ (\text{alcohol}) + R^2\bullet$$

Eq.6



$$R^1-\underset{\underset{O\bullet}{|}}{CH}-R + R^2\bullet \longrightarrow R^1-CO-R\ (\text{ketone}) + R^2H$$

Eq. 6



$$R^1-\underset{\underset{O\bullet}{|}}{CH}-R + RO\bullet \longrightarrow R^1-CO-R\ (\text{ketone}) + ROH\ (\text{alcohol})$$

Eq. 7

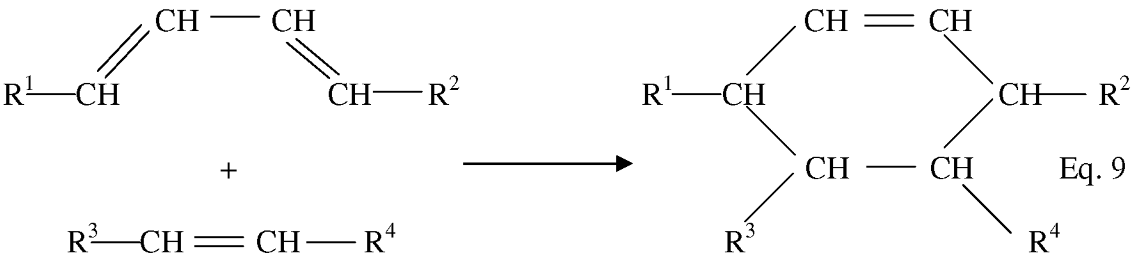
Termination:

$$ROO\bullet + X\bullet \longrightarrow \text{Stable compounds}$$

Eq. 8

The fourth stage is polymerization, which typically increases the viscosity of the oil (1) and it is believed to occur by a Diels-Alder reaction (3).

Polymerization:



Eq. 9

The final stage is degradation, typical of oils in a very advanced state of decomposition (1). Beside these reactions which are the result of the oil-oxygen-temperature interaction, there are other phenomena because of the interaction between food and oil. An overall scheme of the reactions occurring in an actual fryer is depicted in Fig. 2.

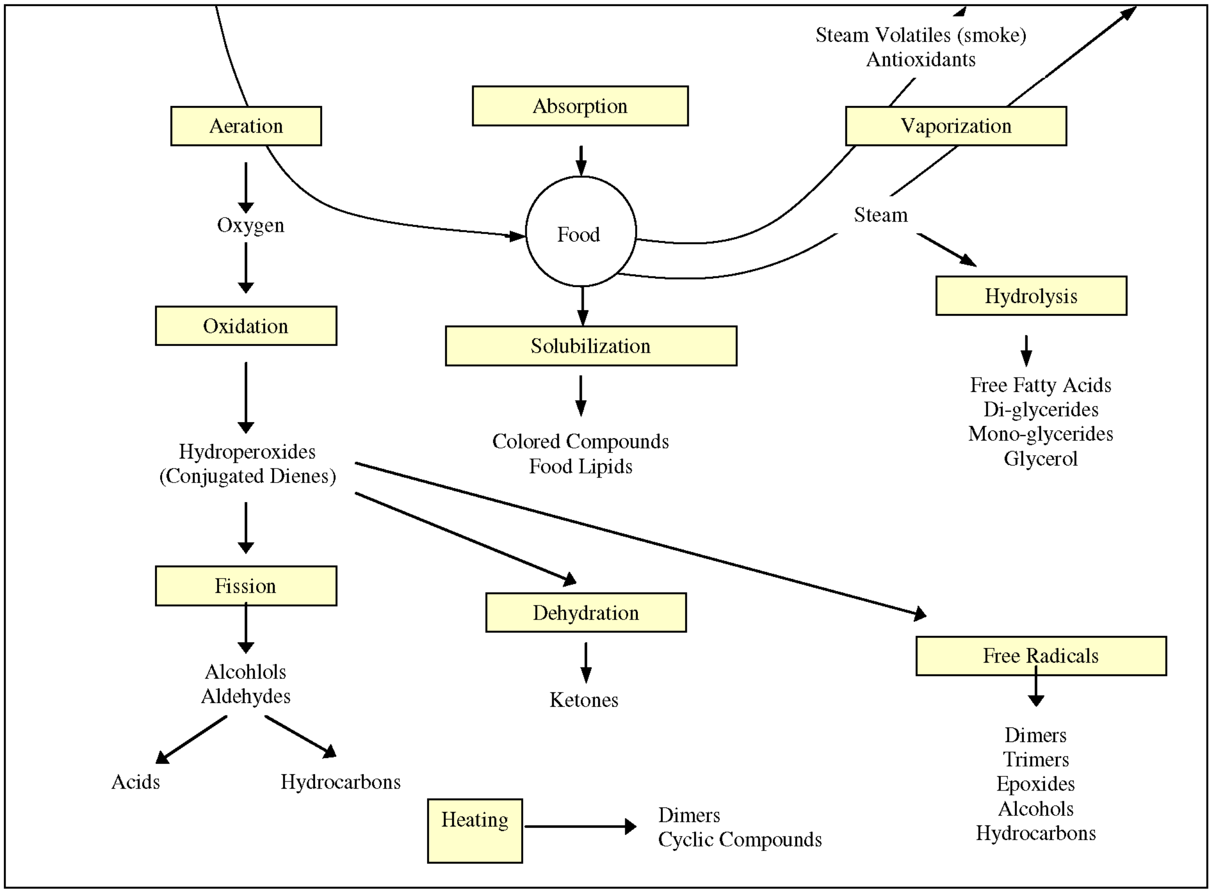


Fig.2. Reactions occurring in a fryer (Adapted from Fritsch (4)).

There are two different types of reactions during frying, physical and chemical reactions. The most important physical changes are oil absorption by the food, solubilization of liposoluble compounds from the food into the oil, vaporization of part of the water naturally present in the food, and the introduction of air into the system. Among the chemical reactions occurring in the oil, besides the oxidative changes already mentioned, hydrolysis of the triacylglycerides is one of the most important. The steam produced by the vaporization of the water promotes the formation of free fatty acids and mono and diglycerides, which have surfactant properties. Hence, they promote foaming (4), which introduces more oxygen as well as making the frying operation more dangerous for the operator (may produce the spillage of the oil). Another effect of the high free fatty acids content in the oil is the smoke produced (5). Simply heating the oil produces dimers and cyclic compounds. Finally, the oxidation of fatty acids produces a broad variety of hydrocarbons, acids, ketones, alcohols, and aldehydes (6, 7), most of them accompanied by noticeable sensory properties (8).

Frying Oils

It is because of the reactions that were previously described that the stability of the oil is of crucial importance when choosing the frying medium. Oil stability is primarily determined by the fatty acid composition of the oil. The higher the concentration of unsaturated fatty acids, especially polyunsaturated ones such as linoleic and linolenic acid, the more unstable the oil (9). It is because of this that the industry has been using hydrogenation as a means of increasing the stability of oils rich in polyunsaturated fatty acids (10) such as soybean and canola oils. This process increases the saturation level of the oil, and also produces *trans* fatty acid isomers (11). The consumption of fats and oils rich in *trans* fatty acids decreases high density lipoprotein cholesterol levels in human blood serum and increases low density lipoprotein cholesterol levels (12). Also, a positive correlation between *trans* fatty acid intake and coronary heart disease in women has been observed in an epidemiological evaluation (13, 14). Because of these effects on human metabolism the American Heart Association (15) advices consuming not more than 1% of total calories in the diet from *trans* fats. The FDA (16) passed a rule that imposed the obligation of including the amount of *trans* fats on food labels starting on January 1 2006, in food products containing 0.5 g of *trans* fats per serving or more.

For all the above reasons, the food industry is trying to find *trans*-free alternatives to hydrogenation. The most promising option is the breeding of oilseeds containing low levels of fatty acids which are very unstable, such as linolenic acid. There are many studies showing the benefits of soybean oil with reduced linolenic acid content. Soybean oil typically contains around 7% linolenic acid. This acid is very unstable because of the presence of three methylene-separated double bonds (17). Fatemi and Hammond (9) have shown that the relative reactivity of linolenic acid is 21.6 times the reactivity of oleic acid (monounsaturated), whereas for linoleic acid (diunsaturated) it is 10.3 times. Because of this propensity to react in the presence of oxygen, a reduced content of this acid significantly increases oil stability.

Oil Quality Determination

There are several parameters used to describe the quality and degradation of oils. The most representative ones are sensory. Flavor, aroma, and color of the oils are the usual attributes used in food service to decide the continued use or discarding of frying oils (18, 19). It is hard to correlate these subjective aspects to objective and consistent measurements. Many times the characteristics (chemical or physical) that describe the situation of the oil the best are difficult or costly to measure. Then, parameters that are directly or indirectly related to the oil quality are measured (20). It is important to make clear that there is no single test that is totally representative of the overall quality of the oil (4). The following methods are some of the most widely used means to assess the actual quality of frying oils (20).

Peroxide value (PV) is a measurement of the total oxidative capacity of the substances formed during the first stages of the oxidation (hydroperoxides). The American Oil Chemists' Society (AOCS) official method (21) to determine the PV of oils utilizes indirect titration. The hydroperoxides present in the oil oxidize potassium iodide to iodine. The iodine formed is further titrated with sodium thiosulfate using starch as indicator. This method is very sensitive and has been modified by Crowe and White (22) to reduce the amount of needed sample making it useful for very small samples (0.5 g). Yildiz et al. (23) compared the performance of three alternative methods to determine peroxide value: NIR spectroscopy, PeroxySafe^{TM} , and FOX^{TM}. They found a very good correlation between the first two methods and the official method. Because of the short life of the hydroperoxides this test is useful to determine the quality of fresh oils or of oils that have not been heat abused (20).

Conjugated dienoic acids (CDA) measures the first change during oxidation of oils rich in polyunsaturated fatty acids. Generally, this change is the shift in the position of one of the double bonds, typically separated by a methylene (17), to form conjugated dienoic acids. The method takes advantage of the capacity of these conjugated double bonds to absorb ultra violet radiation at 233 nm wavelength. The amount of CDA is determined through spectrophotometry (21) and is directly calculated from the absorbance value of the sample. As well as PV, CDA content is a parameter that is representative of the first stages of the oxidative process.

Free fatty acids (FFA) are typically formed through the hydrolysis (chemical or enzymatic) of the triglycerides. During the frying process the chemical hydrolysis is almost exclusively the one producing free fatty acids. These free fatty acids, as it previously was described, are responsible for the smoking and foaming of frying oils (4, 5). The methodology to determine the content of free fatty acids is based on an acid-base titration (21, 24). The method senses not only the acids released from the hydrolyzed triglycerides but the total acidity of the oil. Basically, the oil is dissolved in neutralized ethanol and is titrated with sodium hydroxide using phenolphthalein as indicator. This acidity is expressed as milligrams of potassium hydroxide necessary to neutralize one g of fat or directly as a percentage of oleic acid (21). Percentage as oleic acid is the most preferred way to express acidity for vegetable oils rich in eighteen-carbon fatty acids. There is no amount of free fatty acids established as maximum for frying oils in general. For meat and poultry products, the USDA advices not to continue frying when the free fatty acid level reaches 2% (25).

Fresh refined bleached and deodorized oil is almost completely composed of triacylglycerides. The polarity of these molecules is very low. When the oils are oxidized, the fatty acids that comprise the triacylglycerides specifically react with the oxygen to yield products of a higher polarity. Especially in oils used for frying or that have been heat abused, the amount of these polar compounds is particularly high. Among these compounds there are acids, ketones, aldehydes, alcohols, monoglycerides, diglycerides, dimers and polymers. The total polar material (TPM) content has been found to be a good indicator of the actual abuse that the oil has had. TPM is measured by column chromatography using a mixture of diethyl ether and petroleum ether as developing solvents and a silica column. The polar material is retained by the column and the solvent of the non-polar fraction is evaporated and TPM is calculated by weight difference (26). The maximum amount of TPM allowed in frying oils ranges between 24 and 27% (27) in many European and South-American countries. In the United States, legislation does not establish a TPM limit in frying oils. Even though TPM is a very reliable parameter, the test is time consuming to carry out (26) and the hazardous solvents needed require using fume hoods. Therefore this test is not widely used by the industry as a regular quality control tool in frying operations.

High-Performance Size-Exclusion Chromatography (HPSEC) is used to monitor the formation of high molecular-weight compounds (polymers) in oils that have been heat abused. White and Wang (28) developed a chromatographic methodology using two µ-spherogel size-exclusion columns (500 and 1000Å). They reported the separation of four fractions: conjugated triglycerides, dimeric triglycerides, tetrameric triglycerides, and higher molecular weight compounds. Marquez-Ruiz and Dobarganes (29) reported the separation of the polar fraction of oils into triacylglycerol dimers, oxidized triacylglycerol monomers, diacylglycerols and FFA. They reported the successful separation of the polar portion by solid-phase extraction or by using a silica column and then separating the different polar compounds by HPSEC.

Several rapid methods have been proposed as quality control tools during frying operations. These methods are usually based on colorimetric reactions or the measurement of changes in the dielectric constant of the fat. Dielectric constant has been hard to implement in real frying operations because the instrument is influenced by many external factors (26). Croon et al. (30) tested four methods including Foodoil sensor (FOS), RAU-Test, Fritest™, and Spot test. They found the tests easy to use and accurate enough for evaluating used frying fat. In another study (31), the performance for monitoring oil degradation of the

SafTest^{TM} was evaluated. This test measures malondialdehydes, FFA and peroxides. They found good correlations for the first two parameters but they do not recommend its use to determine peroxides in heat-abused oils. Indeed, peroxides should not be used as a measure of heat abuse in oils, because they are very unstable, and do not give an accurate measure when extensive heat is applied, as with frying.

Oil Stability Index (OSI) is an accelerated method to determine the oxidative stability of the oils (21). Two instruments are available to determine the OSI: the Oxidative stability instrument (Omnion, Inc., Rockland, MA) and the Rancimat (Brinkmann Instruments, Inc., Westbury, NY). The oil is placed in a tube that is heated at 100, 110, 120, 130, or 140º C and air is bubbled in the oil. The volatile compounds formed are absorbed into the water and the change in the conductivity of the water is constantly measured. OSI is defined as the time when the change in the rate of oxidation is maximum (maximum of the second derivative of the conductance with respect to the time). The longer the observed OSI, the more stable the oil.

Improving the Stability of Fats and Oils Without Hydrogenation

1. Plant Breeding

Breeding oilseeds with modified fatty acid composition is a promising tool to develop oils that are as stable as those obtained by hydrogenation. The great advantage of breeding is that it does not produce *trans* fatty acids while increasing the saturation (stability) level of the oil.

Soybean, sunflower, corn, and rapeseed (canola) are major crops that have been altered to obtain oils suitable for frying without the need of further chemical hydrogenation. To accomplish this task, breeders focused their efforts on reducing the amount of linoleic and linolenic acids in soybean and canola, and the amount of linoleic in sunflower and corn oils. Rapeseed had been previously modified to reduce the content of erucic acid (22:1) because of health concerns (32). The result of this work was the development of canola.

Many studies have been conducted to test the performance of these “tailor made” oils (32, 33). The reduction of linolenic acid in soybean and canola oils increased their oxidative stability during storage and frying. In the same way, linoleic acid has been replaced by oleic in sunflower (high and mid-oleic sunflower oils) (34).

In particular, the use of soybean lines with reduced contents of linolenic acid decreases the formation of some obnoxious odors and flavors typical of the soybean oil oxidation (fishy, acrid, burnt) (35, 36). In general, soybean oils containing 3% linolenic acid or less perform better than commodity soybean (36) and cottonseed oils (37). Other studies showed performances of low-linolenic soybean oils to be similar to partially hydrogenated soybean oil (36, 38, 39). The increase in the levels of stearic and palmitic acid (saturated) also increased the oil stability (40, 41). Su and White (42, 43) tested different blends of high-oleic and regular soybean oils, and found that increasing the content of this monounsaturated fatty acid enhances the oxidative and flavor stabilities of soybean oils.

Normand et al. (44) compared low-linolenic and commodity soybean oils. They did not find differences in FFA but based on the TPM content, in contrast to previous work, regular soybean oil performed better. They suggested that the lower content of tocopherol in the low-linolenic oil counteracted the effect of the fatty acid modification. They also proposed tocopherol level as another factor to be considered when breeding crops to enhance oil quality (44, 45).

In corn and sunflower, as well as in soybeans, the stability increased when the unsaturation level of the oil was reduced (34, 46, 47). Another study showed no differences in the performance of high-oleic and regular sunflower oils during frying (48) probably because of the greater tocopherol content in the regular sunflower oil.

2. Extruded-Expelled and Physically Refined Oils

Currently, most of the soybean oil in the United States is solvent-extracted by using hexane. There has been an increase, however, in the number of plants using mechanical extraction to recover the oil from the beans (49). These plants have much lower processing capacities (8-20 tons/day) than do solvent-extraction plants, but at the same time the initial investment is also much lower ($100,000-$250,000) (50). Because of these two attributes, farmers, cooperatives and small companies are taking advantage of this technology to process their grain, especially for processing identity-preserved oilseeds (organic, non-genetically modified and specialty oils) (49, 51).

This type of processing consists of two stages. The first stage is the extrusion of the beans during which the material is cooked by the heat generated through friction. This extrusion process helps to release the oil from the tissues increasing the efficiency of mechanical extraction (52, 53). The second stage is screw-pressing of the extruded material to separate the oil from the meal.

The quality of the crude oils when processing commodity soybeans has been reported to be the same as the quality of solvent-extracted oils (50). However, in beans with increased content of unsaturated fatty acids the expeller-processed oil was more oxidized and contained lower levels of tocopherols than did solvent-extracted oils, although the differences were very small (50).

Another process being increasingly used is physical refining of the oils. Typically, crude oils go through a four-step process after the extraction (degumming, neutralization or refining, bleaching and deodorization) (54). During neutralization alkali is added to the oil to convert the FFA to soap, which is later washed away with water. An alternative to this process is physical refining, which eliminates FFA plus the unsaponifiable fraction by steam stripping (54). This process is cleaner than alkali refining because it does not use sodium hydroxide, and requires less initial investment and energy (54, 55). Providing an adequate pretreatment (degumming and bleaching), the physical refining process is as effective as alkali refining (56). Physical refining of soybean oil requires exhaustive degumming to achieve a phosphorus content of 15 ppm (57) to 20 ppm (58). A high content of phosphatides contributes to darkening of an oil (54).

Because of the small scale and no chemicals needed (hexanes and sodium hydroxide), expeller extraction and physical refining often are coupled, especially in products that are considered organic (49, 59). Several studies have been done to determine the effect of the extraction and refining method on finished oil quality and stability. Leon-Camacho et al. (60) reported the effects of temperature and time on the formation of *trans* isomers of linoleic acid during physical refining of sunflower and soybean oils. They demonstrated that the longer the time and the greater the temperature, the greater the amount of *trans* fatty acid isomers formed. De Greyt et al. (61) reported that the maximum amount of *trans* isomers of linoleic acid formed is 2% and that the isomerization of linolenic acid ranged between 3 to 24% of the initial amount of this fatty acid. Considering soybean oil, these amounts of *trans* fat are not sufficiently enough to be reported on the label of the commercial oils (16). Minor changes in the triglyceride composition of the oils that have been physically refined at high temperatures also have been reported (62).

Regarding the changes in the unsaponifiable fraction, physical refining has been found to significantly decrease the amount of tocopherols (in the same way as screw-pressing extraction) (50) and phytosterols naturally present in soybean oil (63). De Greyt and Kellens (57) reported that the amounts of tocopherols extracted from oil during physical refining can be controlled by controlling the operation parameters. On the other hand, they reported that the phytosterols form fatty acid esters because of the high processing temperature and the substantial FFA (they were not neutralized and washed out) in the medium. These steryl esters are not as volatile as the free phytosterols and remain in the oil.

Warner and Dunlap (64) found that screw-pressed and physically refined soybean oil was as stable as solvent-extracted and alkali-refined soybean oil with tertiary butyl hydroquinone (TBHQ, an antioxidant) and also as partially hydrogenated soybean oil during frying of French fries. They proposed that the increased stability in the expeller-pressed physically-refined oil was due to Maillard browning reaction products formed during oil extraction. Coscione et al. (65) compared screw-pressed, physically refined soybean oil with solvent-extracted low-linolenic soybean oil during pan-heating for 12 min. The screw-pressed oil was more stable than the solvent-extracted low linolenic oil.

Near-Infrared Spectroscopy

Spectroscopic techniques have been widely used in detecting and quantifying many compounds. In general, spectroscopy is based on the capacity of matter to absorb energy.

Molecules have two types of properties: static (atomic composition, stereochemistry, isomeric structure, etc) and dynamic (molecular translation, rotation, and vibration). The last properties can be considered as energy (66). Generally, dynamic properties depend on static ones. By measuring changes in the first properties, it is possible to measure the last properties by extrapolation.

When light hits a molecule, part of the energy is absorbed and the remaining energy is reflected. Different functional groups absorb energy at different wavelengths and most of them absorb energy at several wavelengths. Energy absorption also is influenced by other functional groups close to them. The energy absorbed produces changes in the vibrational energy of the molecule (atoms oscillations through their bonds). Then, by measuring the energy absorbed at different wavelengths it is possible to correlate the measurements with changes in static properties.

Chemometrics is the use of mathematical and statistical methods to correlate experimental data and the chemical composition or physical properties of the tested samples (67). The near-infrared zone of the spectrum includes wavelengths from 780 to 2500 nm. By using chemometric tools such as Partial Least Square (PLS) or Principal Component Analysis (PCA), it is possible to obtain an equation correlating the parts of the spectra that are most representative of the chemical properties measured in the samples.

NIRS is used widely in crop and plant analyses. Calibrations have been developed to determine protein, moisture and fiber content in pulses (68), sugar and malic acid in apple juice, (69) and even fatty acid composition in soybeans (70). Some calibrations have been successfully developed to monitor oil degradation and quality. Che Man and Moh (71) used NIR spectroscopy to determine FFA in palm oil over a range of 0.07 to 6.20%. Successful calibrations were developed to determine PV, anisidine value, and CDA (72), FFA, and TPM (73, 74). NIR spectroscopy is a promising methodology to be used as a clean and fast quality control tool in food processes in which oil quality has to be monitored (72).

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Frying Performance of No-Trans, Low-Linolenic Acid Soybean Oils

A paper to be submitted to the Journal of the American Oil Chemists' Society

Jose Gerde[1], Connie Hardy[2], Walter Fehr[3] and Pamela White[1*]

[1]Department of Food Science and Human Nutrition, Iowa State University, Ames, Iowa 50011

[2]Value Added Agriculture Program, Iowa State University, Ames, Iowa 50011

[3]Department of Agronomy, Iowa State University, Ames, Iowa 50011

Running Title: FRYING PERFORMANCE OF LOW-LINOLENIC ACID SOYBEAN OILS

[*]To whom correspondence should be addressed at 2312 Food Sciences Building, Iowa State University, Ames, IA 50011-1060. Phone: 515-294-9688, Fax: 515-294-8181, Email: pjwhite@iastate.edu

ABSTRACT: Two extruded-expelled soybean oils with reduced contents of linolenic acid, ultra-low linolenic acid (ULL, 1.5%) and low-linolenic acid (LL, 2.6%), and a extruded-expelled control oil (control, 5.3% linolenic acid) were evaluated by frying French fries in a commercial-like setting for 6 h/day during 23 days. The oils became darker, increased in yellow color at the beginning, and became redder and less green throughout the process. Free fatty acids levels were not different among the oils until day 14, after which ULL was different from the control for the remainder of frying. The conjugated dienoic acid values were greatest in the control. Generally, ULL and LL oils had lower percentages of polar compounds than did the control, providing a frying life 2 d longer than the control and a ~30% increase in frying time. A trained sensory panel evaluated the French fries on days 2, 5, and 6. Buttery and potato flavors decreased, and rancid and painty flavors increased over frying time for all products. Rancid flavor was highest in the fries from the control oil. Overall, the ULL and LL oils performed better than did the control oil and ULL tended to perform better than the LL.

KEY WORDS: French fries, frying, oil stability, sensory evaluation, *soybean oil*, ultra-low linolenic acid, extruded-expelled oil, physical refining.

Frying is one of the most common practices used to cook food in both home and industrial operations. The essence of the fast-food industry is the frying process that provides tasty, ready-to-eat food in a relatively short period of time. In addition to saving time, frying reduces the amount of waste because it allows cooking of small batches of food to order. The stability of the oil is a crucial factor when choosing a frying media because of the highly aggressive process involving high temperature in the presence of oxygen, water, and the formation of pro-oxidants. Partially hydrogenated oils have been commonly used as the frying media because of their stabilities. In 2003, the Food and Drug Administration passed a ruling requiring labels of all food products containing 0.5 g or more of *trans* fat per serving to list the *trans* content on the nutrient label by January 1, 2006 (1). Other countries, such as Denmark (2) and Canada (3), have passed legislation that regulates *trans* fat content labeling in food products. Companies are increasingly marketing products that do not contain trans fats (4). *Trans* fatty acid consumption has been linked to health, including increased serum levels of low-density lipoprotein cholesterol and decreased high-density lipoprotein cholesterol (5). Because of these health issues and the accompanying *trans* fats labeling requirements, the food industry has been trying to find alternatives to partially hydrogenated oils.

Typical soybean oil with about 7 to 8% linolenic acid (18:3) is known to be oxidatively unstable, especially during frying (6, 7). Recent studies showed that soybean oil with only 1.5 to 3.5% of the very unstable 18:3 had better flavor scores and increased stability during frying than commodity and even partially hydrogenated soybean oils (8-10). Frying stability of soybean and other oils also is impacted by the extraction method. Indeed, Warner and Dunlap (11) reported that French fries fried in screw-pressed typical soybean oil had better sensory characteristics than fries fried in hexane-extracted soybean oil with TBHQ added, and also better than fries fried in partially hydrogenated soybean oil. Screw pressing is thought to create Maillard browning reaction products that contribute natural antioxidants to the pressed oils (11).

The combination of low 18:3 composition along with extrusion-expelling has not been tested for performance during frying. In this study, the extended frying performance of three extruded-expelled soybean oils was evaluated: two oils from soybean varieties with reduced amounts of 18:3 and one oil from commodity soybeans with a typical amount of 18:3. A main goal of the study was to determine whether substantial differences occurred among these three oil types to help buyers decide the value of selecting one of the low 18:3 acid oils over typical commodity oil.

MATERIALS AND METHODS

Soybean oils: Extruded-expelled soybean (*Glycine max*) oils with three different fatty acid compositions were obtained from American Natural Soy, Inc., Cherokee, IA. An ultra low-linolenic acid oil (ULL), having 1.5% 18:3 after processing, was obtained from soybean cultivar IA2064 produced by Taylor Seeds, Inc. near Hartley, IA in 2003. Low-linolenic acid oil (LL), having 2.6% 18:3 after processing, was obtained from the soybean cultivar IA3018 produced by Pleasant Valley Farms near Iowa City, IA in 2004. Oil with 5.3% 18:3 (control) after processing came from a mixture of conventional soybean cultivars produced by American Natural Soy in 2004. Both ULL and LL oils originated from Iowa State University (ISU) soybean varieties developed through traditional breeding practices to reduce the 18:3 content of the oil.

Frying of French fries: The frying process was performed simultaneously for two replicates of the three oils in a total of six twin frying wells of Star Twin Pot deep-fat fryers, model 530TA (Star Manufacturing International Inc. St. Louis, MO, 7.2 liter per well). Three 0.225-kg batches of commercial extra-long (XL) fancy 0.635-cm (¼ inch) shoestring par-fried frozen French fries obtained commercially were fried per h, for 6 h per day for 23 days. The fries were provided by a single supplier from a single lot and were par-fried using partially hydrogenated vegetable shortening (canola and/or soybean oil) and/or palm oil and/or beef fat. The fatty acid composition of the fat extracted from the par-fried fries was 19.4% 16:0 (palmitic acid), 16.3% 18:0 (stearic acid), 61.9% 18:1 (all isomers), and 2.4% 18:2 (all isomers). The available column did not allow geometric isomer separation. A 100-m column is needed to obtain a complete profile of fatty acids. The manufacturer also claimed the addition of dihydrogen pyrophosphate (to promote color retention), dextrose and natural flavoring. The initial frying temperature was 190°C and each batch was fried for 165 s. The oil temperature was recorded at 30-s intervals and the temperature monitored to ensure consistent frying temperatures for all batches. At the end of each frying day, the oils were filtered through fast flute shortening filters (DF1600FF Disco, McDonough, GA) to remove food particles. Aliquots of the oils were removed for further evaluation and stored at -22°C in glass jars under nitrogen in the dark to prevent further oxidation. The bulk of the oils was left overnight in the fryers at room temperature loosely covered with aluminum foil. The following day, oil was added to bring the level back to normal before heating.

Fry chef evaluations: Fry chefs (9 chefs x 2 frying replicates = 18 total observations) from the ISU dining service served as an expert panel to evaluate each replicate of the frying oils during the operation. They were familiarized with the frying set-up and trained to use the scoring sheet provided for them. They visited the frying operation on days 2, 5, 9, 11, 14, 16, 19, 21, and 23 and at each visit were asked to independently judge the unidentified oils for their need to be changed, based on their expert judgment as to when they would typically change the oil during normal use. Frying continued until all the chefs agreed that the oils (both replicates) needed to be changed (day 23).

Fatty Acid Methyl Ester (FAME) composition: The FAME composition of each oil was determined by gas-liquid chromatography and was reported in relative area percentage. The FAME were obtained by using the method described by Hammond (12) and analyzed with an HP 5890 GC chromatograph. The chromatography conditions were similar to those described by Onal-Ulusoy et al. (13). Based on FAME composition, oxidizability was calculated (14). The oils were analyzed fresh and periodically throughout the frying operation.

Free Fatty Acids (FFA): The FFA concentration expressed as oleic acid was determined by titration following AOCS Official Method Ca 5a-40 (15) as modified by Rukunudin et al. (16).

Conjugated Dienoic acid (CDA): The CDA content expressed as percentage was spectrophotometrically determined according to AOCS Official Method Ti 1a-64 (15).

Total Polar Compounds (TPC): TPC were determined according to AOCS Official Method Cd 20-91 (15).

Peroxide value (PV): PV of each oil was determined before frying according to AOCS Official Method Cd 8-53 (15).

Oil Stability Index (OSI): The oil resistance to oxidation, called OSI, was evaluated according to AOCS Official Method Cd 12b-92 (15) using an Oxidative Stability Instrument (Omnion Inc., Rockland, MA). OSI was run at 100°C.

Tocopherol content: The α-, γ-, and δ-tocopherol contents of the fresh oils were determined by HPLC following the AOCS Official Method Ce 8-89 (11).

Color: Oil color was analyzed by using a Hunter Lab LabScan XE colorimeter (Hunter Lab, Reston, VA). The illuminant used was D65 and the standard observer was set at 10°. The oil aliquots were placed in 60 x 15 mm Petri dishes with the edge previously covered with two layers of white, 1.27-cm width tape (Fisherbrand, Fisher Sc. 11-880A) to avoid light dispersion caused by sample translucence. The Petri dish was placed on a standard white tile for oil color measurement. The color results were expressed in Hunter Lab units.

Sensory evaluation: Sensory evaluations were performed on French fries fried in the oils on days 2, 5 and 6 to correspond with the typical timing of fast food operations, in which frying oil is typically changed on a weekly basis. Rancid, painty, potato, and buttery flavors were assessed by a sensory panel of 12 individuals, previously trained during three separate sessions to recognize and quantify these attributes. The attributes were rated on a 15-cm line, with the perceived flavor increasing in intensity from 0 to 15. French fries were randomly coded and served to all panelists on a monadic sequential order (randomized among sessions).

Statistical analysis: All data were analyzed by using analysis of variance (ANOVA) with the SAS mixed models procedure (17). For tests performed over time, repeated measures were used. Multiple comparisons between means were assessed by F-protected contrasts. The level of significance was set at α=0.05.

RESULTS AND DISCUSSION

The 18:3 concentration in the fresh oils was different for all the treatments (Table 2.), but for the ULL was greater and for the control was less than expected. The 18:3 of ULL was measured at 1.0% in the 2003 seed, whereas for LL was measured at 2.5% (Unpublished data). Also, the control blend, at 5.3%, was lower than is typical for commodity soybean oil (7). During processing, there likely was some carryover of previously processed commodity oil into the ULL oil, then of ULL and/or LL oil into the control oil, thus slightly altering the anticipated 18:3 concentrations of the processed oils. It is possible there also was an environmental impact on the oil compositions during growing. The reduction of 18:3 in LL and ULL, compared to the control, was accompanied by increased linoleic (18:2) and oleic (18:1) acid levels, but the 18:2 acid concentrations were not different between ULL and LL.

Also the amount of stearic acid (18:0) was greater in the ULL than in the control and LL. These changes were reflected in the calculated oxidizability (Table 1.). ULL had the lowest value (highest theoretical stability), LL had an intermediate value, and the control had the highest value.

Throughout the frying study the percentages of the unstable 18:3 and 18:2 decreased at the beginning and the percentages of the more stable 18:1, 18:0 and palmitic (16:0) acids increased. This same tendency was reported by Onal-Ulusoy (13) for soybean oil heated at frying temperatures. After approximately day 9, however, the changes in the percentages of each fatty acid reached a plateau, probably because of an equilibrium between the degradation and the turnover rates of the oils (Table 1).

The α-, γ-, and δ-tocopherol concentrations of the fresh oils were different for each of the oils, and the total tocopherol concentration was greater for LL than for both ULL and the control which were not different from each other (Table 2.). Warner suggested that although fatty acid composition is crucial in determining oxidative stability in oils, tocopherol content also plays an important role in oil stability (18). The greater tocopherol content may have given LL a slight stability advantage over ULL and the control. Previously, the tocopherol content affected the TPM content in oils and triglyceride mixtures heated at frying temperatures (19, 20).

The PVs of the three fresh oil treatments were all less than 1 meq/kg, indicating that all oils were unoxidized and of high quality, although statistical differences occurred among the oil types (Table 1). The OSI of the fresh oils was greater (more stable) for ULL and LL than for the control, which was likely a direct result of the lower level of 18:3 in ULL and LL (Table 1). These values were consistent with the calculated oxidizability, which showed that the lower the 18:3 the greater the theoretical stability. OSI predicts the oxidative stability of the oils under the severe conditions employed by this method, but does not necessarily indicate stability during deep-fat frying of food, because of the differences in the systems (Unpublished data).

Figure 1 shows the FFA evolution over frying time for each of the oil treatments. There was no evidence of differences in FFA among the oils until 14 days of frying. At that point, and generally during the rest of the frying period, the control had a greater FFA level than did LL and ULL. The control generally had a higher FFA level throughout frying. Oils with high FFA are known to have a lower smoke point (21, 22) and the surfactant effect of FFA contributes to the foaming which leads to further oxidation of the oil (23).

The concentrations of polar compounds were not significantly different among the oils throughout frying. However, the control tended to have the greatest values, probably a result of its higher level of 18:3 and overall greater oxidizability (Fig. 2). In many countries 25% polar compounds is considered as the discarding point for frying oils (24). With that criterion and by interpolating the polar compound levels presented in figure 2, both ULL and LL had a frying life 2 d longer than control (~30% increase in frying time).

Throughout frying, the control had greater levels of CDA (Fig. 3), which was directly related to its higher 18:3 content. ULL and LL were not different from each other. Even though the LL had greater 18:3 content, its higher tocopherol content may have helped reduce the CDA formation. The greatest changes in CDA content occurred at the beginning of the frying period, and after day 5 the evolution in the CDA content was much slower. A previous study showed the same trend in CDA development during the initial stages of frying (25). All the oils had reached their maximum levels of CDA by day 6. At that point, the CDA of the control and LL started to decrease in value but ULL remained at the maximum level until day 9. The further decrease might be explained by the degradation of the CDA to form other secondary breakdown products, such as the FFA, which began to form more quickly at about day 9 for all treatments.

There was no clear tendency with respect to Hunter a value changes among the oils. The control was more red (higher a) than were ULL and LL on days 5 and 6. ULL was still less red than the control on day 9. On day 16, LL was redder than ULL, the only point at which ULL and LL were significantly different from each other. After 21 days and until the end of frying, LL became redder than the control as did ULL on day 23. In the fresh oils, the Hunter b value was greatest in the control (most yellow), followed by ULL and then LL (fresh oils). On days 14, 19, and 23, LL and ULL were more yellow than the control. Hunter L values decreased (oils became darker) throughout frying. On day 9 the rate of darkening decreased and, starting on day 14 and until the end, ULL was significantly lighter (higher Hunter L value) than the control. The darkening of the oils during frying has been previously associated with the formation of polymers (22). It is also probable that Maillard browning products formed in the fries leached into the oil also contributing to its darkening.

Overall, Hunter a values for all oils tended to increase (became more red) during frying, with a subsequent decrease during the last 4 days. In general, Hunter b values increased during the first 2 days of frying and then decreased (became less yellow). The initial rapid increase in darkness, redness and yellowness in the first phase of the process was likely related to the accumulation of the Maillard browning reaction products from the fries. Color formation then gradually changed as the oil degradation products formed. These findings agree with the study of Su and White in which bread cubes were fried in various soybean oils (26). In the current study, CDA and color evolved at faster paces during the first phase of the process; after day 9 the changes in these two parameters were less pronounced. At this point, the changes in FFA accelerated. Generally, CDA and color changes were reflective of the early changes in the oil during frying, whereas changes in FFA were more pronounced later in frying.

There were strong linear correlations among all the treatments between total polar compounds content and Hunter L value (Table 3).This decrease in the lightness of the oils with the increase of the total polar compounds content in the measured range agrees with the results obtained by Paul and Mittal (27), who noted a third-degree correlation between total polar material and lightness in canola oil shortening during frying.

Figure 5 shows the mean cumulative number of fry chef observations that stated at least one replicate of the frying oils ready for changing by the day noted. By day 9, eight out of eighteen possible observations stated that the control needed to be changed, whereas only one established ULL and two established LL needing replacement. After day 9, the control continued to be recommended for changing at a greater rate than the other two oils. Thus, a longer fry life, and potential monetary savings could arise from use of the ULL or LL.

Finally, there were no differences in buttery, potato, and painty flavors among the different oils (Fig. 6). All values, except for potato, were relatively low in intensity throughout testing, indicating there were few rancid and painty off flavors and a low amount of buttery flavor, with potato flavor predominating. There was a tendency, however, for both ULL and LL to score lower (better) than the control with respect to painty flavor. For rancid flavor, ULL and LL were not different from each other, but both were lower (better) than the control.

In general, both ULL and LL oils performed better than the control. ULL tended to be more stable than LL. Both LL and ULL may be good alternatives to partially hydrogenated oils in frying operations.

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TABLES AND FIGURES

TABLE 1
Initial Oil Quality Values of Ultra Low-linolenic acid (ULL), Low-linolenic acid (LL), and Control Soybean Oils[1]

Oils[2]	Oxidizability[3]	Tocopherol (μg/g)				OSI[4]	PV[5]
		α	γ	δ	Total	(h@100°C)	(meq/kg)
ULL	6.4^c	67^c	759^a	245^c	1071^b	19.40^a	0.72^a
LL	6.6^b	117^b	803^a	261^b	1181^a	19.34^a	0.18^c
Control	6.9^a	136^a	676^b	272^a	1084^b	14.65^b	0.24^b

[1] Values in the same column with the same superscript letters are not significantly different ($P<0.05$).

[2] ULL = ultra low-linolenic soybean oil, LL = low-linolenic soybean oil, Control = typical soybean oil.

[3] Oxidizability = [oleic acid % + 10.3(linoleic acid %) + 21.6(linolenic acid %)] (14).

[4] OSI = oxidative stability index.

[5] PV = peroxide value.

TABLE 2

FAME Composition (%) of Ultra Low-linolenic acid (ULL), Low-linolenic acid (LL), and Control Soybean Oils throughout Frying[1,2]

	Oil	16:0	18:0	18:1	18:2	18:3
Fresh	ULL	9.9^{b}	6.0^{a}	26.0^{b}	56.6^{a}	1.5^{c}
	LL	10.0^{b}	4.5^{c}	26.5^{a}	56.4^{a}	2.6^{b}
	Control	10.9^{a}	4.7^{b}	25.5^{c}	53.7^{b}	5.3^{a}
2 days	ULL	10.8^{b}	6.9^{a}	28.8^{b}	52.3^{a}	1.2^{c}
	LL	10.9^{b}	5.5^{c}	29.6^{a}	51.9^{a}	2.2^{b}
	Control	12.1^{a}	5.8^{b}	28.5^{b}	49.0^{b}	4.7^{a}
5 days	ULL	11.5^{b}	7.9^{a}	31.0^{b}	48.6^{a}	1.0^{c}
	LL	11.6^{b}	6.3^{c}	31.5^{a}	48.7^{a}	1.9^{b}
	Control	12.7^{a}	6.7^{b}	30.7^{b}	46.1^{b}	3.9^{a}
9 days	ULL	12.2^{b}	8.6^{a}	32.9^{a}	45.5^{a}	0.9^{c}
	LL	12.1^{b}	7.1^{c}	33.2^{a}	45.9^{a}	1.8^{b}
	Control	13.0^{a}	7.3^{b}	32.2^{b}	43.8^{b}	3.7^{a}
14 days	ULL	12.2^{b}	8.9^{a}	33.6^{b}	44.4^{a}	0.9^{c}
	LL	12.1^{b}	7.5^{c}	34.1^{a}	44.6^{a}	1.7^{b}
	Control	13.1^{a}	7.7^{b}	33.2^{b}	42.5^{b}	3.6^{a}
19 days	ULL	12.2^{b}	9.1^{a}	33.6^{b}	43.9^{a}	0.9^{c}
	LL	12.3^{b}	7.8^{c}	34.1^{a}	43.4^{a}	1.7^{b}
	Control	13.2^{a}	8.1^{b}	33.2^{b}	41.9^{b}	3.5^{a}
23 days	ULL	12.2^{b}	9.1^{a}	34.3^{a}	43.5^{a}	0.9^{c}
	LL	12.2^{b}	7.6^{c}	34.3^{a}	44.2^{a}	1.7^{b}
	Control	13.4^{a}	8.2^{b}	34.4^{a}	40.6^{b}	3.4^{a}

[1] Values in the same column within the same day with the same superscript letters are not significantly different ($P<0.05$).

[2] FAME= fatty acid methyl esters of 16:0 (palmitic acid); 18:0 (stearic acid); 18:1(oleic acid); 18:2 (linoleic acid); 18:3 (linolenic acid).

TABLE 3.

Relationship between Hunter L Value and Total Polar Compounds in Ultra Low-linolenic acid (ULL), Low-linolenic acid (LL), and Control Soybean Oils throughout Frying

Oil type	Equation	Correlation coefficient[1]
ULL	$L = -0.960TPC+54.119$	0.98*
LL	$L = -1.045TPC+56.324$	0.97*
Control	$L = -1.087TPC+58.094$	0.98*

[1] * Denotes significance at $P<0.001$ level

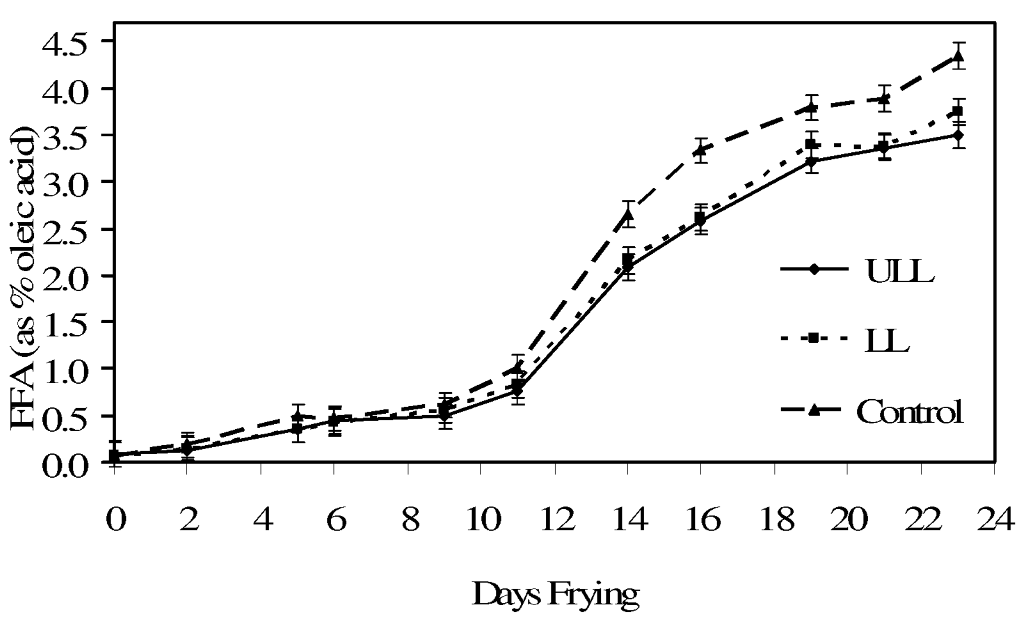

FIG. 1. FFA evolution in ultra low-linolenic acid (ULL), low-linolenic acid (LL) and control soybean oils throughout frying. Each value represents the mean of two replications. Bars around each data point indicate standard error of the mean for all data points.

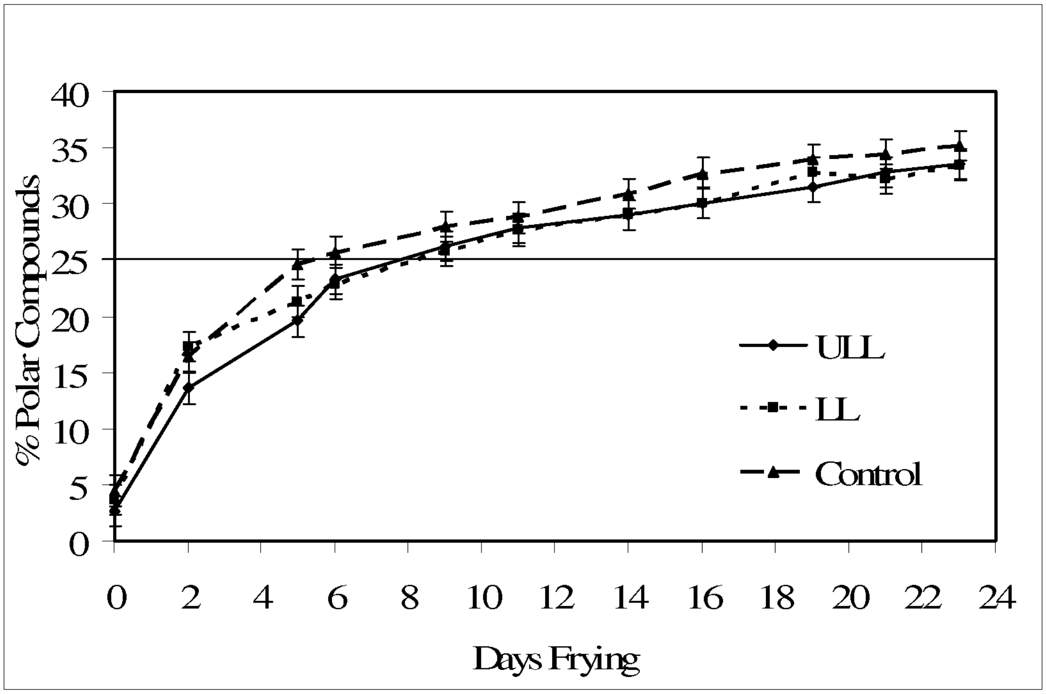

FIG. 2. Total polar compounds in ultra low-linolenic acid (ULL), low-linolenic acid (LL) and control soybean oils throughout frying. Each value represents the mean of two replications. Bars around each data point indicate standard error of the mean for all data points. The value of 25% polar compounds is used in some countries as the maximum discard value for frying oils (24).

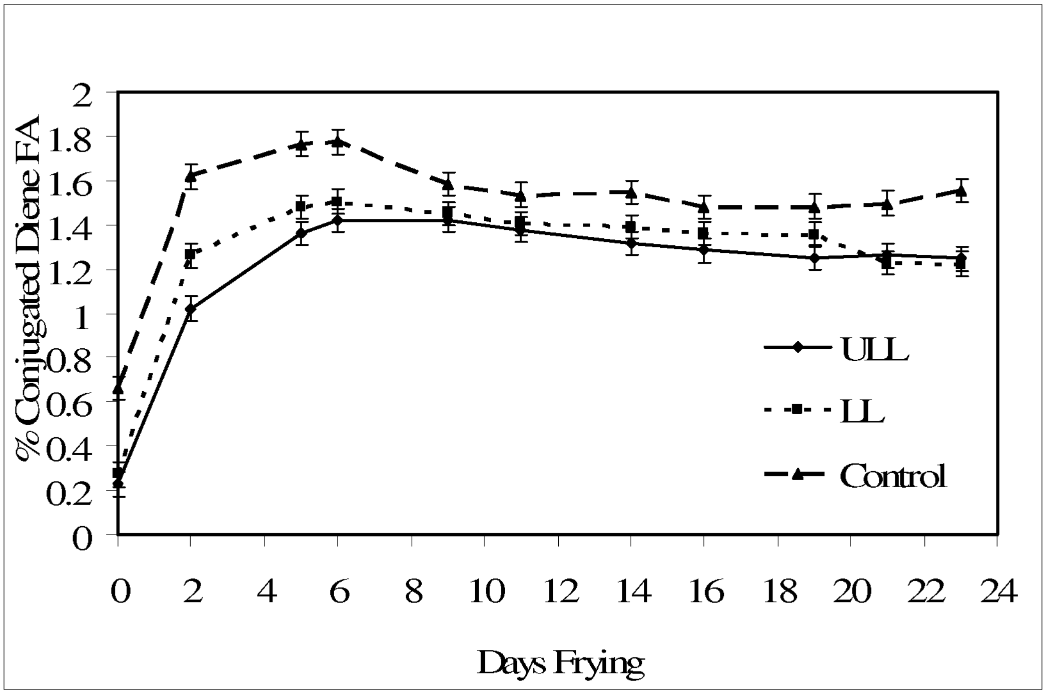

FIG. 3. Conjugated dienoic acid content in ultra low-linolenic acid (ULL), low-linolenic acid (LL) and control soybean oils throughout frying. Each value represents the mean of two replications. Bars around each data point indicate standard error of the mean for all data points.

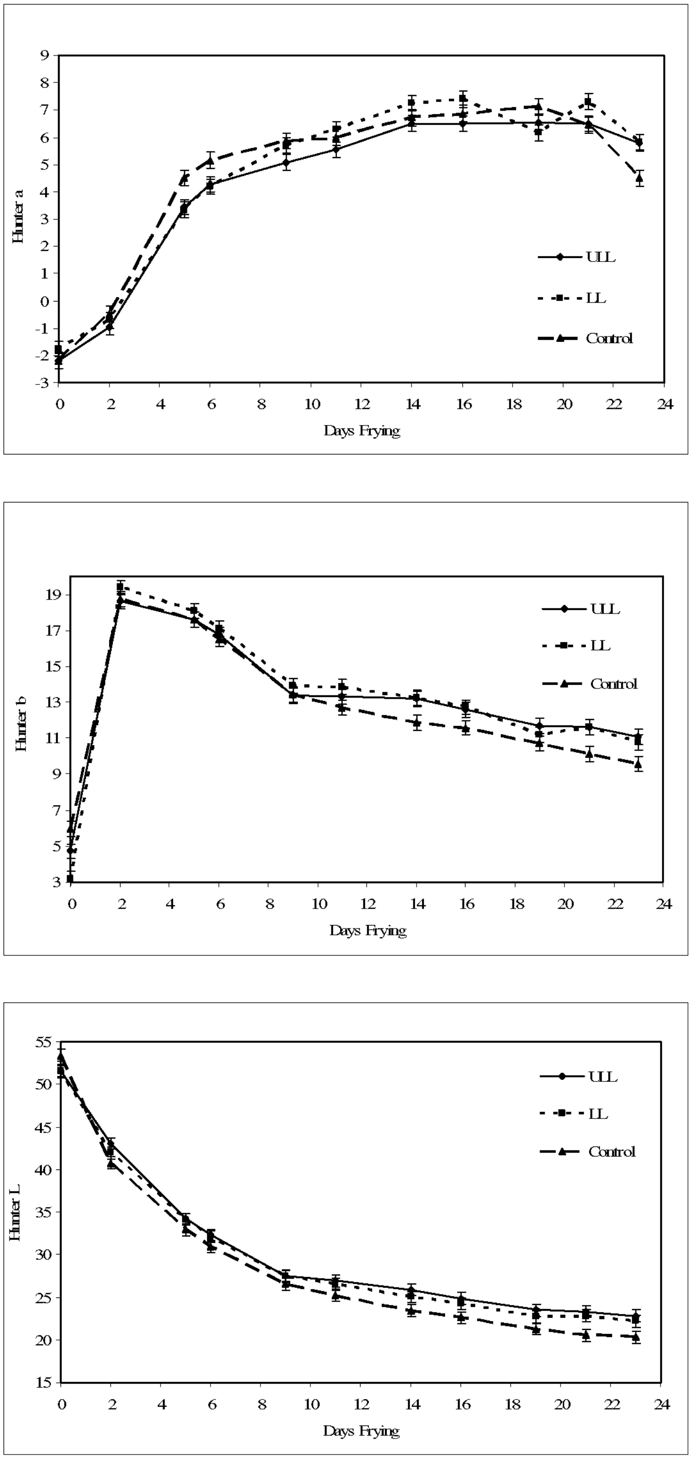

FIG. 4. Color Hunter L, a, and b values in ultra low-linolenic acid (ULL), low-linolenic acid (LL) and control soybean oils throughout frying. Each value represents the mean of two replications. Bars around each data point indicate standard error of the mean for all data points.

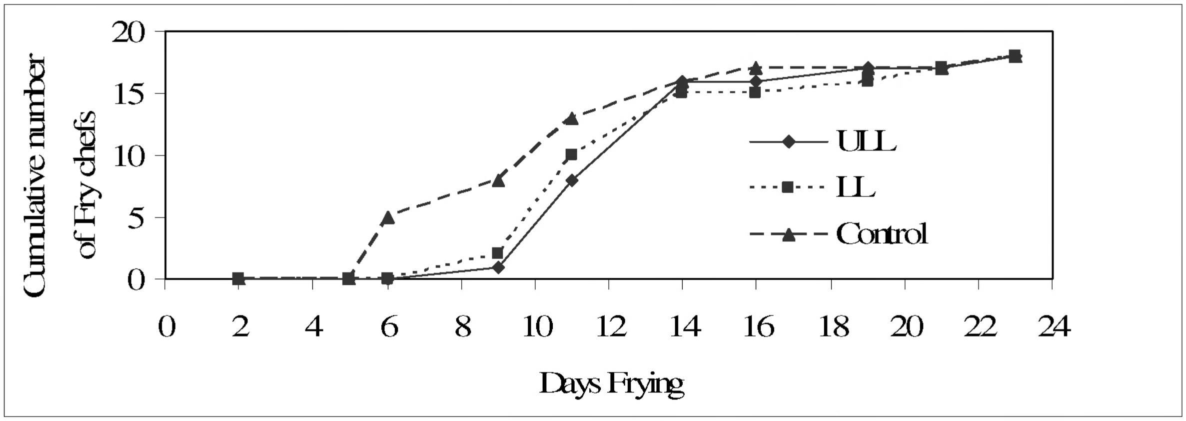

FIG. 5. Cumulative number of fry chefs who judged at least one of the replicates of ultra low-linolenic acid (ULL), low-linolenic acid (LL) and control soybean oils ready for changing during frying (9 chefs x 2 replicates = 18 total observations).

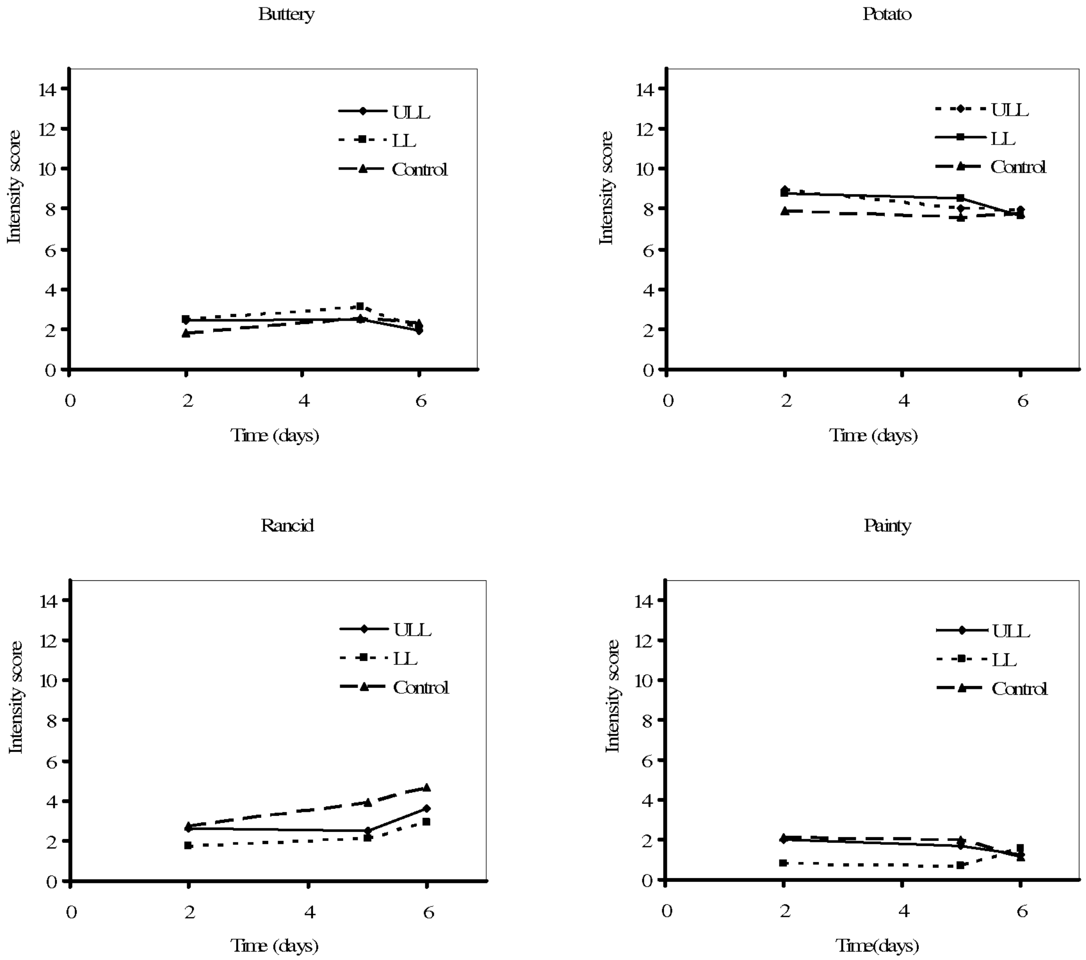

FIG. 6. Sensory scores for buttery, potato, rancid, and painty flavors in French fries fried in ultra low-linolenic acid, low-linolenic acid and control soybean oils throughout the first week of frying. Data are the average of two replications.

Rapid Determination of Degradation in Frying Oils by NIR Spectroscopy

A paper to be submitted to the Journal of the American Oil Chemists' Society

Jose Gerde[1], Connie Hardy[2], Charles Hurburgh[1,3], and Pamela White[1*]

[1]Department of Food Science and Human Nutrition, Iowa State University, Ames, Iowa 50011

[2]Value Added Agriculture Program, Iowa State University, Ames, Iowa 50011

[3]Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, Iowa 50011

Running Title: NIR MEASUREMENT OF OIL DEGRADATION

[*]To whom correspondence should be addressed at 2312 Food Sciences Building, Iowa State University, Ames, IA 50011-1060. Phone: 515-294-9688, Fax: 515-294-8181, Email: pjwhite@iastate.edu

ABSTRACT: Free fatty acids (FFA), total polar material (TPM), and conjugated dienoic acid (CDA) contents are typical indices of oil degradation. Soybean oils with different linolenic acid concentrations were used to fry French fries. Oil aliquots were taken daily and analyzed to determine FFA, TPM and CDA. These aliquots also were scanned with a reflectance spectrometer by using a wavelength range of 350 to2500 nm. By using partial least squares and one-out cross validation, calibrations were developed to quantitatively determine FFA, TPM, and CDA by NIR spectroscopy (NIRS). Successful calibrations were obtained for the measurement of FFA and TPM. The coefficients of determination (R^2) when compared to the standard procedures were 0.974 for FFA and 0.958 for TPM. The use of NIRS for the determination of CDA was less effective (R^2= 0.775). NIRS was an accurate and fast method to determine FFA and TPM in oxidized oils. The ability to obtain different parameters simultaneously makes NIRS a potentially valuable tool for food quality assurance.

KEYWORDS: calibration, conjugated dienoic fatty acids, free fatty acids, frying, *NIR spectroscopy*, soybean oil, total polar material.

The frying industry uses several parameters to determine the quality of oil in deep-fat fryers. Speed and consistency are extremely important characteristics in choosing measurement methodologies to be used. Acidity expressed as free fatty acid (FFA) content is one of the most common oil quality assays used to assess the quality of frying oils. The official methodology has been modified to use small oil samples in order to reduce cost and waste (1).

Total polar material (TPM) content is also a reliable indicator of frying oil deterioration. TPM uses hazardous organic solvents (petroleum ether and diethyl ether) and requires 3.5 h per sample (2). This index is not commonly used by the industry as a daily quality control index; its use is often limited to research studies.

Conjugated diene fatty acids (CDA) in polyunsaturated oil is an indicator of the initial oxidation stages. This index is not commonly used by the food industry but is very useful in scientific studies. Measurement of CDA is done by spectrophotometry (3).

Near infrared spectroscopy (NIRS) is a clean, fast, and nondestructive method proven to be useful in determining fatty acid composition in soybeans (4). It also has been used to determine the quality of edible oils (5-7). Previous work by Ng et al. (8) showed strong spectral correlations between FFA and NIRS using transmission spectra in samples of oils heated at 190ºC with the added water to promote the formation of FFA and TPM. The FFA range was 0.020 to 0.568 % oleic acid. Relative predictive determinants (RPD) (9), were between 2.5 to 6.0 for the FFA calibration, and between 15.3 and 19.7 for TPM. For TPM, the oil samples ranged between 2.18 and 62.93% polar material. It is generally accepted that a calibration with an RPD $\geq$ 5.0 is a good calibration and can be applied in quality control operations; if the RPD is $\geq$ 8.1 the calibration can be used in any application (9).

Büning-Pfaue and Kehraus (10) developed multiple partial least squares (PLS) models for FFA in the range of 0.03 to 2.76% as oleic acid and for TPM in the range of 7.6 to 48.1%. RPD were 5.5 for the FFA calibration and 5.0 for the TPM calibration. In this case, the oils being tested were obtained from actual fryers in restaurants and bars.

Yildiz et al. (11) reported a PLS calibration for CDA determination in soybean oils using transmittance NIRS, with RPD of 3.6 and 4.5 for two path lengths.

The previous studies were limited because the oxidation of the oils was done by heating and pumping water into the oils or by inducing the oxidation with a fluorescent lamp (9, 11) and when done with actual frying oils the number of samples used was too small (10). The objectives of this study were to determine FFA, TPM, and CDA with NIRS in actual frying oils with ranges typical of food service use.

MATERIALS AND METHODS

This NIRS study was conducted as part of a frying stability test of oils with varying linolenic acid content (12).

Oils: Extruded-expelled, physically refined soybean oils with three different levels of linolenic acid were obtained through Innovative Growers from American Natural Soy, Inc., Cherokee, Iowa. The cultivars from which the oils came were: IA2064 produced by Taylor Seeds, Inc. near Hartley, IA in 2003, ultra low-linolenic acid oil (ULL) and IA3018 produced by Pleasant Valley Farms near Iowa City, IA, in 2004, low linolenic acid oil (LL). The third oil was obtained from conventional beans produced by American Natural Soy (Control (Ctrl)). The starting linolenic acid contents of the oils were: 1.5 (ULL), 2.6 (LL), and 5.3% (Ctrl) The two lines with reduced content of linolenic acid originated from Iowa State University soybean varieties developed through traditional breeding practices.

French fries: Extra-long (XL) fancy 0.635-cm (¼ inches) shoestring par-fried frozen French fries were obtained from a commercial supplier. The fries were par-fried by the processor in partially hydrogenated shortening (canola and/or soybean oil) and/or palm oil, and/or beef fat. They also contained dihydrogen phosphate (to retain color), dextrose, and natural flavoring.

Frying operation: Three Star Twin-Pot deep-fat fryers model 530TA (Star Manufacturing International Inc., St. Louis, MO, 7.2 liter per well) were used to heat the oils. Oil treatments were heated in duplicate and French fries were fried according to Gerde et al. (12). The oil in the fryers was replenished to the starting level with fresh material.

Oil sampling: Aliquots from the filtered oils were taken at the end of each frying day for further analysis. The samples were stored at -22°C in glass jars under nitrogen in the dark to prevent further oxidation.

Free Fatty Acids (FFA): FFA content was measured daily from the oil aliquots (n = 138) by titration using a modification of the AOCS Official Method Ca 5a-40 (3) for small samples (1). The acidity was expressed as percentage of oleic acid. FFA are formed during the frying process from hydrolysis of triglycerides, however, the AOCS method does not discriminate between acidity from actual fatty acids and acidity from other organic acids formed during oil oxidation. Because the AOCS method is a titration procedure, with a colorimetric end point, it is not easy to get consistency among different laboratories and operators, and even from an individual operator.

Total Polar Compounds (TPC): TPC content was measured by column chromatography with AOCS Method Cd 20-91(3). The TPC content was measured after days 2, 5, 6, 9, 11, 14, 16, 19, 21, and 23 (n = 60).

Conjugated Diene Fatty Acids (CDA): The CDA content was determined as described in the AOCS Official Method Ti 1a-64 (3). The sample is dissolved in isooctane and the absorbance of the solution is measured in a spectrophotometer at 233 nm. The concentration of oil needs to be adjusted to fit the absorbance values between 0.2 and 0.8 (3). The oil samples were from the same days as for TPM, with the total number of samples again being 60.

Near Infrared Spectroscopy: Daily oil aliquots were allowed to come to room temperature in the dark and poured into 64/51 mm approximate internal diameter top/base weighing boats (Fisherbrand, Fisher Scientific, Pittsburgh, PA). They were scanned with a reflectance spectrometer using a wavelength range of 350-2500 nm (LabSpec Pro, Analytical Spectral Devices, Boulder, CO). The samples were not tested on-line and the test does not include temperature compensation.

Spectra were analyzed with Unscrambler 9.6 using Partial Least Squares (PLS) modeling, with three Principal Components (PC) for FFA and TPM and nine PC for CDA. Wavelengths in the range of 445 to 1675 nm were selected for CDA and TPM analyses and 1141 to 1675 nm for FFA analysis. These ranges contained the most useful information about the parameters measured. The validity of the models was tested by cross validation.

RESULTS AND DISCUSSION

Free Fatty Acids: The FFA level of the oil aliquots measured was 0.10 to 4.35 % oleic acid equivalent, with an average of 1.80 %. The best PLS model (3 PC) using one-out cross validation yielded a coefficient of determination (R^2) of 0.974 and a standard error of cross validation (SECV) of 0.219 with an RPD of 6.4. Eight aliquots out of the 138 were removed as spectral outliers, but no particular oil type or frying stage showed a tendency to produce spectral outliers. Figure 1 shows the regression between the reference and the predicted values.

Total Polar Compounds: The number of aliquots used for the TPM calibration was 60, rather than the 138 used for the FFA calibration, because of the time and resources needed to analyze all the samples. The TPM contents of the samples used ranged between 15.04 and 39.20 %, with a mean of 28.39%. The maximum TPM value was far above 24 to 27% that many countries accept as the maximum allowable for frying oils (12). Figure 2 shows the regression curve between the reference and the predicted values. The best PLS model yielded a R^2 of 0.958 with a SECV of 1.051 and an RPD of 4.9. Seven outliers were removed. The removed samples belonged to different stages in the frying process and did not show any tendency to produce outliers.

Conjugated diene fatty acids: Figure 3 shows the regression curve between the reference CDA method and the predicted values. The R^2 for by this model was 0.775 with a SECV of 0.080 and an RPD of 2.1. The range of CDA measured in the oil was from 0.86 to 1.80%, with a mean of 1.41%. Four outliers were removed.

In general the tested samples had a wider range of FFA and CDA compared to previous work (9, 11), however the range of TPM was narrower. Reflectance NIRS spectroscopy is a reliable, accurate and fast technique to determine the FFA and TPM contents in actual frying oils after lengthy use. The calibration to determine CDA was not as strong as for FFA and TPM. NIR spectroscopy can be used for quality control of frying operations in the food industry.

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TABLES AND FIGURES

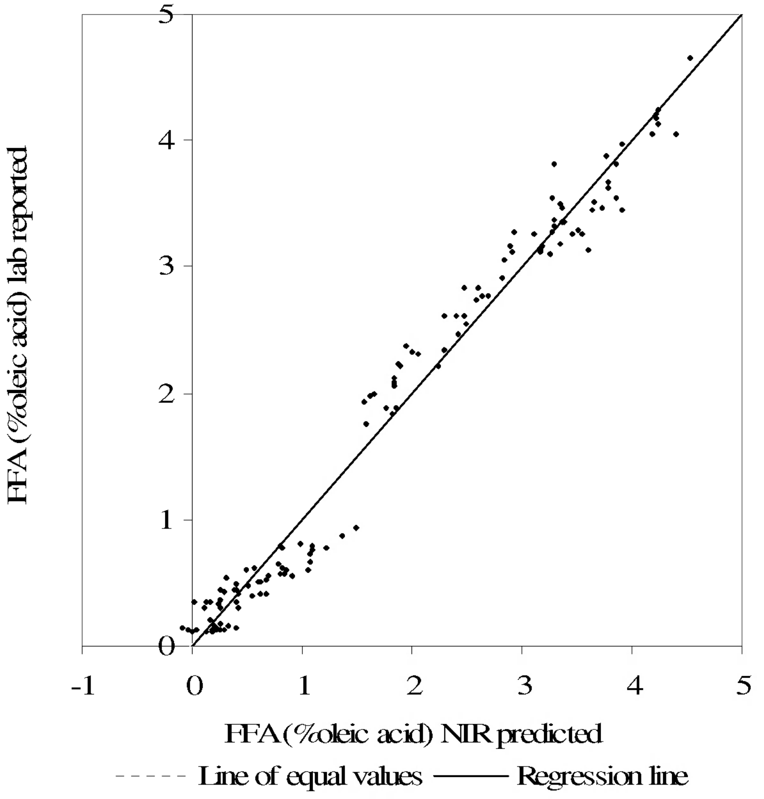

FIG. 1. Relationship between the lab reported and the NIR determined FFA values.

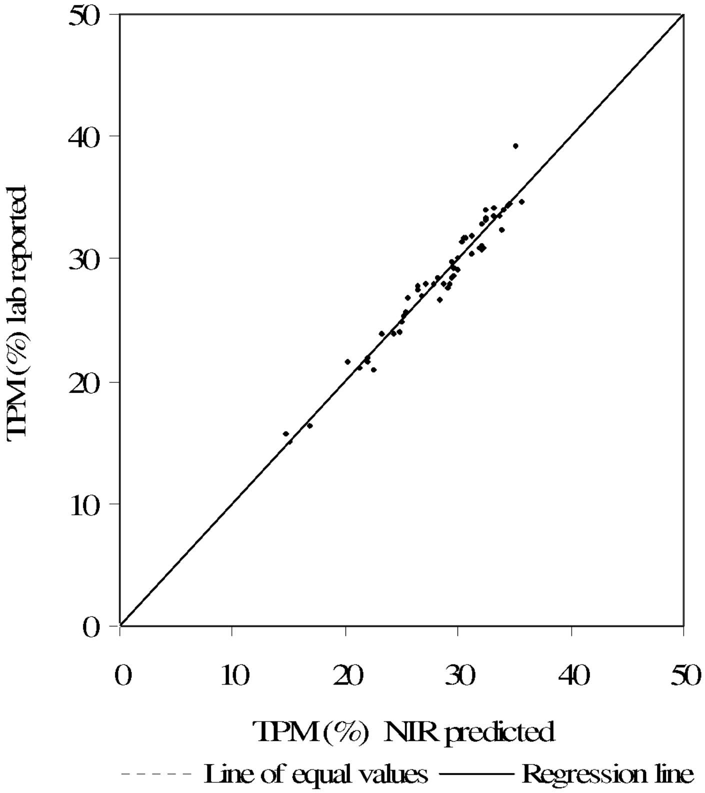

FIG. 2. Relationship between the lab reported and the NIR determined TPM values.

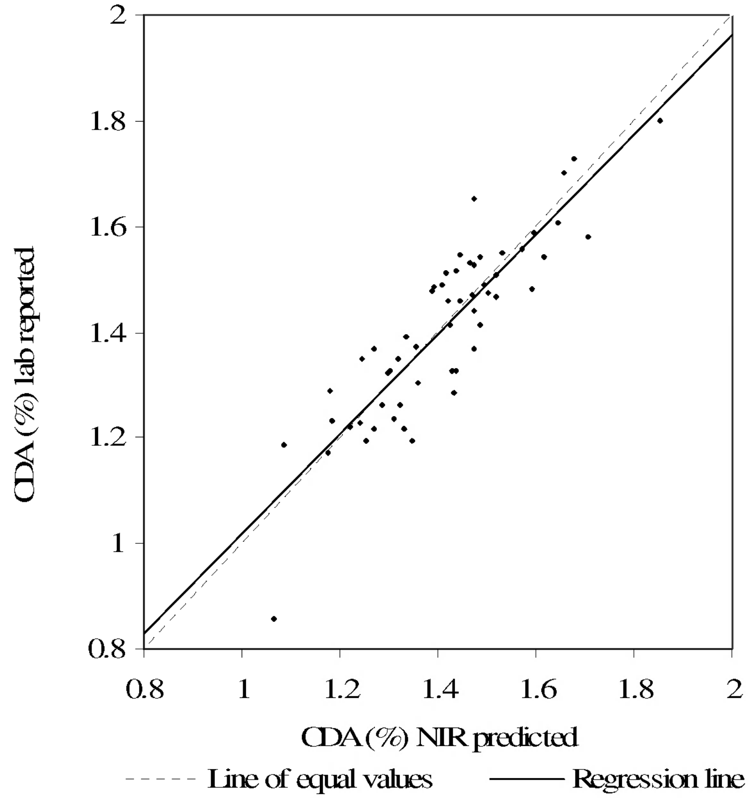

FIG. 3. Relationship between the lab reported and the NIR determined CDA values.

General Conclusions

This study demonstrated that the use of extruded-expelled soybean oil with reduced contents of linolenic acid improved the stability of soybean oil during frying. Both, ULL and LL performed better than the commodity oil and ULL tended to be more stable than LL according to the chemical parameters measured. Based on the TPM content, the frying life of both ULL and LL was ~30% longer than regular soybean oil. Indeed, the fry chefs' evaluation showed control was judged to be changed much earlier than both ULL and LL. The sensory evaluation of the French fries did not show differences among the treatments for potato, buttery, and painty flavors. For rancid flavor, fries fried in both ULL and LL scored lower (less intensity) than when fried in the control oil. The small differences between ULL and LL might be due to the higher content of tocopherols in LL and to the small difference in linolenic acid contents between the oils. In general, both ULL and LL oils seem to be promising alternatives to partially hydrogenated oils in frying processes.

For the evaluation of the oil degradation during frying using near-infrared spectroscopy, successful correlations were obtained for the determination of FFA and TPM. For CDA, the correlation was not as robust as for the other two parameters. Near-infrared spectroscopy was a fast and clean tool for determining the degree of degradation of frying oils in food quality assurance.

Continued development of soybean lines with enhanced fatty acid composition is desirable to meet the changing market demands for new oil types. For example, the linoleic acid content is a crucial factor in the stability of the oil, as well as in the diet. It will be necessary to explore the performance of oils with not only reduced content of linolenic acid but linoleic, too. Testing the NIR calibrations with an independent set of frying oils is needed to evaluate the usefulness of NIR as a quick testing method under different conditions.