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Frying Oils

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1. INTRODUCTION

Fried foods have provided culinary delight to people worldwide for centuries. It is difficult to determine when and where frying was first used by mankind. However, there is evidence that man used fried products long before the modern civilization reinvented fried products. Modern day frying involves sophisticated equipment, techniques, ingredients, and packaging. This is because the industrial fried products require long shelf life for warehousing, distribution, and sale.

In the frying process, food, such as vegetables, meat, or seafood, is brought in direct contact with hot oil. The food surface becomes golden yellow to dark brown in color and develops a pleasant fried food flavor.

Frying is done in homes, restaurants (food services), and at large industrial operations. Pan frying or griddle frying is done mostly at homes or at the restaurants. In this process, a thin layer of oil is heated on a skillet or a griddle. The food is fried in a layer of oil and fried until completion.

Restaurants also use batch fryers, where the food is placed in a wire basket, which is lowered into a bed of hot oil. The basket is removed from the hot oil when the product is fully fried.

The restaurants follow their guidelines on the frying temperature and time of frying. Frying temperature and frying time vary with the products fried.

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Large-scale production of snack food is done in deep fat fryers. These are either batch or continuous fryers. In a batch fryer, the food is added into a large pan of hot oil. The oil is heated either directly from under the fryer or in an external heater. In the latter case, the oil is continuously recirculated into the pan and it is stirred with a stirrer. Formerly, manual stirring was common but modern kettles are generally equipped with mechanical stirrers. Fried product is removed and spun through a centrifugal device to remove the excess oil from the surface. The product is seasoned and packaged. The recovered oil is reused.

In a continuous fryer, the food enters the fryer at one end, is fried and taken out from the other end. The product is submerged in a bed of hot oil for a specified time depending on the type of food being fried. The oil is heated directly or indirectly as described above for the batch fryers.

Products in the above procedures are fully fried and are ready for consumption. There is another industrial method of frying that is used quite extensively. This is known as the par-frying process. The food is partially dehydrated in an industrial fryer and flash frozen at -20° C. The packaged par-fried food is stored at -5° F (20.6°C) to -10° F (23.3°C) and distributed in freezer trucks. The product remains in a freezer at the destination. It is taken out of the freezer and fried immediately without thawing. Most common par-fried products are French fries, potato wedges, breaded chicken, coated or uncoated vegetables, cheese-filled vegetables, coated cheese sticks, etc. This reduces the manpower and preparation times at the restaurants and provides a great deal of convenience and cost savings to the restaurants and food services.

Advancement in the packaging materials and packing methods has enabled the industrial frying operations to extend the shelf life of the fried products so they can be stored, distributed, and marketed over several weeks to several months, without losing freshness in the product. This has provided a tremendous boost to the growth of the packaged fried food industry.

Oil plays a great role in determining the storage stability quality of the fried product. However, oil is also prone to oxidation, which leads to rancidity of the product in storage. Use of packaging material with high oxygen, nitrogen, and moisture barrier properties can significantly reduce oil degradation and increase the shelf life of packaged fried food.

Frying oil has been available to man in various parts of the world. Most of the time a specific oil has been selected for frying because it is locally available. Man also has moved from the crude expelled oils to refined oils as the oil technology advanced. In addition, the availability of most oils across the world has also increased due to improved transportation and storage systems developed over the years. Consumers have been exposed to the taste of products fried in different types of oil for quite sometime. Production of other than the indigenous oils has also become common where the local climate, soil conditions, and overall agronomy have been favorable to a particular type of oilseed or oil palm trees.

In spite of the widespread distribution of various types of oils across the world, it is found that there are regional preferences for particular oils in fried foods. For example, cottonseed oil is considered as the "gold standard" for potato chips in the United Sates. This is largely because cottonseed oil was the primary vegetable oil grown in the United States when potato chips were introduced 150 years ago at Saratoga Falls, New York (1).

Similarly, the Mexican consumers prefer sesame seed oil or safflower oil in fried snack foods. Consumers in the Indian sub-continent prefer peanut (groundnut) oil in fried snacks. Bias towards the original indigenous oil can be found in every oil-producing country. Availability and the necessity for sufficient supply of the oil have played a great role in local selection of oil for frying products. For example, the Mexican consumers have accepted palmolein for frying snack foods because the fried food has good flavor and taste, although they prefer safflower oil or sesame seed oil. Acceptance of palmolein in Mexico has been influenced by the fact that sesame seed and safflower oils are in short supply and more expensive and palmolein produces good fried food at reduced cost.

2. ROLE OF OIL OR FAT IN FRYING

Oil provides several important attributes to the fried product that makes the fried food palatable and desirable to the consumers, these include:

- Texture
- Fried food flavor
- Mouthfeel
- Aftertaste

Fortunately, oil has also been an excellent heat transfer medium for dehydration of the food during frying. Some mechanical engineers in the frying industry tend to treat the oil as a true heat transfer medium. Subsequent discussions in this chapter will show that oil plays a much greater role than just being a heat transfer medium in frying.

3. APPLICATIONS OF FRYING OIL

As previously mentioned, frying oil is used in homes, restaurants (food services), and industrial frying operations. Home fried food is consumed almost immediately after preparation. At restaurants, the fried food is generally made to order and consumed within minutes of its preparation. Frying oil is always considered acceptable at homes or restaurants when it produces good flavor and texture in the food. There is little or no concern regarding the shelf life of the fried product at either of these locations.

Industrial products, on the other hand, are packaged and distributed for sale. Some of these products may require weeks or months for their distribution and sale. Therefore, these products must maintain good flavor and texture in order to

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be acceptable to consumers when they are purchased. The oils (fats) used for industrial frying must have good oxidative and flavor stability in order to achieve good shelf life for the products. In this chapter, one will be able to understand the requirements that are critical for industrial frying oil. All subsequent discussions on oils in this chapter will be pertaining to industrial frying, although, the same criteria apply in restaurant frying.

4. SELECTION OF FRYING OIL

The following criteria (2) are applied for the selection of oil for industrial frying:

- 1. Product flavor
- 2. Product texture
- 3. Product appearance
- 4. Mouthfeel
- 5. Aftertaste
- 6. Shelf life of the product
- 7. Availability of the oil
- 8. Cost
- 9. Nutritional requirements

Flavor, aroma, and appearance are generally the first three attributes that the consumer looks for in the fried food. Subsequently, the consumer judges the fried food for texture, mouthfeel, and aftertaste. Thus, the first five items from the above list are important for consumer acceptance of the product.

Product shelf life is important for quality and economic reasons. All products require a certain number of weeks or even months for distribution and sales. The product flavor and texture must be acceptable to the consumer at the time it is used. The texture of the product (staleness) is caused by moisture pickup during storage. This can be corrected through proper initial moisture control and the use of appropriate packaging with a good moisture barrier property.

Oil quality and oil flavor stability greatly influence the flavor stability of the product in storage.

Availability and cost of oil are important economic factors. Even the best performing frying oil is not beneficial to the business if it is not available in sufficient quantities. The cost of oil is extremely critical for the industry. Most fried snack foods contain 20–40% oil. Therefore, the snack food company has to minimize the delivered cost of oil at the plant. Sometimes, the procurement department purchases oil from a supplier that does not have good control over their operation. This ends up costing money and goodwill for the snack food company in the long run.

Nutritional value of oil in the snack food has become important. To meet today's consumer desire's, the frying oil must have the following attributes:

- 1. Low in saturated fat
- 2. Low in linolenic acid
- 3. High oxidative and flavor stability
- 4. Not hydrogenated (trans-fat free)

This is a difficult challenge for the snack food industry to meet because the modified composition oils are in very limited supply. Palmolein has no *trans*-fat but it is high in saturated fat. Soybean oil and canola oil must be hydrogenated for industrial frying. Thus, they will have *trans*-fat. Moreover, it is important to recognize the fact that the joint supply of palm oil and soybean oil constitutes almost 80% of the world's oil consumption (2). There is not enough of either of these two oils to supply the world's total oil needs. Corn oil, cottonseed, modified sunflower, and modified canola oils are in limited supply. They are grown in limited geographic areas where they are facing stiff competition against other cash crops. Therefore, nutritional needs in fried snack foods can be met in limited geographic areas and at a significantly higher cost.

5. THE FRYING PROCESS

Frying is a complex process where simultaneous heat and mass transfer as well as chemical reactions take place (3). In this process, the hot oil supplies the heat to the product being fried. Heat turns the internal moisture of the food product into water vapor. The water vapor comes out of the product through the outer surface (see Figure 1). This is why one can always see bubbles around the food being fried. Bubbling is vigorous at the beginning when the food is added into the hot oil and stops when the moisture in the product drops to a low level.

The food product undergoes dehydration. At the same time, several physical changes and chemical reactions occur in the food as well as the frying oil, as described below:

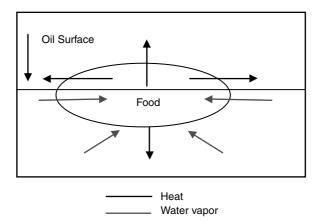


Figure 1. Conceptual heat and mass transfer during frying.

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5.1. The Changes Occurring in the Food

- The food loses moisture
- The food surface develops a darker color (sometimes, hard crust)
- The fried food develops a firmer texture (or crust)
- The food also develops fried flavor and aroma

5.2. The Changes Occurring in the Oil

- The fresh oil passes through a breaking-in period during which the fried food appears quite bland
- Fried food flavor develops as the frying process continues
- Along with flavor development, the oil undergoes the following chemical reactions:
 - 1) Hydrolysis
 - 2) Autoxidation
 - 3) Oxidative Polymerization, and
 - 4) Thermal Polymerization
- The oil in the fryer becomes darker

The oil quality and the fried food flavor go through an optimum stage. Thereafter, both oil quality and product flavor decline (4). All of the above chemical reactions alter the chemical structure of the oil molecules. The unsaturated fatty acids are mostly affected. Some desirable as well as undesirable chemical compounds are formed in the oil during frying (5). Oil in the freshly fried foods contains the same compounds that are present in the fryer oil. The desirable compounds help provide good flavor to the freshly fried product. Sometimes, the undesirable oil components can affect the fresh product flavor. In many instances, a fried product with good initial flavor may develop oxidized or rancid flavor during storage. This is because the products of oil oxidation are strong catalysts and cause further degradation of the oil (contained in the product) during storage. This phenomenon is quite pronounced when the oil is abused in the frying process. This is even more evident in products fried in oil with poor fresh oil quality. Therefore, oxidative stability of the oil in packaged fried foods is critical for achieving the desired shelf life for the product.

Darkening of the product surface, also called the browning reaction, is produced by the chemical reaction between the frying oil or oil present in the food (lipids in general) and proteins, and saccharides present in the food. This reaction is known as Maillard reaction (6, 7), which is responsible for the following:

- 1. Brown or dark brown surface appearance of the fried product
- 2. Fried flavor of the product

Browning reaction also provides some protection against photooxidation (8, 9), which will be discussed later.

6. CHEMICAL REACTIONS OCCURRING IN OIL DURING FRYING

It has been mentioned earlier that several chemical reactions take place in the oil during frying (10, 11). These include hydrolysis, autoxidation, oxidative polymerization, and thermal polymerization, as explained below.

6.1. Hydrolysis

In this process, an oil (triacylglycerol, also known as triglyceride) molecule reacts with a molecule of water, releasing a molecule of fatty acid (12), commonly known as free fatty acid (FFA), and a molecule of diacylglycerol (DG, also called diglyceride). The reaction scheme is shown below:

Triacylglycerol + H_2O = Free Fatty Acid(FFA) + Diacylglycerol

Although, it is common for the oil to undergo this reaction during frying, presence of a surfactant is required for hydrolysis to occur. Hydrolysis cannot occur unless oil and water form a solution (13). Oil and water do not mix except at very high temperatures under high pressure at 500° F (260° C) or higher, water boils at 212° F (100° C), at sea level. Therefore, one can expect that very little oil and water solution should result at frying temperatures ($300-415^{\circ}$ F or $149-213^{\circ}$ C), unless there is a small amount of surfactant present in the fryer (14, 15). A surfactant can facilitate the formation of an oil/water solution during frying. This is primarily responsible for generating the FFA in the fryer oil. Several sources of surfactants are listed below.

6.1.1. Fresh Oil. Fresh frying oil is obtained by refining palm oil or seed oils. It would be appropriate to briefly discuss the vegetable oil refining process for the readers to understand how various processing steps impact the quality of freshly refined oil. Vegetable oils are refined principally by:

- 1. Physical refining method
- 2. Chemical refining method

Palm oil and coconut oil are refined by the physical refining method. The crude oil is bleached with acid-activated clay and citric acid at elevated temperatures under vacuum. The objective is to remove phosphorus (phospholipids), trace metals, oil decomposition products, and some of the color bodies from the crude oil. The volatile impurities in the bleached oil are then removed via steam distillation under very low absolute pressure and high temperature in a deodorizer.

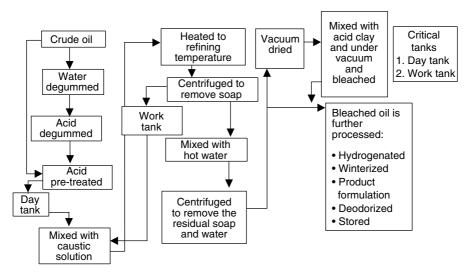


Figure 2. Chemical refining process.

Physical refining process is fairly simple and is environmentally friendly and more economical for palm oil, coconut oil, and palm kernel oil. The process may not remove the trace impurities if the bleaching step is not done properly.

Seed oils are refined mostly by the chemical method where the crude oil is intimately mixed with a caustic (sodium hydroxide) solution under controlled conditions. The caustic primarily reacts with the free fatty acids to form soap (in this case, sodium soap of fatty acids). The soap is removed from the refined oil using a centrifuge. Aside from free fatty acids, some of the phospholipids, trace metals, and some of the color bodies from the crude oil are also removed and they appear in the soap phase. The soap is processed further to regenerate fatty acids. The refined oil is water washed to reduce the soap and then bleached with acid-activated clay and citric acid at elevated temperatures under vacuum. The bleached oil is either deodorized to make liquid oil or is hydrogenated to make shortening and margarine and the formulated product is then deodorized. The schematic flow diagram for the chemical refining process is shown in Figure 2.

Various processing steps are involved in vegetable oil refining. Each step is controlled under specific operating and oil quality standards in order to produce the best quality oil. Oil-refining procedures have been discussed in another chapter in this series. However, the processing steps, and their impact on the hydrolytic and oxidative stability of fresh oil, have been discussed briefly. The impacts of improper processing on hydrolytic stability of the freshly refined vegetable oil are listed below.

1. Higher than the normal level of phospholipids, calcium, or magnesium left in the fresh oil (16, 17) as a result of:

- Poor quality crude oil
- Incomplete refining that leaves high levels of phosphorus, calcium, and magnesium
- Poor bleaching condition, leaving high levels of phosphorus, calcium, and magnesium
- Poor harvest and storage conditions for the seeds before crushing, producing crude oil that is hard to refine
- 2. Soap left in the oil as a result of poor water washing and bleaching (18).
- 3. High levels of diacylglycerol and monoacylglycerol in the refined oil as a result of the (19) factors listed below:
 - Poor-quality crude oil that requires excess caustic treatment
 - Repeated refining of the crude oil because of poor crude oil quality
 - Caustic overdose in the refining step as a result of poor process control
 - High temperature in refining

6.1.2. Food. Surfactants can originate from the food itself. Food products contain many naturally occurring components that have surface-active properties. The metals, naturally present in the food, can form soap by reacting with the free fatty acids in the oil. The coating materials on breaded products contain acid-phosphates of sodium or calcium. These metal ions react with free fatty acids in the oil to form soap. Soap, thus formed in the oil, can produce an oil/water solution in the fryer and promote hydrolysis in the oil.

6.1.3. Oil Decomposition Products. Some of the oil decomposition products have surface-active properties. These compounds can promote hydrolysis of the fryer oil somewhat similar to soap.

6.1.4. Poor Rinsing of the Fryer After Sanitation. Soap is left in the fryer when it is not completely rinsed after sanitation, leaving residual caustic or soap in the system. This can promote hydrolysis in the fryer oil.

6.2. Autoxidation

Oil is oxidized during frying. Oxidized fatty acids develop flavor in the fried food (20). The compounds known to impart good fried food flavor are lactones and certain aldehydes. Most of these compounds originate from linoleic acid. Autoxidation is one of the major reactions taking place during frying (20–24) and, subsequently, in the oil present in the packaged product in storage.

Autoxidation of unsaturated fatty acids is initiated by a free radical, which is formed in the oil when an unsaturated fatty acid is exposed to oxygen in the presence of a metal initiator, such as iron, nickel, or copper. The fatty acid could be a fatty acid moiety on a triacylglycerol molecule or it could be a free fatty acid molecule that is either present in the fresh oil or produced in the oil from hydrolysis during frying. The reaction mechanism for autoxidation involves several steps as described below:

6.2.1. Step 1: Initiation. Metal initiator produces a free alkyl radical from an unsaturated fatty acid molecule. The following conditions are required for this reaction step:

- There must be a metal initiator (iron, nickel, copper) in contact with the unsaturated fatty acid
- Heat generally accelerates the process of free radical formation and the subsequent reaction steps
- Phospholipids, monacyloglycerol, and diacylglycerol can reduce the interfacial tension between oil and air. This increases the amount of contact between the oil and oxygen in frying, promoting autoxidation
- Calcium and magnesium form soap in reaction with the free fatty acid in the fryer oil, forming soaps. These can behave in the same way as the phospholipids, causing increased autoxidation in the fryer oil.

6.2.2. Step 2: Reaction with Oxygen. The free radical reacts with a molecule of oxygen, forming a peroxy (alkoxy) radical. Presence of oxygen is absolutely necessary. This is why oil does not oxidize when it is stored under vacuum or saturated with nitrogen.

6.2.3. Step 3: Propagation. In this step, the peroxy radical reacts with a molecule of unsaturated fatty acid, forming a molecule of hydroperoxide and releasing another free alkyl radical, which can then react with an oxygen molecule to form a peroxy (alkoxy) radical. This step becomes rapid and more complicated when the oil contains linolenic acid.

Hydroperoxides are very unstable and decompose into a series of aldehydes, ketones, hydrocarbons, alcohols, and many more reaction products as the oil-oxidation process continues. In reality, these reactions can continue during storage of the packaged product, as the oil in the product continues to break down via autoxidation and develops oxidized or rancid flavor in the product.

6.2.4. Step 4: Termination. Free radicals can react with each other. This occurs when:

- 1. There are no more unsaturated fatty acids left in the system, or
- 2. When there is no more oxygen present in the system

7. SOURCES OF FREE RADICALS

Free radicals are formed whenever oil containing unsaturated fatty acids is heated in the presence of a metal initiator, (25) such as iron, nickel, or copper. Free radicals are formed in the oil during frying. The metal initiator in the frying process can come from several sources as given below:

- 1. The food being fried
- 2. The oil itself

Trace metals are present in crude vegetable oils at parts per million (ppm) levels. Researchers have shown that soybean oil flavor can deteriorate from autoxidation, even at an iron content as low as 0.3 ppm (26) in the deodorized oil. Metal initiators initiate autoxidation in all vegetable oils and animal fats.

Trace metals in the crude oil are removed in the refining and, primarily, in the bleaching steps (27–32). Inadequate bleaching of the oil can leave trace metals at high concentration in the oil. This can promote autoxidation in the fryer. In addition, atmospheric bleaching, poor vacuum in the vacuum bleacher, high temperature in the bleacher, or poor vacuum in the deodorizer can produce free radicals in the fresh oil (33). These free radicals can rapidly oxidize the oil in a fryer.

8. POLYMERIZATION

There are two types of polymers formed in the fryer oil (25). These include:

- Oxidative polymers
- Thermal polymers

8.1. Oxidative Polymers

Oxidative polymers are formed in autoxidation when the free radicals terminate each other as under autoxidation. When a triacylglycerol molecule breaks down during autoxidation, the partial triacylglycerol molecules are not removed in the deodorization process and can react with each other, forming dimers, trimers, or polymers.

These oxidative polymers do not always impart an off flavor to the freshly fried food. However, an off flavor in the packaged product might be observed within a few days after production and may exhibit oxidized or rancid flavor in the product before expiration of the code date on the package. This is because of the following events that might occur:

• The oxidative polymers are strong free radicals and can decompose while the fried product is in storage

- Some of oxidative polymer molecules may contain a higher amount of oxygen than the triacylglycerol molecule. When these oxidative polymers decompose, they produce free radicals and release some oxygen (34)
- The free radicals and the released oxygen can continue the autoxidation process in the product during storage
- This phenomenon can be observed in packaged fried products, even when the package is nitrogen flushed, using a film that has high nitrogen barrier property
- This reaction can progress even when the above product is stored in a freezer
- Some researchers have called this reaction "hidden oxidation" (35)

Improperly processed oil can have high concentrations of free radicals even after deodorization (34). This can compound the situation, producing rapid oxidation of oil during frying.

8.2. Thermal Polymers

Polymerization of oil occurs under heat with or without the presence of oxygen. Heat can cleave the oil molecule or fatty acid. These cleaved compounds can then react with each other, forming large molecules. These polymers are referred to as thermal polymers. In the frying process, excessive fryer heat and excessive fryer down time can produce high levels of thermal polymers. Thermal polymers can be detected in the fresh product by expert panelists because they generally impart a bitter aftertaste to the fried food.

9. COMPLEXITY OF OIL REACTIONS IN FRYING

The reactions in the oil in the frying process are very complex. Figure 3, published by Carl W. Fritsch, illustrates the various pathways for oil reaction in the fryer (10).

Figure 3 shows that the autoxidation reaction produces alcohols and acids, among others. Some of these are dibasic acids, i.e., they contain two carboxylic acid groups (- COOH). This is why oil expelled from a highly oxidized or rancid fried product can exhibit a higher free fatty acid content than the fryer oil sampled at the same time as the product. This does not mean that the oil in the product was hydrolyzed in storage. It means the oil was abused at the time the product was packaged. The above phenomenon is observed in fried food even if the product is packaged under nitrogen flush.

Figure 3 indicates that there are several reactions that take place simultaneously in the fryer. Also, the degradation of product flavor is associated with oxidation and other reactions in the oil. Therefore, it is important to note that measurement of free fatty acid in the fryer oil does not necessarily represent the absolute quality of the oil. This is because the free fatty acid content in the fryer oil ranges from 0.25% to 0.40% for most snack food products. In many frying operations, a portion of the fryer oil is replaced by fresh oil when the free fatty acid level exceeds 0.35%. At this low level of free fatty acid, there is little correlation between the free fatty acid

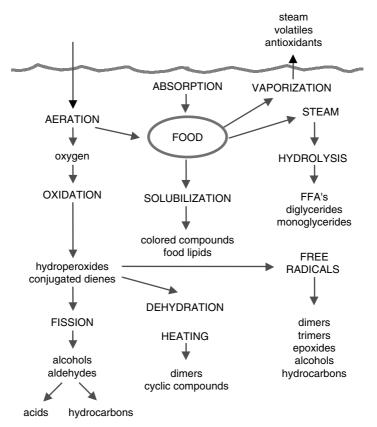


Figure 3. Reactions in oil during frying.

and the degree of oxidation of the fryer oil. Free fatty acids in the fryer oil could be considered as a valid oil quality indicator, where the free fatty acids are allowed to go up to >0.5% in the fryer.

In fact, the author conducted the following experiment on a commercial potato chip fryer to prove that the high level of free fatty acid in the oil was not a determinant for poor flavor in the fresh product. The test procedure and the observations are listed as follows:

- The fryer was filled with fresh oil
- Pure oleic acid at 2% level was added into the fryer oil and circulated for complete mixing
- The make-up oil also contained 2% of added oleic acid
- The fryer was operated under normal operating conditions
- The fresh product did not have any objectionable flavor from high free fatty acid content of the fryer oil
- The flavor of the product was affected only after the oil began to oxidize

It was mentioned earlier that the standard procedure in the snack food industry is to discard oil when the free fatty acid in the fryer oil reaches or exceeds 0.5%. The experimental oil contained 2% free fatty acids, and yet the product flavor was unaffected until the oil began to oxidize.

Referring to Figure 3, one can see that a multitude of reactions occur in the fryer oil simultaneously. This includes hydrolysis, autoxidation, polymerization, and many others. Therefore, the fryer oil should also be analyzed for the state of oxidative and polymeric degradation aside from free fatty acids. These analyses will not be the same for all types of fried food. The specific analysis needs to be established through shelf life study and consumer acceptability tests on the product.

It is a difficult and lengthy process to identify and quantify the specific compound or compounds in the fried food that makes the consumer reject it for poor flavor.

The following techniques are generally applied by the snack food companies to identify and quantify the compound or compounds (markers) that are responsible for consumer rejection of the product for unacceptable flavor:

- A well-designed shelf life test protocol including oil and corresponding product sampling procedures are outlined
- Highly skilled analysts to analyze oil breakdown products in the fryer oil and in the product (fresh and stored)
- A well-designed consumer test or multiple tests to determine the point at which the product flavor is found to be unacceptable
- Identification and quantification of the oil-degradation compounds that are responsible for the rejection of the product for unacceptable flavor
- Statistical correlation are established between the oil-quality parameters (also called markers) and consumer test results to establish the threshold value for the marker/markers responsible for product failure.
- The data are correlated with the initial oil quality in the product to establish the standards for the fryer oil quality in the process.

The markers and the threshold values are expected to be different for different products.

10. ANALYTICAL REQUIREMENTS FOR FRESH FRYING OIL

Based on the prior discussions, it can be stated that frying oil must meet the following quality criteria:

- 1. Good oxidative stability
- 2. Low levels of trace impurities in the fresh oil to prevent rapid hydrolysis and oxidation during frying

Oxidative stability of the oil depends primarily on its polyunsaturated fatty acid content. This includes linolenic and linoleic acids. Linolenic acid-containing

three-double bonds is most prone to oxidation; linoleic acid is less reactive than linolenic acid. As the number of double bonds increase in the fatty acid, the relative rate of oxidation increases at higher than a linear rate (36).

Fatty Acid	Relative Rates of Oxidation
Stearic acid	1
Oleic acid	10
Linoleic acid	100
Linolenic acid	150

Linolenic acid content must be low in order to provide maximum oxidative stability to the oil. This is why soybean and canola oil, which contain about 8% linolenic acid in the natural state, are hydrogenated to reduce their linolenic acid content to less than 2% determined by the capillary GC Method (2). Poor frying stability in sunflower oil comes primarily from the high level of linoleic acid. Therefore, sunflower oil must also be hydrogenated to reduce its linoleic acid content to 35% or lower for industrial frying. Table 1 lists the analyses of the most commonly used industrial frying oils.

Analysis	PH Soy	PH Canola	Corn	Cottonseed	PH Sun	Palm Olein	Frying Shtg.
FFA%	< 0.05	<0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
PV	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
IV	100	90	118–130	98–118	100	55–58	75–78
	+/- 4	+/- 2			+/- 4		
M.Pt °F	75	70	—	—	70	75	105–109
(Max)							
AOM	35	70	16	16	25	60	>100
hrs (minimum)							
FAC (%)							
C-14	—		_	_	—	1.0–1.5	—
C-16	10	4	11	22	7	39–43	_
C-18	5	2	2	2	4	4–5	—
C-18:1	55	75	20	19	53	40–44	_
C-18:2	28	12	60	53	35	12–14	—
C-18:3	<1.5	<1.5	<1.0	<1.0	<1.0	<0.5	_
C-20	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	_
C-22	—	_	_	_	_	_	_
C-22.1	_	<0.5	_	_	_	_	_
% Trans	25	25	_	_	25	_	35
SFI @ °F							
50°F	<10	<10	_	_	<10	_	20–26
70°F	<1	<1	_	_	<1	_	18–24
82°F	_	_	_	_	_	_	14–18
92°F	_	_	_	_	_	_	12–16
104°F	—	_	_	_	_	_	4–8

TABLE 1. Analyses of Common Industrial Frying Oils and Fats.

PH—Partially hydrogenated; Frying Shtg—Frying shortening; FFA—Free fatty acid; PV—Peroxide value; IV— Iodine Value; M.Pt.—Melting Point; AOM—Active oxygen method; FAC—Fatty acid composition; SFI Solid fat index ($50^{\circ}F = 10^{\circ}C$; $70^{\circ}F = 21.1^{\circ}C$; $80^{\circ}F = 26.7^{\circ}C$; $92^{\circ}F = 33.3^{\circ}C$; $104^{\circ}F = 40^{\circ}C$). It has been mentioned earlier that linoleic acid is more stable than linolenic acid, but far less stable than oleic acid. This is why regular sunflower oil, which contains as much as 65% linoleic acid, is not suitable for frying shelf-stable industrial products. However, Table 1 indicates that liquid cottonseed and corn oil are used for industrial frying, although both oils contain over 50% linoleic acid.

Sunflower oil contains 10–12% higher linoleic acid than corn or cottonseed oil. However, this does not fully explain why corn or cottonseed oil has much higher frying stability than sunflower oil. The value of AOM does not fully explain why corn oil and cottonseed oil have higher frying stability than sunflower oil. This is discussed further in the following section.

11. IMPACT OF TOCOPHEROLS AND TOCOTRIENOLS IN FRYING OIL

Tocopherols are natural antioxidants present in all vegetable oils (30). The seed oils contain four types of tocopherols at varying amounts as listed in Table 2.

It is important to note the difference between the seed oil and palm oil. Seed oils contain tocopherols. Palm oil contains tocotrienols in addition to tocopherols, and also a small amount of coenzyme Q10. Both tocotrienols and coenzyme Q10 high antioxidant properties. Gamma- and delta-tocopherols, and their corresponding tocotrienols, are very effective in protecting oils from autoxidation (37).

Alfa-tocopherol is a good antioxidant against photooxidation (38). Table 2 shows that corn and cottonseed oils are rich in gamma-tocopherol, while sunflower oil contains very little gamma-tocopherol. This may explain why cottonseed oil and corn oil have superior frying stability than the sunflower oil even without hydrogenation.

Palm oil (also its fraction, palmolein) has good frying stability because of its high contents of gamma- and delta-tocotrienols, aside from the corresponding tocopherols. Tocotrienols contain three unsaturated double bonds as compared with the

Tocols (ppm)	Sunflower	Cottonseed	Soybean	Canola	Palm Oil ⁺
Tocopherols:					
Alpha	403–935	136–674	9–352	100–386	130-260
Beta	ND-45	ND-29	ND-36	ND-140	22–45
Gamma	ND-34	138–746	89-2306	189–753	19–20
Delta	ND-7	ND-21	154–932	ND-22	10–20
Tocotrienols;					
Alpha	ND*	ND	ND	ND	44–90
Beta	ND	ND	ND	ND	44–90
Gamma	ND	ND	ND	ND	260-525
Delta	ND	ND	ND	ND	70–140
Total Tocol (ppm)	440–1520	380-1200	600–3370	430–2680	600–1200

TABLE 2. Tocol Content in Typical Oils (Source: Food Codex).

ND-Nondetectable.

corresponding tocopherols. This makes tocotrienols more effective as antioxidants against autoxidation in the frying process.

12. FACTORS AFFECTING FRYING OIL QUALITY

Table 3 lists the desired quality attributes for frying oils. It indicates that the oil must be low in free fatty acids, peroxide value, conjugated dienes, anisidine value, monoacylglycerols, diacylglycerols, and trace impurities, such as iron, phosphorus, calcium, and magnesium. Each of these quality parameters has specific significance in influencing the performance of the frying oil.

Quality of the oil starts from the seeds (39) for seed oils and from fruit palm (for palm oil and palmolein). Seeds that are physically damaged, insect-infested, moldy, too dry, or too moist produce poor-quality crude oil (40–43). Crude oil derived from such seeds can have high free fatty acids and oil oxidation products that inherently make the oil less stable, even after complete refining.

•			
Analysis	Desired Level	Maximum Level	AOCS Method
Free fatty acid, FFA (%)	0.03	0.05	Ca 5a-40 (97)
Peroxide value, PV, meq/kg	<0.5	1.0	Cd- 8b-90 (97)
Para anisidine value, pAV, AVU Unit	<4.0	6.0	Cd-18-90 (97)
Conjugated dienes, (%)	Trace	<0.5	Th-1a-64 (97)
Polar compounds, (%)	<2.0	<4.0	Cd-20-91(97)
Polymers, (%)	<0.5	<1.0	Cd-22-91(97)
Phosphorus, PPM	<0.5	<1.0	Ca-12b-92 (97)
Iron, PPM	<0.2	<0.5	Ca-17-01 (01)
Calcium, PPM	<0.2	<0.5	Ca-17-01 (01)
Magnesium, PPM	<0.2	<0.5	Ca-17-01(01)
Monoacylglycerol, (%)	ND	Trace	Cd-11b-91(97)
Diacylglycerol*, (%)	<0.5	<1.0	Cd-11b-96 (97) Cd-11b-91 Cd-11b-96
Lovibond Red Color:	-1.0	<1 E	Cc-13b-45 (97)
Soybean oil Canola oil	<1.0	<1.5	
	<1.0	<1.5	
Sunflower oil	<1.0	<1.5	
Cottonseed oil Corn oil	<3.0	<3.5	
Palmolein	<3.0 <2.5	<3.5 <3.0	
	<2.5 <1.5		
Peanut (Groundnut) oil	< 1.5 460	<2.5	Cc-9a-43 (97)
Smoke point,**°F (minimum)	400	—	00-98-43 (97)
Soap, PPM	_	0.0	Cc-17-95 (97)
Flavor grade	8	0.0	Cg-2-83 (97)
Chlorophyll (ppb)	8 <30	 <30	Cg-2-83 (97) Cc-13d-55 (97)

TABLE 3. Recommended Analytical Parameters for Fresh Frying Oil (RBD oil).

*Commercial palm oil may contain 5-11% diacylglycerol.

**420°F for commercial palm oil or palmolein.

Excessive rain before harvest can increase chlorophyll content of the crude oil. There are two types of chlorophylls found in oilseed: Chlorophyll-A and Chlorophyll-B. Chlorophylls are oil soluble and produce green color in the oil. At normal concentrations, they are easily reduced in the bleaching process. It is very difficult to reduce the chlorophylls from the crude oil if it is obtained from seeds that are not mature or have developed higher chlorophylls because of excessive rain before the harvest. The normal practice is to use an excess amount of bleaching clay to reduce chlorophylls. This reduces the natural antioxidants in the oil, produces higher amounts of free radicals in the oil, and reduces its stability.

A high concentration of chlorophyll catalyzes photosensitized reaction (photooxidation) in the product fried and stored in clear packages. In addition, extra bleaching of the oil can decompose chlorophylls into pheophytenes, pheophorbides, and pyropheophorbides, which do not have visual green color but are ten times more active photosensitizers than their parent compounds (44–46).

Seeds must be dried before storage. Failure to do so can increase enzyme activity in the seeds and damage the oil inside. Moisture content, the drying process, and the storage condition of the seeds impact the quality of the crude oil obtained from the seeds. In extreme cases, it becomes very difficult to obtain refined oil with high stability and good color from poor quality or poorly handled seeds.

Damaged seeds, whether resulting from the harvest, subsequent handling, insect infestation, mold infestation, or weather conditions can trigger the activities of several enzymes in the seeds (47). These are summarized below.

12.1. Lipase Reaction

Lipase hydrolyzes the triacylglycerol molecules in presence of moisture and form free fatty acids, diacylglycererols, or even monoacylglycerols. Monoacylglycerols are mostly removed from the oil during deodorization, but a great majority of the diacylglycerols remain in the processed oil after deodorization. It has been mentioned earlier, high concentration of diacylglycerols in the fresh oil can accelerate the process of hydrolysis in the fryer.

12.2. Lipoxygenase Reaction

Lipoxygenase oxidizes the unsaturated fatty acids in the oil in the seeds during storage under the conditions described above (48). There are different types of lipoxygenases in oilseeds. Lipoxygenase- Type-II and Type-IV are more reactive than the others (48).

12.3. Phospholipase-D Reaction

This enzyme converts the hydratable phospholipids present in the seeds into nonhydratable phospholipids (42), when the seeds contain 14% moisture or higher and stored at $115^{\circ}F$ (45°C) or higher. It is undesirable to have a high level of nonhydratable phospholipids in the crude oil because extra caustic treatment or longer contact time between caustic and crude oil is required to reduce the nonhydratable phospholipids in crude oil. This increases the potential for increased diacylglycerol content in the refined oil.

The crude oil with high nonhydratable phospholipids requires acid pretreatment before refining. This may increase the chlorophyll breakdown, forming pheophytenes, pheophorbides, and pyropheophorbides and make the finished oil more susceptible to photooxidation (44).

High temperature storage of seeds can also produce darker color crude oil as a result of color fixation (49) (this is also true for oil storage). This crude oil requires extra caustic or stronger caustic treatment as well as extra bleaching treatment to reduce the red color. Sometimes, it is difficult to obtain a light bleached color in color-fixed oil even after heavy bleaching. Extra refining and bleaching not only increases the potential to have higher concentration of diacylglycerols in the refined oil but also removes tocopherols from the refined oil. This reduces oxidative stability of the refined oil (50).

Storage of crude oil is also critical. Prolonged storage or high temperature storage of crude oil can greatly affect the quality of the refined oil (51). Long-term storage of crude oil increases oxidation, free fatty acids, and nonhydratable phospholipids in the crude oil, resulting in poor-quality refined oil. Crude oil with a high peroxide value can be refined to meet the fresh oil analytical standards but can oxidize very rapidly during frying.

Aside from free fatty acid, peroxide, aldehydes (by para-anisidine, pAV test), and conjugated dienes, the oil must also be low in trace components as listed in Table 3.

13. QUALITY STANDARDS OF OILS (TABLE 3)

- 1. The oil is either improperly processed or it is derived from poor-quality crude if the fresh oil analysis indicates the following:
 - FFA >0.05%
 - Lovibond Red color is higher than normal (see Table 3 above)
 - Tocopherol content is lower than normal (see Table 4)

2. The FFA in the oil rises rapidly in storage if it contains high levels of (47):

Phosphorus	>1 ppm
Calcium	>0.3 ppm
• Magnesium	>0.3 ppm
• Sodium	>0.2 ppm
 Diacylglycerols 	>1.5%
 Monoacylglycerols 	>0.4%

Tocopherol (ppm)	Cottonseed	Corn	Soybean	Palm [*]	Sunflower
Alfa-tocopherol	320	134	75	256	487
Beta-tocopherol	—	18	15	—	—
Gamma-tocopherol	313	412	797	316	51
Delta-tocopherol	—	39	266	70	8
Total tocopherol	633	603	1153	642	546

TABLE 4. Typical Values of Tocopherols in Refined Seed Oils (ppm).*

Source: Bailey's Industrial Oils and Fat Products, 5th ed., pp. 133 and 194 (52). 2nd ed., p. 131 (53) The Lipid Handbook, (54)

*150 ppm of tocotrienols.

3. The oil will oxidize rapidly in the fryer if the oil contains high levels of (47):

• PV	>1.0
• pAV	>6.0
• Iron	>0.3 ppm
• Conj. Dienes	>0.5%
• Polars	>4.0%
• Polymers	>2.0%
• Iron	>0.3%

Frying oil needs certain amounts of solid fat to fry foods that require crunchy texture or crispness. Table 1 lists the typical industrial frying fats and their analyses.

14. COMMENTS ON PALM OIL

Palm oil is the second largest source of oil in the world, next to soybean oil (55). Worldwide production of palm oil is increasing at a rapid rate and the volume of palm oil in the world may surpass that of soybean oil in the near future. Palm oil and palm olein (the liquid fraction) show excellent frying performance. In addition, both palm oil and palm olein produce a highly desirable fried food flavor (56, 57).

Sometimes the commercial palm oil and palm olein contain high amounts of diacylglycerols and phospholipids. This makes the oils prone to rapid hydrolysis in frying.

Diacylglycerols are produced in the fruit palm after harvest. The fruits are required to be processed within 24 hours after the harvest in order to control hydrolysis of the oil in the fruit by lipase. This guideline cannot be followed by all palm oil processors during the peak harvest season. As the trading rule for palm oil allows 5% free fatty acids in crude palm oil and 0.25% free fatty acid in neutralized palm olein (58), there is no incentive for the common palm oil processors in producing oils with lower free fatty acids. Commercially available palm oil and palm

olein may contain higher than 1 ppm of phosphorus after refining, which may make the free fatty acids go up rapidly in the oil during frying.

It is possible to produce crude palm oil with less than 1.5% free fatty acid and less than 4% diacylglycerols through careful separation of the damaged fruits from the bulk and by exercising some other process precautions.

Some palm oil processing companies in Malaysia are producing and exporting fully processed palm oil and palm olein with low free fatty acids, diacylglycerols, phosphorus, and trace metals. They guarantee the delivered quality for the oil. These oils have shown excellent frying stability.

15. ENHANCEMENT OF FRYING OIL PERFORMANCE

Natural as well as synthetic antioxidants can improve the oxidative stability of edible oils. Most common natural antioxidants are mixed tocopherols. Tertierybutylhydroquinone (TBHQ) is one of the most common synthetic antioxidants used in commercial frying oils. This also costs only a fraction of the natural antioxidants.

Tocopherols are already present in the oil. The amounts and the types of tocopherols vary with the type of oil. Most common types in seed oils are alpha-, gamma-, and delta-tocopherols. These compounds protect the oil from oxidation during processing, storage, transportation, and, also, later in the fryer. Tocopherols terminate the free radicals by reacting with them in the autoxidation reaction. This is why they are considered as free radical scavengers/quenchers.

For various reasons, as described earlier, the freshly refined oil may contain lower than the desired level of tocopherols. In those cases, supplementing the oil with gamma- and delta-tocopherols or gamma- and delta-tocotrienols can significantly improve oxidative stability of the oil. This is not commercially practiced because of the high cost of the antioxidants.

As antioxidants are free radical quenchers, the level of the added antioxidants in the refined oil decreases while the oil is in storage or in transit. However, one must recognize the fact that, because of the presence of antioxidants, the free radical content of the oil is going to be low at the time it is added to the fryer (provided the oil is not stored for too long or oxidized as a result of mishandling before use).

A large portion of the TBHQ is lost during frying as a result of high heat and agitation. Therefore, some suggest that addition of TBHQ in frying oil is not beneficial. However, it is known that, despite the loss of TBHQ in the fryer, the finished product will have a better chance to retain good oil flavor during storage and distribution because of the lower concentration of free radicals in the fresh oil used in frying. It must be emphasized that the added antioxidant does not necessarily protect the oil against abusive treatment during storage, handling, or frying.

There are various synthetic antioxidants, such as butylated hydroxytoluene (BHA), propyl gallate (PG), ethylenediaminetetraacetic acid (EDTA), etc. that are used in commercial oils; TBHQ is known to produce the best results in frying applications.

Many countries have regulations regarding the type of antioxidants permitted for use and also on the maximum allowable limits in foods. The snack food companies must be aware of local regulations regarding the use of synthetic and natural antioxidants in foods.

Added tocopherols, tocotrienols, or synthetic antioxidants must be declared on the label, according to the USFDA (United States Food & Drug Administration), if they are added to the oil after deodorization.

16. STORAGE AND TRANSPORTATION OF FRYING OIL

Deodorized oil must be cooled, saturated with nitrogen, and stored in nitrogenblanketed tanks (59). The storage tanks can be made of carbon steel. It is not necessary to have stainless steel tanks for freshly deodorized oil with a low free fatty acid content as shown in Table 3. The following guidelines are recommended for oil storage:

- Liquid oils should be stored under $86^{\circ}F(30^{\circ}C)$ and should not be stored at a temperature higher than $104^{\circ}F(40^{\circ}C)$
- The storage temperature of hydrogenated fats must not exceed its melt point by 10° F (5.6°C)

The best results are obtained when the deodorized oil is cooled to the above recommended temperatures, saturated with nitrogen as it leaves the deodorizer, and stored in nitrogen-blanketed tanks. The headspace in the storage tank should have maximum oxygen content of 0.5% (see Figure 4).

Loading trucks or rail cars are also critical for the quality of the oil delivered at the point of destination. The oil can pick up air (oxygen) at the loading station, which can initiate autoxidation in the oil during transit. The clearest indication

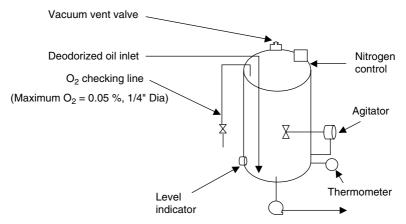


Figure 4. Schematic for deodorizer oil storage. (Copyrighted by: MG Edible Oil Consulting, Int'l.).

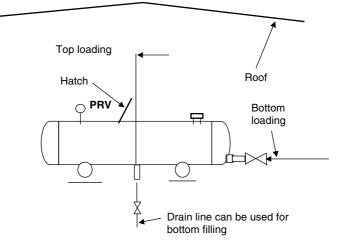


Figure 5. Schematic diagram for truck loading. (Copyrighted by: MG Edible Oil Consulting, Int'l.).

of such a situation is found when the oil, at delivery, shows a higher peroxide value than the certificate of analysis (written at the time of loading and sent with the oil shipment). In addition, partially loaded trucks or rail cars have more air space above the oil. This causes higher oxygen absorption by the oil during transit. The following steps are recommended to minimize the oxygen absorption by oil during loading and transit:

- Follow the guidelines provided above on oil temperature
- Saturate the oil with nitrogen at the discharge of the loading pump
- Bottom load the truck or rail car
- Extend the loading boom to the floor of the truck or rail car to avoid splashing of the oil and air entrainment during loading
- Fill the truck or rail car to the maximum limit to minimize air space at the top

See Figure 5 for truck or rail car loading.

Unloading and storage of the oil is equally critical at the snack food company. Care must be taken not to overheat any solidified hydrogenated oil. The oil must be saturated with nitrogen and stored under nitrogen as described for the deodorized oil.

17. HYDROGENATION AND TRANS-FAT

Sabatier and Senderens (59) conducted the first hydrogenation reaction in the vapor phase. In 1903, Normann (60) patented the liquid-phase hydrogenation process for oils. Later, Crossfield and Sons, a British company, purchased the patent.

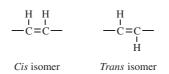


Figure 6. Cis- and trans-isomers of unsaturated fatty acids.

Procter & Gamble Company of USA acquired the patent right from Crossfield and Sons (59) in 1909 and started to produce Crisco shortening from cottonseed oil in 1911. The American patent on hydrogenation was under Burchenal (61) patent, which was declared null and void in the country to clear the way to allow an all out expansion of hydrogenation by every American oil company.

In the hydrogenation process, unsaturated fatty acids are reacted with hydrogen gas with the help of nickel catalyst. In this process, two hydrogen atoms are attached to the double bond in unsaturated fatty acids. Complete hydrogenation of vegetable oils converts essentially all of the unsaturated fatty acids to stearic acid.

During the course of transformation of the unsaturated fatty acids to saturated fatty acids, positional isomers of unsaturated fatty acids are produced. These unsaturated fatty acid isomers are known as *trans*-fatty acids (62), as shown in Figure 6.

Scientists recognized the benefits of the hydrogenation process, which revolutionized the fats and oils industry for a century. Hydrogenation of oils provides the following benefits to the oils:

- Increased oxidative stability due to reduced level of unsaturation
- Higher concentration of saturated fatty acids
- Higher melting point
- Unique functional products like shortening and margarine

Improved oxidative stability of selected hydrogenated oil is demonstrated in Table 5.

Liquid soybean oil and liquid canola oil contain 8% linolenic acid. This makes both oils very prone to oxidation, especially in the frying application. Light hydrogenation can reduce the linolenic acid to less than 2% (measured by the capillary GC method). This makes the oils suitable for industrial frying of shelf-stable products.

Table 4 shows that hydrogenation of soybean oil to a linolenic acid content of less than 2% increased the AOM value from 15 hours to over 30 hours. Simlarly, the AOM value rose from 20 hours to over 75 hours for canola oil after hydrogenation. However, hydrogenation also produced significant levels of *trans*-fats in both oils (2).

During the past century, while *trans*-fats were *not* on the "unwanted list" in diet, the oil technologists found that these fatty acids possessed some unique properties and used this to achieve the following:

Analysis	Soybean Oil Before Hydrogenation	Soybean Oil After Hydrogenation	Canola Oil Before Hydrogenation	Canola Oil After Hydrogenation
Iodine Value (Typical)	130	100	115	90
M.P.(°F)	—	<75	—	<75
AOM, hr (minimum)	12–20	>30	12–20	>70
Palmitic acid (%)	10	10	4	4
Stearic acid (%)	5	5	2	2
Oleic acid (%)	25	55	62	75
Linoleic acid (%)	50	28	21	12
Linolenic acid (%)	8	1.5	8	1.5
Erucic acid (%)	—	—	<2.0	<0.5
Gadeloic acid (%)	—	—	1	0
Trans-fat (%)	_	>30	_	>20

TABLE 5. Effect of Hydrogenation on AOM.

- Formulate margarine with sharp melting curve, similar to butter
- Beta-prime stable crystals in the shortening, which is desirable in the baking industry

Without hydrogenation, one could not make these products using only seed oils. In recent years, *trans*-fats have been under the scrutiny of nutritionists and regulatory agencies in various countries. Multiple clinical studies have revealed *trans*-fats elevate of the low-density lipoprotein (LDL), depression of high-density lipoprotein (HDL), and elevation of triacylglycerol (TG) in human blood serum (63–68). In this respect, *trans*-fats behave like saturated fats. The U.S. Food & Drug Administration has released a mandatory labeling requirement that shows that, beginning January of 2006, all food packages must indicate the level of *trans*-fats on the food packaging (69). This is to be shown as a separate line item. The FDA has not recommended daily value for *trans*-fat intake. Some European countries and Canada have also issued labeling requirements on *trans*-fat in all food packages.

18. ALTERNATIVES TO TRANS-FATS

Home frying does not require any shelf life for the fried food. Therefore, use of any liquid oil is acceptable for home frying. High oxidative stability is required for the

frying oil used at the restaurants or food service operations as well as for manufacturing shelf-stable products that are packaged and distributed. The standard seed oils, such as those from soybean or canola, must be hydrogenated to different degrees depending primarily on the type of fried product and their required texture, flavor, and mouthfeel.

Three basic alternatives are available to make *trans*-free oils for industrial frying as well as other uses. These are described below.

18.1. Modified Composition Oils

These oilseeds have been developed over the past two decades. These oils are very low in linolenic acid (except high oleic canola). All of these oils can be used for industrial frying without hydrogenation. Fatty acid compositions of these oils are listed in Table 6. These oils are in limited supply and they are expensive. Corn oil, cottonseed oil, and palmolein have been included along with the others for comparison.

18.2. Pourable Shortening

This is made from a mixture of 90–98% liquid oil and 2–10% fully hydrogenated soybean oil. The blend is specially processed to obtain the pourable consistency. The fully hydrogenated component can also be made from canola or corn oil.

Standard liquid shortening sold in the market contains lightly hydrogenated soybean or canola oil. These contain approximately 20–30% *trans*-fats. Substitution of this lightly hydrogenated oil with one of the oils listed in Table 6 would produce *trans*-free pourable shortening.

18.3. Alternative Catalysts

Platinum, palladium, or copper catalyst can produce hydrogenated oils with a lower *trans*-fat content (70–72). The hydrogenated oils produced by these catalysts

Analysis	NuSun	HO Sun	HO Canola	LL Canola	Cotton-Seed	Corn	Palm Olein
C-14	<1	<1	<1	<1		_	1.0–1.5
C-16	5	6	6	4	22	11	39–43
C-18	4	2	2	3	2	2	4–5
C-18:1	50–65	83	76	65	19	20	40–44
C-18:2	20–35	11	13	22	53	60	12–14
C-18:3	<1	<2	4.5	3	<1	<1	<0.5
C-20	_	_	_	<1	<1	<1	<1.0
C-22	—	—		—		—	—
C-22.1	—	—		—		—	—
% Trans	—	—	_	_	_	—	_

TABLE 6. Typical Fatty Acid Composition of Modified Composition Oils (weight %).

NuSun-Mid-oleic sunflower oil; HO Sun-High oleic sunflower oil; HO Canola-High oleic canola oil; LL Canola-Low linolenic canola oil.

contain higher stearic acid and higher solids compared with nickel catalysts. One could choose to use either platinum or palladium catalysts to make shortenings or frying fat with less *trans*-fat contents. Platinum and palladium catalysts are very costly and not commercially competitive with the nickel catalysts.

Copper catalysts are cheaper and work just as well as the precious metal catalysts. However, complete removal of catalyst from the hydrogenated oil is never possible. Copper, present in the oil even at very low concentrations (less than 0.05 ppm) can cause rapid hydrolysis in the oil during frying.

18.4. Hydrogenation Under High Pressure and High Agitation

Use of high reactor pressure (10–20 bars) with a high rate of agitation can produce similar results as the precious metal catalysts (62). However, this process cannot be carried out in the United States, because the reactors are designed to operate at a maximum pressure of 5 bars. There is only one oil processor in the United States that owns a high-pressure reactor, but it has not been used to any great extent. There are high-pressure hydrogenation reactors in Europe.

18.5. Interesterification for Frying Shortening

In this process, two oils are reacted under special conditions to exchange the fatty acids from one another (73–76). A fully hydrogenated oil, such as cottonseed, palm, soybean, canola, or corn oil, can be interesterified with any of the liquid oils in Table 5 to produce *trans*-free shortening to suit the need for frying, baking, margarine, etc. Fully hydrogenated cottonseed or palm oil will produce beta-prime shortening, which is desirable for baking applications.

Interesterification is done by two methods: chemical and enzymatic. The cost for making interesterified producs is very similar for both processes. The enzymatic interesterification process is becoming more popular because it is environmentally friendly.

18.6. Fractionation

This is commonly done with palm oil because of the higher concentration of the triand disaturated acylglycerol molecules. This technique is highly developed and used in Europe, South America, Far East, Mexico, and Canada. The seed oils are not suitable for this process because of the lack of natural solids in them. This is why seed oils require hydrogenation to create solids to make functional products.

19. FRYING SHORTENING VERSUS FRYING OILS

Oils are used mostly for frying snack foods. Some snack foods use a topical coating on the product to hold the seasoning on the surface. In most cases, the spray oil needs a certain amount of solid fat for proper adherence of the topical seasoning and also to reduce the oily surface appearance. Coating oil or spray oil, made from seed oils, is partially hydrogenated and contains *trans*-fats. It is possible to produce coating oil with no *trans*-fats by using a blend of liquid oil, such as listed in Table 6, mixed with a very small amount of fully hydrogenated fat. This small amount of saturated triacylglycerol provides the solids needed to hold the seasoning and reduce the oily appearance of the product.

Fried products with harder texture, such as French fries, extra crunchy fried chicken, and like products require solid shortening. The standard frying shortening in the United States is made from hydrogenated oils. It is possible to make *trans*-free shortening using either liquid shortening or interesterified technology, as described above.

It is unfortunate that palm oil is not acceptable to some consumers in the United States. Supply of modified composition oil is also very low. This makes it difficult to produce *trans*-free shortening in large volumes in the country at present.

20. SUMMARY

Frying is a mature industry. There are two major sectors of industrial frying, namely restaurant (food services) and large-scale manufacturing of shelf-stable products. Most large-scale manufacturers use continuous fryers, although there are some products that are strictly fried in batch (or kettle fryers) to achieve the desired product texture and appearance. Products made in either type of fryer are packaged in appropriate packaging material and distributed.

Par-fried products, such as French fries, chicken, coated vegetables, etc., have become extremely important to the fried food industry. These products are partially dehydrated, packaged, and shipped in the frozen state. The end users store these products in the freezers and fry them without thawing.

The longer shipping and distribution time required for the fried products has increased the need for oils with higher oxidative stability in order to meet the shelf life for all fried products. Soybean, sunflower, or canola oil needs to be hydroge-nated for industrial frying. Heavy-duty frying shortening, used for frying French fries, donuts, and chicken, require a high degree of hydrogenation. Hydrogenation of oil produces *trans*-fatty acids. These are unsaturated fatty acids that behave like saturated fatty acids in terms of promoting coronary heart disease (CHD). Therefore, several countries, including the United States, have focussed their attention on the *trans*-fatty acid content in the prepared foods.

Palm oil and palm oil fractions contain natural solid triacylglycerols and no *trans*-fat. Palm oil is used extensively by many countries to make *trans*-free shortening and margarine (except the United States). Interesterification is also applied in Europe, the Far East, and South America. Some modified composition oils have been introduced in the United States, but they are in very limited supply. Several of these oilseeds are grown in specific geographic areas where there is stiff competition from other cash crops. This will continue to be a challenge for the United States in producing sufficient amounts of *trans*-free frying fats, unless palm oil or palm olein is accepted by the consumers in the country. On the other hand, palm oil will be in extremely short supply, if the United States begins to use it because there is not enough surplus palm oil in the world at present (55).

The Better Bean Initiative from the United Soybean Board of USA is developing the mid-oleic soybean oil, which will not require hydrogenation for industrial frying applications. Full commercialization of this oil will take at least six to ten years. In the meantime, the food industry in the United States will have to be very creative to reduce *trans*-fats in fried foods as well as in other products.

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