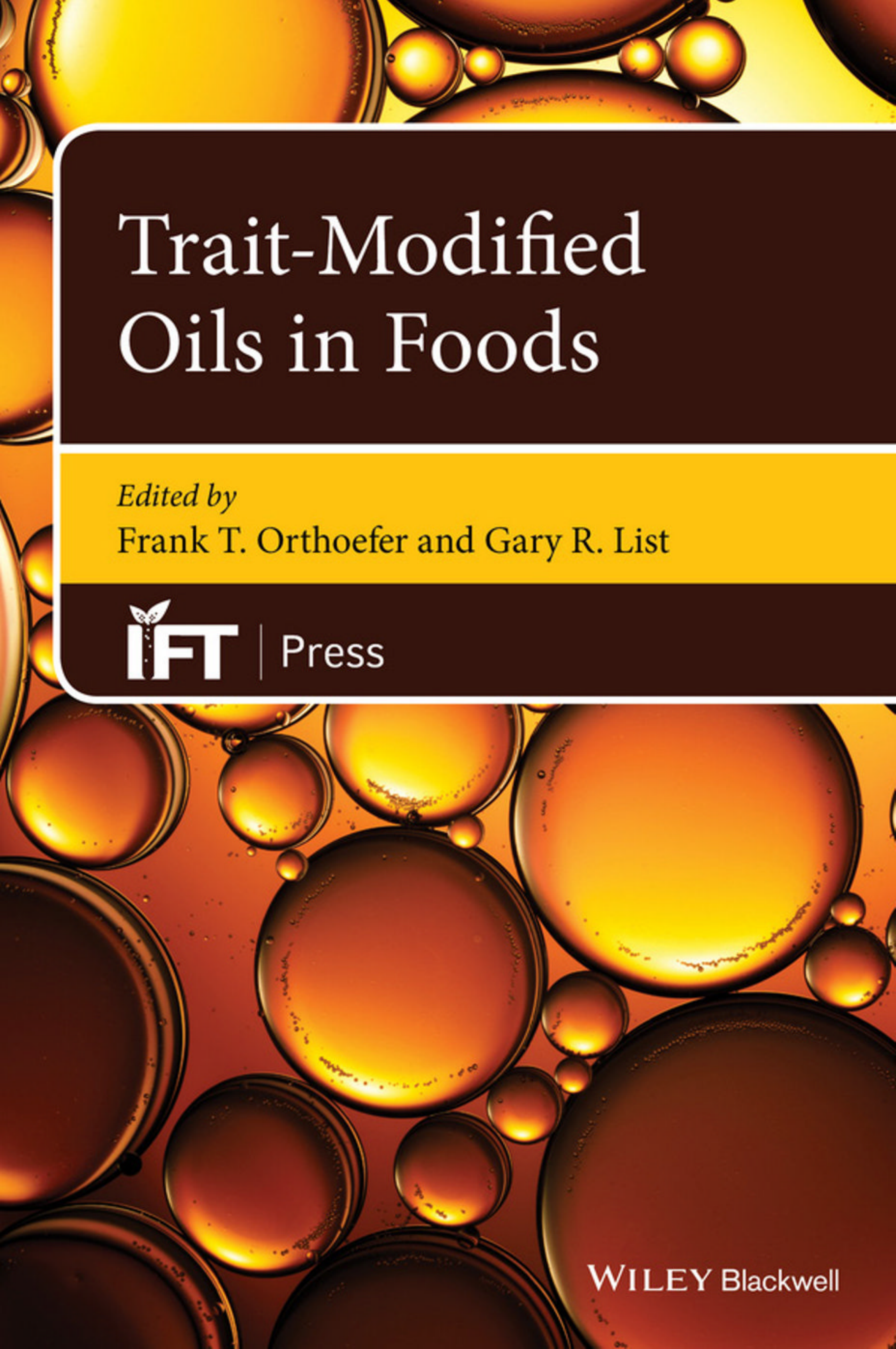

Trait-Modified Oils in Foods

Edited by
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Trait-Modified Oils in Foods

Edited by

Frank T. Orthoefer
FTO Foods, Knoxville, TN, USA

Gary R. List
USDA ARS NCAUR, Peoria, IL, USA

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This edition first published 2015 © 2015 by John Wiley & Sons, Ltd.

Registered Office
John Wiley & Sons, Ltd., The Atrium, Southern Gate, Chichester, West Sussex,
PO19 8SQ, UK

Editorial Offices
9600 Garsington Road, Oxford, OX4 2DQ, UK
The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK
111 River Street, Hoboken, NJ 07030-5774, USA

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Library of Congress Cataloging-in-Publication Data

Trait-modified oils in foods / edited by Gary List, USDA ARS NCAUR, Peoria, IL, USA,
Frank Orthoefer, FTO Foods, Knoxville, TN, USA.
pages cm. – (Institute of food technologists series)
Includes bibliographical references and index.
ISBN 978-0-8138-0872-7 (hardback)
1. Oils and fats, Edible. 2. Food–Composition. 3. Oils and fats–Biotechnology.
I. List, Gary R. II. Orthoefer, Frank T., 1941–
TP671.T73 2015
664′.3–dc23
2015009528

A catalogue record for this book is available from the British Library.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Cover image: oil-amp-water-abstract-background-red-macro-33964882,
Stock photo © ThomasVogel

Set in 11/14pt Times by SPi Global, Pondicherry, India

1 2015

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Contents

Contributors

Don Banks
Edible Oil Technology,
Dallas, TX, USA

Neal A. Bringe
White Wave Foods,
Bloomfield, CO, USA

Joseph W. Burton
USDA ARS NCSU (Retired),
Ligon St
Raleigh, NC, USA

Monoj K. Gupta
MG Edible Oil Consulting,
Richardson, TX, USA

Ernesto M. Hernandez
Lipid Consultants,
Houston, TX, USA

Larry W. Kleingartner
National Sunflower Association (Retired),
Mandan, ND, USA

Gary R. List
USDA ARS NCAUR (Retired),
University St.
Peoria, IL, USA

Dilip K. Nakhasi
Bunge Oils Inc,
Bradley, IL, USA

Frank T. Orthoefer
FTO Foods
Knoxville
TN, USA

Thomas G. Patterson
Dow AgroSciences LLC,
Zionsville Rd
Indianapolis, IN, USA

Roman Przybylski
University of Lethbridge,
Department of Chemistry and Biochemistry,
University Drive,
Lethbridge, Alberta, CA

Tom Tiffany
Archer Daniels Midland,
Decatur, IL, USA

Richard S. Wilkes
Wilkes Food Technology Consulting,
Township of Washington, NJ, USA

Richard F. Wilson
Oilsccds & Biosciences Consulting,
Raleigh, NC, USA

1 Introduction

Frank T. Orthoefer[1] and Gary R. List[2]

[1]FTO Foods, Knoxville, TN, USA
[2]USDA ARS NCAUR (Retired), Peoria, IL, USA

The fats and oils industry has changed and continues to renew itself. Historically, two major technological events have had a significant impact. These are (1) the development of new oils with modified fatty acid composition and/or distribution: the *trait-modified oils* (TMO) and (2) the substitution of animal fats for vegetable oils.

Trait-modified oils owe their existence to the development of new fats and oils through plant breeding biotechnology with the need for more suitable crop varieties to meet the demands of the marketplace. Two new oil examples are high oleic acid sunflower oil, developed through breeding and selection, and low linolenic acid soybean oil developed through mutation. Using analytical methods, mainly gas chromatography, has enabled the application of molecular biology to the modification of fatty acid composition. The rapid changes in molecular genetics and plant breeding have made what was once considered "novel" now routine practice. No longer necessary was conventional hydrogenation, a process that made all oils "equal" for food applications, all the way from frying to hard butter applications. Soybean oil could be stabilized by hydrogenation and its physical properties modified such

Trait-Modified Oils in Foods, First Edition. Edited by Frank T. Orthoefer and Gary R. List.

that it met the needs of most bakery or imitation dairy users. The formation of trans acids in this process was part of the expanded applications of hydrogenated oils which are no longer desired. Traits of oils based on fatty acid composition permitted the use of by-product oils: soybean, corn, and cottonseed oils.

The oil biotechnologist was motivated by loftier goals. Most of the impetus for these food scientists was not functionality but rather the negative health effects of trans fatty acid (Mensink and Katan 1990) and the mandate for labeling trans acids in the diet (reviewed by Hunter 2005). The Food and Drug Administration (FDA) mandates of 2003 regarding labeling of trans fats from partially hydrogenated oils in foods was the major push. Food technologists were challenged in the fields of reformulation, processing, and handling. All these methods were used to make the substitution seamless. Suddenly, oil producers and consumers were looking to the alternatives already available. Today's trait-modified oils include those from selective breeding, mutation, and genetic modification. Food formulators now, have a class of food oils that are not only more healthy but have a longer shelf-life. These "new" oils meet processor and consumer demands and are the functional alternative ingredients for foods.

1.1 SOURCES

There is a long list of plant and animal derived edible oils (Box 1.1). Four crops account for 84% of the total North American consumption of edible oils. Box 1.2 shows these oils, in their order. Soybean, corn, canola, and cottonseed oils are the top four. Prior to 1997, about 10% of the world's edible supply was consumed by industrial uses. Edible oil used industrially has now increased to 20.6%.

The characteristics of the trait-modified oils suitable for frying are:

1. Low linolenic – moderate stability, high deep fat flavor intensity.
2. High oleic – high stability, low deep fat fried flavor intensity, waxy/plastic flavor.
3. Mid Oleic- high stability, high deep fried flavor intensity.

Sharp differences exist between saturated fatty acid content, saturated short chain fatty acids, saturated long chain fatty acids, monounsaturated, and polyunsaturated fatty acids. The diversity in fatty acid composition

Box 1.1 Typical Fatty Acid Compostion of the Principal Vegtetable and Animal Fats and Oils in the U.S.

(% of total fatty acids)

	Butyric	Caproic	Capriylic	Capric	Lauric	Myristic	Pentadec Anoic	Palmitic	Margaric	Stearic	Arachidic	Behenic	Lignoceric	Myristoleic	Palmitoleic	Oleic	Margaroleic	Gadoleic	Linoleic	Linolenic
	SATURATED													MONO-UNSATURATED					POLY-UNSATURATED	
	4:0	6:0	8:0	10:0	12:0	14:0	15:0	16:0	17:0	18:0	20:0	22:0	24:0	14:1	16:1	18:1	17:1	20:1	18:2	18:3
Oil or Fat																				
Beef tallow						3	1	24	2	19				1	4	43	1		3	1
Butterfat	4	2	1	3	3	11	2	27	1	12					2	29			2	1
Canola								4		2						62			22	10
Cocoa butter								26		34						34			3	
Coconut		1	8	6	47	18		9		3						6			2	
Corn								11		2						28			58	1
Cottonseed						1		22		3					1	19			54	1
High oleic canola								4		2						75			17	2
High oleic safflower								7		2						78			13	
High oleic sunflower								4		3						79			11	
Lard						2		26		14					3	44		1	10	
Mid oleic sunflower								4		5						65			26	
Olive								13		3	1				1	71			10	1
Palm kernel			3	4	48	16		8		3						15			2	
Palm						1		45		4						40			10	
Peanut								11		2	1	3	2			48		2	32	
Safflower								7		2						13			78	
Soybean								11		4						24			54	7
Sunflower								7		5						19			68	1

From: Food Fats and Oils. Institute of Shortening and Edible Oils. 1750 New York Ave., NW Suite 120, Washington DC. 2006. Ninth Edition Pg 26

Box 1.2 North American Edible Oil Consumption by Partial Hydrogenation Level

Type of Edible Oil	Amount* 10^6 lb	% of Total	% Partially Hydrogenated†	Amount of Partially Hydrogenated Oils, 10^6 lb
Soybean	17820	70.3	41.7	7431
Canola	2609	10.3	26.7	697
Corn	1722	6.8	36.1	622
Coconut	895	3.5	0	0
Cottonseed	695	2.7	17.7	123
Palm Kernel	529	2.1	0.4	2
Palm	434	1.7	0	0
Sunflower	423	1.7	23.5	99
Peanut	233	0.9	11.6	27
TOTAL	25360	100	35.5	9001

*Based on data from the Oil World Annual Report 2006.

†Based on a propriatary report conducted for Dow AgroSciences.

imparts differences in functional properties important for some food manufacture, for example frying, bakery shortenings, and salad oils.

Even processing technology is affected. Melt point, melting characteristics, and oxidative stability are associated with the degree of saturation and component fatty acids. Minor compounds also have an effect (O'Brien 2004).

Food processors have learned how to manufacture basestocks and blends for foods to optimize flavor, mouth feel, texture, and functionality. This led to interchangeability of whole oils with similar physical properties or processed products that may be based on them. Accessing suitable fats and oils has been left to price and availability. The trait-modified oils with modified fatty acid profiles may be positioned to enter the market as commodity oils with premiums either for contract supply or actual cost of identity preserved production, storage or processing.

1.2 PROCESSING

Through processing methods and blending, oil processors have extended the functional properties and utility of edible oils (O'Brien 2004; Weiss 1983). Hydrogenation further extended the range of modification and utility of edible oils in shortenings, margarines, and frying fats. Hydrogenated basestocks and functional additives were used to create foods with appealing flavors, mouthfeel, lubricity, and texture. Meeting these standards through hydrogenation led to the ability to interchange various vegetable oils for formulation of processed products.

The most sustainable oil crops are palm, soybean, and canola oils. Other oils will continue to be produced but may require an advantage for market success. The trait-modified oils may provide another distinction for crops. The value or need for other oils will be to find means to use viable competitive edge through nutrition, production, processing or functionality. The genetic modification of oil traits is a new level of distinction for crops.

1.3 CONSUMER PREFERENCE AND LEGISLATION

Consumers are now more selective and have been conditioned to the dietary health benefits of fats and oils. The health benefits of polyunsaturated fats led to a restriction of dietary saturates, generally meat fats, and the emphasis on use of liquid vegetable fats (Kearney 2007). The extent of the health claims led to the Nutrition Labeling and Education Act of 1990 that limited claims such as “low in saturated fats” to food containing less than 1 g of saturated fat per serving. This restricted the use of the claim to vegetable oils with 7% or less saturated fats.

The health claim was extended to include process rearrangement of the TAG molecular structure. The implication was that process induced trans fatty acids formed in partially hydrogenated oils with a deviation of serum levels of low density lipoprotein (LDL), the “bad” cholesterol. The Institute of Medicine, National Academy of Science published a report suggestingthat trans fat consumption should be kept as low as possible. The Center for Science in the Public Interest (1994) filed a petition with the FDA requesting the agency take steps to require trans fats to be listed on nutrition labels. The FDA later proposed a rule based on a number of credible scientific reports and expert panels: Trans Fatty Acids in Nutrition Labeling. Nutrient Content Claims and Health Claims 2003. The Final Rule became effective in January 2006.

Today the link between trans fat and coronary heart disease is no longer disputed by consumers (Mensink and Katan 1990). An overreaction occurred, with several cities and state governments imposing bans on restaurant foods that contain trans fats. Several major food producers switched to trans free alternatives. Alternatives to partially hydrogenated oil were sought. Overall, the outcome has impacted the commodity markets. Credits for the reductions in trans fat is shared by food industry, oil processors and seed developers in developing healthier oils. (Journal of the American Medical Association, Feb 8, 2012).

Oilseed processing technology had no solution to reverse the trend. Consumers were introduced to soybean oil with genetically modified, low linolenic acid concentration by Pioneer, Dupont/Bunge/Monsanto/Cargill, and Iowa State University. The low linolenic acid soybean oil had been shown to produce better tasting fried products retaining desirable flavor in shelf-life testing. However, in many trials by various food manufacturers, the increased stability of these new oils was insufficient to drive a market structure that can accommodate new commodity streams for additional edible oils with trait modification. Some of these oils include ultra low linolenic acid oil, mid oleic acid soybean oil, high oleic acid soybean oil, and high saturated soybean oil.

Other oils may fit the current oil market: mid and high oleic canola oils with reduced linolenic acid content, and mid and high oleic sunflower oils. The low linolenic canola oil met the increased stability requirements for baking and snack food frying. The combined low linolenic high oleic oils are ideally suited to be a substitute for high stability oils required for deep fat frying. Generally, the modified composition of frying oils (Warner 2007) has an undesirable effect on flavor.

1.4 SUBSTITUTION WITH TRAIT-MODIFIED OILS

The goal of biotechnology with respect to food oil is to develop or modify plants to produce desirable characteristics or traits. The focus has been on output quality traits with improved composition of seeds. With dietary oils, the target is to modify the fatty acid composition of the plant oil. Multiple oils have been modified (Box 1.3).

Fats and oils make up a major portion of many finished foods. Consumer oil products are those based on a specific commodity: soybean, corn, canola, cottonseed, sunflower, safflower, olive, and cocoa butter.

Box 1.3 Oils That Have Been Trait-Modified by Plant Breeding and/or Biotechnology

- Low linolenic soybean
- Mid oleic soybean
- High saturate soybean
- High oleic soybean
- High stearodonic acid soybean
- Low linolenic canola
- High oleic, low linolenic canola
- Low saturate canola
- High lauric canola
- Low saturate sunflower
- High oleic sunflower
- Mid oleic sunflower
- High oleic safflower

Consumer expectation is that the label ingredient for a particular oil type is what is in the bottle. Trait identification for a retail oil is not required because of the need for minimum shelf-life of the oil and possibly shelf-life of consumer prepared foods at the table.

Determining performance of oils in formulated foods is much more challenging. Shortening may be prepared in several physical forms: solid shortening, fluid shortening, liquid shortening, and powdered shortening.Oil sales and products may also be in various functional forms such as: all purpose, specialty bakery, donut fry, and bakery spray oils.

Oils formulated for food service frying may be targeted to industrial frying, institutional frying, and fast food frying. The characteristics of the trait-modified oils suitable for frying are:

- low linolenic – moderate stability, high deep fat fried flavor intensity
- high oleic – high stability, low deep fat fried flavor intensity, waxy/plastic flavor
- mid oleic – high stability, high deep fat fried flavor intensity.

Specialty applications for oils may include margarine, spreads, imitation dairy, mayonnaise, salad dressing, confectionery coatings or popcorn seasoning. A majority of trait-modified oils are targeted to be either liquid oils or solid fats dispersed in liquid oils. Yet many foods require a solid or semi-solid fat ingredient for functionality. The liquid oils with high stability can be targeted to frying, consumer/retail oils or as a component of a blend of trait-modified oil. To make an all purpose shortening (more solid), it is based on blending with a trait-modified oil and the addition of a fully hydrogenated hard fat component; 15–25% of the hard fat is blended. A high oleic, low linolenic canola oil may be interesterified to produce shortenings with better melting (Orthoefer 2005). A finished votated shortening blend has the appearance and consistency of a traditional all purpose shortening. Performance in cakes was equivalent to an all purpose shortening based on a hydrogenated soybean oil blended with a cottonseed oil hardstock.

Both physical blends and interesterified oil blends have been formulated into shortenings. Performance of interesterified blends was similar to conventional shortenings. Both chemical and enzymatic interesterification achieved similar positive results.

Use of trait-modified oils in food service frying was investigated by Przybylski (2007). He found that high oleic, low linolenic canola oil (70% plus oleic acid content) was found to have the best frying performance as measured by formation of polar compounds and carbonyl components. The best nutritional quality fried foods occurred when this oil was used. The oil contained only trace trans content (no trans), had a low rate of oxidative deterioration, and received high scores from consumer taste panels. Frying durability could be extended beyond that for partially hydrogenated soybean oil.

1.5 FATS AND OILS – NUTRITION

Most dietary fats are 95–100% absorbed. Fats broken down to monoglycerides and free fatty acids in the intestine are absorbed, then recombined in the intestinal wall. If the carbon chain is longer than 10 carbon atoms, they are transported via the lymphatic system. If the carbon chain is less than 10 atoms, they are transported via the portal vein to the liver where they are metabolized. Triglycerides, whether from diet or endogenous sources, are transported in the blood as lipoproteins. The triglycerides are stored in adipose tissue until they are needed as a source of calories. Excess calories are stored as fat. The body can make saturated and monounsaturated fatty acids by modifying other fatty acids or by de novo synthesis from carbohydrate and protein. Polyunsaturated fatty acids, such as linoleic acid, cannot be made by the body and must be supplied in the diet.

Cardiovascular disease (CVD) is a leading cause of death in the US. These are chronic degenerative diseases often associated with aging. The relationship of dietary fat and coronary heart disease has been examined since the 1950s. Diet affects serum cholesterol and the risk of "heart attack" increases with elevated serum cholesterol levels. Diet modification to achieve lower serum cholesterol levels is recommended. This includes reducing consumption of total fat, saturated fat, trans fats, and cholesterol.

The largest portion of total cholesterol is in the LDL fraction. High density lipoprotein (HDL) cholesterol has been associated with protection against coronary heart disease. A national program was established in the mid-1980s by the National Heart, Lung, and Blood Institute and the National Institutes of Health, to increase public awareness regarding the importance of lowering elevated serum cholesterol levels.

The three major types of dietary fatty acids (saturated, monounsaturated, and polyunsaturated) appear to influence total LDL and HDL differently. Monounsaturated and polyunsaturated fatty acids are cholesterol lowering when they replace significant levels of saturated fatty acids in the diet. Studies have shown that polyunsaturates lower LDL and total cholesterol (Gardner and Kraemer 1995). Monounsaturated fatty acids decrease LDL cholesterol to a greater extent than polyunsaturated fats, while maintaining HDL cholesterol levels (Committee on Nutrition 1992; Mata et al. 1992).

Cardiovascular diseases declined from 1984 to 1994. Specific reasons for this are not known (AHA 1998). Increased public awareness and more effective treatment of heart diseases may have played a role.

Cancer is the second leading cause of death in the US. Cancer is a group of diseases caused by external and internal factors. Many cancers are related to dietary factors and are believed to be preventable. No markers exist to indicate that a cancer is developing.

Some associations exist between dietary factors such as high fat intake and appearance of cancer at certain sites. A causal relationship has not been established (Ip and Marshall 1996).

Trans fatty acid content of dietary fats and oils is linked to CVD. These have a greater negative effect with respect to coronary heart disease than saturated fatty acids (British Med Journal, 2006). Complete or near avoidance of trans fats may be necessary. The alternatives should be low in both trans fats and saturated fatty acids (British Med Journal, 2006).

Trans fat consumption among US adults has decreased by 58% over the past decade. This coincides with regional bans and government regulation on labeling of trans content.

1.6 MARKETS FOR TRAIT-MODIFIED OILS

Essentially three major markets exist for trait-modified oils:

- consumer/retail
- food service
- food ingredient.

The consumer market consists mainly of bottled oils with specific identity (soybean, cottonseed, corn, canola, sunflower). A major nutritional issue is the fatty acid composition, whether saturated, monounsaturated or polyunsaturated, stability and taste. Stability of consumer/retail oil is not an issue with excellent packaging and controlled distribution.

The food service market is largely performance driven, combined with price concerns. The extreme conditions used in frying impact cost and price. For example, a frying oil with twice the fry life is more economical than using a similar oil with half the fry life. Food service fry oils are a major source of trans fatty acids from partial hydrogenation. Shelf-life of food service fry oils is of less importance since most fried products are consumed shortly after preparation. Of greater concern to the food service handler is the performance of the oil in the fryer (Przybylski 2007). Food service handlers want a healthy oil, but also one that performs well in the fryer.

Oils as food ingredients may require fry stability or stability during storage before consumption, and stability during processing. The oil component must allow the production of a food of desired appearance, good texture, excellent taste, creaming, etc. Melting points, solids content, lubricity, and moisture barrier properties (spray oils) are among the quality attributes sought (List 2007). Bakery shortenings (all purpose, roll in, bakery margarine), filler fats, fry oil for donuts, meltable fats for dairy replacers (margarines, spreads, coffee creamers) are produced. The combination of hard fats with trait-modified oils by interesterification may substitute for traditional products.

Trait modification for edible oils has seen noted improvement in nutritional content and functionality. This includes reduction in saturated and trans fatty acid content with improved stability, and creation of specific fatty acid profiles for functional foods. The Major factors for determining consumer acceptance of trait-modified oils includes:

- Cost/price vs commodity oil
- Consumer resistance to purchase the better oil because of familiarity
- Supply, availability
- Identity preservation
- Some are genetically modified organism (GMO) oilseeds
- It's a niche marketing product.

1.7 FUTURE OF TRAIT-MODIFIED OILS

Trait-modified oils will continue to improve. The composition of commodity based TMO will assist in satisfying supply, availability, functional products, and healthy formulations. Concepts for trait-modified oils include:

- balance of omega 3, omega 6, and omega 9 fatty acids
- very low saturated fatty acid content
- minor components and performance and nutrition.

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2 Overview of Trait-Modified Oils

Richard F. Wilson

Oilsccds & Biosciences Consulting, Raleigh, NC, USA

2.1 HOW CONSUMER INFLUENCE HAS DRIVEN THE EVOLUTION OF EDIBLE OIL MARKETS

Prior to the 20th century, lard, tallow, and butter were the principal forms of edible fats and oils. Evidence of the dietary importance and abundance of animal fats in those times is captured for posterity by 17th century “Dutch masters” such as Gerret Heda or Pieter Claesz in certain still-life paintings that portray hams with at least a 1-inch outer ring of fat as an ideal. In sharp contrast, pork products available today are typically lean with relatively little fat. This condition represents an economic reality of modern, more efficient animal production methods, but the accompanying decline in dietary consumption of animal fats is a function of dynamic change in consumer preference for more convenient and more healthful food ingredients which was inspired by increased availability of liquid vegetable oils.

Those who are old enough to remember how our grandparents would reheat skillet-grease to fry the next meal probably also recall the welcome transition to better tasting vegetable oil frying agents.

Trait-Modified Oils in Foods, First Edition. Edited by Frank T. Orthoefer and Gary R. List.

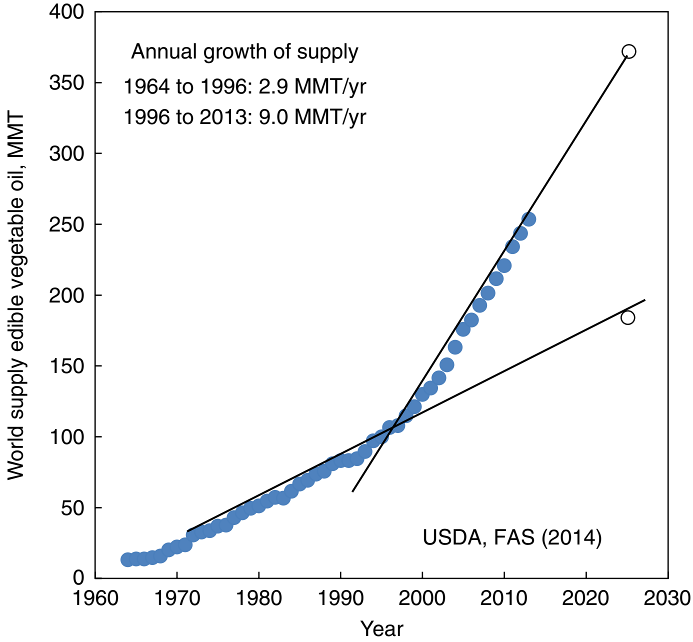

Figure 2.1 Trends in world supply of major edible vegetable oils (USDA FAS 2014).

Consumer demand for liquid vegetable oils stimulated expansion of commercial oilseed production and has supported linear growth in the supply of vegetable based frying and baking fats for decades. United States Department of Agriculture (USDA FAS 2014) estimates of world edible oil supply (based primarily on coconut, olive, palm, palm kernel, peanut, rapeseed, soybean, and sunflower oils) show an annual increase of 2.9 million metric tons (MMT)/year (12.9 to 106.4 MMT) from 1964 to 1996 (Figure 2.1). Thereafter to 2013, the annual rate increased threefold to 9.0 MMT/year (106.4 to 253.5 MMT), principally due to adoption of genetic engineering technology in soybean, canola, and cotton (USDA ERS 2013), and to considerable expansion of palm plantations in Malaysia and Indonesia (May 2012). Continued linear expansion of the total global edible oil supply is expected through the next decade. Yet, more remarkable is the fact that consumer demand has kept pace with the escalated availability of edible vegetable oils. Annual endstocks have held within a consistent range, averaging 7.0 ± 1.1% of total global vegetable oil supply over five decades from 1964 to 2013 (USDA FAS 2014). Such a response suggests the market for edible vegetable oils will not soon be saturated, and that advances in productivity are still needed to satisfy untapped consumer demand.

Consumer desire for edible vegetable oils is enhanced by inherent differences in fatty acid composition that confer a broad range of functional properties as food ingredients (Wilson and Hildebrand 2010). Most commercially available oils may be distinguished by a predominance of saturated, monounsaturated or polyunsaturated fatty acids (Reeves and Weihrauch 1979). Saturated oils such as nutmeg butter, coconut, palm kernel, cocoa butter, palm, and sheanut are endowed with high levels of lauric (12:0), myristic (14:0), palmitic (16:0) and/or stearic (18:0) fatty acids (Table 2.1). These oils typically exhibit melting points above 30°C and may contribute to the solid structure of food products. Crop oils that exhibit comparatively high levels of monounsaturated fatty acids, primarily oleic (18:1) and erucic (22:1), include hazelnut, olive, avocado, almond, mustard, apricot kernel, canola, peanut, and sesame. Crops that provide an economical source of 22:1 often find application in nonedible products such as plastic wraps whereas oils rich in 18:1 are associated with dietary health benefits. The third grouping exhibits relatively high levels of polyunsaturated fatty acids, primarily 18:2 and 18:3. Commercial sources of these oils (including corn, soybean, sunflower, cottonseed, and safflower) comprise the core commodity base for oilseed production, accounting for about 50% of total global supply and over 80% of total North American supply of edible vegetable oils (Table 2.2). Trend analyses for each commodity promulgate continued domination of the global edible vegetable oil markets by palm, soybean, canola, and sunflower, and North American markets by soybean and canola.

2.2 WHY IS THERE NEED FOR TRAIT-MODIFIED EDIBLE OILS?

Given the array and functional diversity of commercial sources, raw commodity oils are often interchangeable or blended to meet specifications for particular food applications. However, business decisions on

Table 2.1 Typical Fatty Acid Distribution Among Edible Seed Oils

Commodity (*Genus species*)	**Fatty acid concentration, %**																				
	6:0	**8:0**	**10:0**	**12:0**	**14:0**	**16:0**	**18:0**	**20:0**	**22:0**	**24:0**	**16:1**	**18:1**	**20:1**	**22:1**	**18:2**	**18:3**	**18:4**	**20:4**	**Sat***	**Mono**	**Poly**
Nutmeg butter (*Myristica fragrans*)	0	0	0	3	87	5	0	0	0	0	0	5	0	0	0	0	0	0	95	5	0
Coconut (*Cocos nucifera*)	1	8	6	47	18	9	3	0	0	0	0	6	0	0	2	0	0	0	92	6	2
Palm kernel (*Elaeis guineensis*)	0	3	4	50	17	9	3	0	0	0	0	12	0	0	2	0	0	0	86	12	2
Cocoa butter (*Theobroma cacao*)	0	0	0	0	0	27	35	0	0	0	0	35	0	0	3	0	0	0	62	35	3
Palm (*Elaeis guineensis*)	0	0	0	0	1	46	4	0	0	0	0	38	0	0	10	0	0	0	51	39	10
Sheanut (*Butyrospermum paradoxum*)	0	0	0	1	0	5	41	0	0	0	0	46	0	0	5	0	0	0	48	46	6
Hazelnut (*Corylus avellana*)	0	0	0	0	0	5	2	0	0	0	0	82	0	0	11	0	0	0	8	82	11
Olive (*Olea europaea*)	0	0	0	0	0	11	2	0	0	0	1	76	0	0	8	1	0	0	14	77	9
Avocado (*Persea americana mill.*)	0	0	0	0	0	11	1	0	0	0	3	71	0	0	13	1	0	0	12	74	14
Almond (*Prunus dulcis*)	0	0	0	0	0	7	2	0	0	0	1	73	0	0	18	0	0	0	9	73	18
Mustard (*Sinapis alba*)	0	0	0	0	2	4	1	0	0	0	0	13	7	48	18	7	0	0	7	68	24

Apricot kernel (*Purnus armeniacia*)	0	0	0	0	0	6	1	0	0	0	2	61	0	0	31	0	0	0	7	63	31
Canola (*Brassica napus*)	0	0	0	0	0	4	2	1	0	0	0	59	2	1	21	10	0	0	7	62	31
Rice (*Oryza sativa*)	0	0	0	0	1	15	2	0	0	0	0	50	0	0	32	0	0	0	18	50	32
Peanut (*Arachis hypogaea*)	0	0	0	0	0	10	2	1	2	1	0	48	1	0	34	0	0	0	17	49	34
Sesame (*Sesamum* spp)	0	0	0	0	0	9	5	0	0	0	0	41	0	0	43	0	0	0	14	42	44
Corn (*Zea mays*)	0	0	0	0	0	11	2	0	0	0	0	25	0	0	61	1	0	0	13	25	61
Soybean (*Glycine max*)	0	0	0	0	0	11	4	0	0	0	0	24	0	0	54	7	0	0	15	24	61
Sunflower (*Helianthus annuus*)	0	0	0	0	0	7	4	0	0	0	0	21	0	0	69	0	0	0	11	21	69
Walnut (*Juglans regia*)	0	0	0	0	0	7	2	0	0	0	0	23	0	0	56	11	0	0	9	24	67
Cottonseed (*Gossypium* spp)	0	0	0	0	1	24	2	0	0	0	1	18	0	0	54	0	0	0	27	19	54
Grapeseed (*Vitis vinifera*)	0	0	0	0	0	7	3	0	0	0	0	17	0	0	73	0	0	0	10	17	73
Safflower (*Carthamus tinctorius*)	0	0	0	0	0	7	2	0	0	0	0	12	0	0	78	0	0	0	9	13	78

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*Saturated fatty acids: 6:0 to 24:0; monounsaturated fatty acids: 16:1 to 22:1; polyunsaturated fatty acids: 18:2 to 20:4. (Reeves & Weihrauch, 1979).

Table 2.2 Estimates of Edible Vegetable Oil Supply

	World supply		**N. American supply**	
Oil (MMT)	**2013**	**2025**	**2013**	**2025**
Soybean	56.8	68.8	11.1	10.5
Rape	32.7	53.6	6.4	11.4
Palm	107.5	171.7	2.1	3.6
Coconut	5.8	6.5	0.8	0.9
Cottonseed	5.4	5.7	0.5	0.4
Palm kernel	10.8	17.3	0.4	0.5
Olive	4.2	3.6	0.4	0.5
Sunflower	24.4	37.8	0.3	0.1
Peanut	5.9	6.9	0.1	0.1
Total	**253.5**	**371.9**	**22.1**	**28.0**

Source: USDA FAS; 2025 projections derived from regression analysis of trends from 2005 to 2013. Palm oil supply for N. America represents imports only.

ingredient choice for scaled manufacturing operations are largely influenced by adequate and timely delivery of raw products. Although relatively small but strong markets may be established for “specialty” oil ingredients, only those commodities with the largest commercial production systems have the capacity to satisfy growth in consumer demand. Palm, soybean, canola, and possibly sunflower currently have the strongest market positions. Yet, industry dependence on fewer sources of raw material increases economic risk not only in sustainability of supply but also in limitations posed by the intrinsic functional utility of those resources for food product development. For example, refined-bleached-deodorized (RBD) soybean and canola oils are prone to relatively rapid degradation and off-flavor formation during high temperature frying (Nzikou et al. 2009; Tan et al. 2002). Therefore, innovations in processing technology, such as hydrogenation, have been deployed to modify fatty acid composition and extend oil utility in the manufacture of shortenings, margarine, and high temperature frying fats. Advances in food processing technology have also led to the discovery of how whole oils, basestocks, and functional additives may be blended to create foods with appealing flavors, mouth feel, and texture.

Apparently, the chemical and physical technologies deployed by the food industry for oil trait modification have been adequate for decades. So, why is a different approach to trait-modified oils necessary?

Probably the most obvious reason for innovation in oil trait modification is the influence of health claims on US public opinion of the dietary benefits of fats and oils (Wells and Buzby 2008). As a protective measure, subsequent governmental intervention became manifest in a number of policies and legislative acts such as the Final Rule pursuant to the Nutrition Labeling and Education Act of 1990 (FDA 1999) which defined and limited the use of health claims for vegetable oils with less than 7% saturated fat. The association of dietary saturated fatty acids with incidence of arteriosclerosis then was extended to connect trans fatty acids found in partially hydrogenated oils with an elevation of serum levels of low density lipoproteins. The Institute of Medicine, National Academy of Science and other academic groups fortified this argument with recommendations that dietary trans fat consumption should be as low as possible (Schrimpf-Moss and Wikening 2005). Petitions from special interest groups eventually compelled the Food and Drug Administration (FDA) to issue a Final Rule: Trans Fatty Acids in Nutrition Labeling, Nutrient Content Claims, and Health Claims which required trans fat to be listed on nutrition labels and food product claims (FDA 2003). The Final Rule became effective in 2006.

Recently, academic certainty that the daily caloric intake of trans or saturated fat by most Americans causes a detrimental impact to health has been challenged by a metaanalysis involving over 640,000 participants in 76 studies (Chowdhury et al. 2014). The conclusion drawn from that paper did not clearly support cardiovascular guidelines that encourage lower consumption of total saturated or trans fats. Nevertheless, the link between trans or saturated fat and increased risk of coronary heart disease has been firmly entrenched in consumers' minds. In response to consumer demand for more "heart healthy" foods, about 95% of the 38,000 bakery, snack food, and margarine products launched in the US from 2006 to 2010 carried a "no trans fat" label (Rahkovsky et al. 2012). This deliberate food industry action has facilitated a nearly 70% decline in US dietary consumption of trans fat derived from partially hydrogenated oils (Bunge 2013). In particular, consumption of partially hydrogenated soybean oil (PHSBO) has fallen from 9 billion pounds per year and is expected to decline to less than 1 billion pounds by 2023 (Gorton 2013).

However, in spite of this progress, on November 8 2013 the FDA published a rule for comment that would deny Generally Regarded As Safe (GRAS) status to partially hydrogenated oils (FDA 2013). Such action would immediately impact about 3 billion pounds of PHSBO that are still in the process of being replaced in the US. Thus implementation of the proposed FDA ruling would significantly preempt the ability of food manufacturers to develop and adopt alternative technologies to eliminate dietary trans fats in an orderly and timely manner (Watson 2014). Other unintended consequences of such a ruling include an increase in dietary saturated fat intake, lost market share for soybean oil, and greater reliance on imported palm and canola oil. Indeed, these trends are already evident in the North American supply of major edible vegetable oils (Figure 2.2) and projections based on those data present a future scenario where palm and canola oils essentially could account for the entire estimated net increase in North American edible oil supply, unless countermeasures are taken (see Table 2.2).

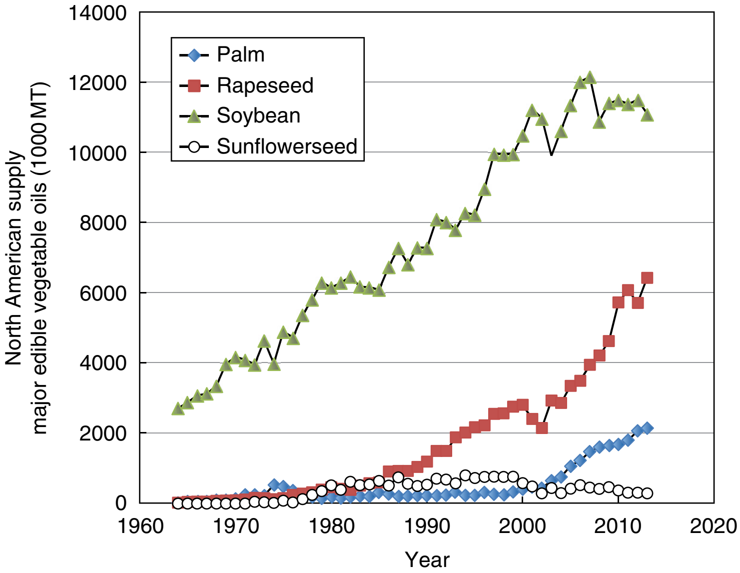

Figure 2.2 Trends in North American supply of major edible vegetable oils (USDA FAS 2014).

2.3 WHAT IS BEING DONE TO INCREASE SUPPLY OF HIGH STABILITY VEGETABLE OILS?

Substitution of palm and canola for soybean oils presents an uncomfortable situation for North American food manufacturers who are diligently reformulating established products to eliminate trans fat. Palm production is beset by environmental sustainability issues (Watson 2013a), palm oil is the leading source of dietary saturated fat, and canola oil would need to be partially hydrogenated to improve oxidative stability and to replace PHSBO in bakery and frying applications. A preferred US food industry strategy is to transition toward vegetable oils that are enriched in oleic acid for improved oxidative stability, and to blend with "interesterified" oil ingredients to enable use of high stability oils in shortenings and bakery applications (Bunge 2013). However, implementation of that strategy requires an adequate raw ingredient supply chain, and current world supply of all commercially available sources of high stability oils (see Table 2.1) is less than 45 MMT. Fortunately, years of effort invested in the biological modification of vegetable oil composition (Wilson 2004) have enabled genetic enhancement of oleic concentration in major oilseed crops. The efficacy of this approach was demonstrated decades ago by the development of canola from interspecific hybrids (Shahidi 1990), and now can be further applied to other crops such as sunflower and soybean to help ensure adequate supply of high stability oil.

Genetic modification of oleic acid concentration of sunflower oil through conventional breeding established a modern blueprint for commercial production of enhanced stability oils (Sandbakken 2012). About 80% of North American sunflower production has been converted to "NuSun" cultivars which exhibit about 56% oleic acid, and current "Hi-Oleic" cultivars with about 82% oleic acid account for the remainder. The oxidative stability index (OSI) for NuSun sunflower oil is 9 hours, and 25 hours for Hi-Oleic sunflower oil (Romano et al. 2013). Stratus Foods and MycoGen Seeds control world distribution of high oleic sunflower (Mullally 2011). However, with expiry of the Hi-Oleic sunflower patent, new nongenetically modified (GM) products are being developed by Seeds 2000 (NUSeed Americas) that guarantee 85% oleic acid (Mullally 2013). Dow AgroSciences also is developing

Omega-9™ sunflower cultivars with 93% oleic acid for production now in Argentina, and North American production by 2016 (Larry Sernyk, Dow AgroSciences, personal communication).

Thus, high stability sunflower oil is an important factor in the consumer driven industry effort to eliminate dietary trans fat but it cannot be the single remedy because North American sunflower oil production accounts for only 1.3% of world production (USDA FAS 2014). Even with ongoing efforts to boost North American supply, availability of Hi-Oleic sunflower oil will remain relatively low compared to soybean and canola.

Another Omega-9™ product is high oleic canola oil (Dzisiak 2013). The OSI of canola with 75% oleic acid is 21 hours (Liu 2012). Cargill also markets an alternative high oleic canola oil product under the Clear Valley® 80 brand (Cargill 2013). Omega-9™ canola is advertised as non-GM oil, but the patent application includes claims for resistance to imidazoline, 2,4-D, and glyphosate herbicides which may be GM traits (Kubik 2009). "Identity preservation" protocols for crop production most likely will be required to minimize adventitious presence to maintain oleic acid levels since canola is notorious for "gene flow" or outcrossing (Beckie 2003; Légère 2005). Nevertheless, high stability canola production in North America is estimated at 1.2 billion pounds, and could increase to 2.2 billion pounds by 2017 (Larry Sernyk, Dow AgroSciences, personal communication).

In addition to sunflower and canola, geneticists are developing other trait-modified commodities that may help diversify the North American supply of edible vegetable oils (Wilson 2012). High stability oil products in peanut (Chu et al. 2009), palm (Ong and Abdullah 2013, Malaysian Palm Oil Board, personal communication), cottonseed (Liu et al. 2002a, 2002b), safflower (Quick 2012), and algae (Anon 2013a, 2013b) could become available by 2025. As indicated below, these products are in various stages of development and some are enabled by transgenic modifications of the genes that mediate oleic acid concentration.

- US peanut production accounts for 5.8% of world supply (USDA FAS 2014) of which 12–15% is high oleic (Patrick Archer, American Peanut Council, personal communication). Conversion of the remainder of US peanut production to high oleic varieties is expected by 2020. This tactic is facilitated by industry cooperation and deployment of genome sequence guided breeding methods. Use of allele specific FAD2-1 gene markers enables selection of elite yielding high oleic peanut cultivars in only 26 months, a time saving of about 2 years compared to traditional breeding methods (Chu et al. 2009). Hi-Oleic peanuts are desired in manufacture of peanut butter and confections to improve shelf-life and improve product flavor. About 78% of US peanut production is consumed as whole kernels or in peanut butter (USDA ERS 2014). Only 12% of annual US peanut production is crushed for oil, which averages about 0.07 MT/year (USDA FAS 2014). Therefore, supply of high oleic peanut oil as a food ingredient will remain extremely low compared to other high stability oil sources.

- Global supply of palm oil could reach 171 MMT by 2025 (USDA FAS 2014). About 25 countries produce palm oil. Indonesia and Malaysia account for about 50% of world production. Indonesian palm oil supply is growing at 2.0 MMT/year compared to 0.6 MMT/year in Malaysia. This rate differential is biased toward ability to expand plantation area in Indonesia, a practice that has raised consumer concern for the environmental impact of deforestation of rainforests and other nonagricultural sources on biodiversity. The palm industry has responded by forming the Roundtable on Sustainable Palm Oil (RSPO). The RSPO is commissioned to oversee a system for certifying transactions made by major food manufacturers that have pledged to source palm oil produced in a sustainable manner (Watson 2013b). Euromonitor estimates that 15% of global palm oil is sanctioned as a fully traceable product, and sale of "GreenPalm" certificates continues to rise (Cottam 2014). The palm industry also has engaged genomic research to evaluate oleic acid and total oil concentration for next generation plantations. Palm oil concentration may be enhanced by 30% by two alleles of the "Shell" gene (Gray 2013). Hi-Oil palm plantings could increase commercial oil production from 4 MT to 6 MT/ha/year by 2020 (May 2012). Hi-Oleic palm oil plantations will not be in production before 2035 (Ong and Abdullah 2013, Malaysian Palm Oil Board, personal communication).
- The Commonwealth Scientific and Industrial Research Organization (CSIRO) has received regulatory approvals for cultivation, food,

and/or feed use of GM cottonseed varieties with high oleic acid in Australia (Liu et al. 2002a, 2002b). In addition, Hi-Oleic safflower varieties developed by CSIRO are being grown on about 100,000 ha in Australia (Quick 2012). OSI for safflower oil with 75% oleic is 14 hours (Romano et al. 2013).

- High oleic algal oil is being produced by Solazyme (Anon 2013c). Strains fit for purpose can be found in nature that yield a wide range of different oils, proteins, and nutritional ingredients. Microalgae can also be optimized using traditional molecular biology techniques to modify composition, which expands the functionality and benefits yielded by the resulting ingredients (Anon 2013b). Native algae species typically have 20–40% palmitic acid, 2–40% palmitoleic acid, 3–12% oleic acid, 0–15% eicosapentoenoic acid (EPA), and produce only about 10% oil (Schlagermann et al. 2012). By contrast, Solazyme has produced algal oil that contains 88% or more oleic acid by composition and 2% or less polyunsaturates (Rakitsky 2013). Oxidative stability (OSI standard method) of this high oleic algal oil as described is over 40 hours neat at 110°C, and over 100 hours with the addition of 200 ppm tert-butylhydroquinone (TBHQ) (Pietz et al. 2014). Solazyme has optimized strains of heterotrophic microalgae to produce 80% oil content (by dry weight) by fermentation. Oils produced from optimized algal strains do not require GM labeling under European Union (EU) regulatory standards because the algae are considered a processing aid and no genetic material is in the final product, similar to the labeling requirements for wines and cheeses that are produced with enzymes from modified microbes. Algal oil is being produced by Solazyme at an Archer Daniels Midland facility with capacity for 20,000 MT (44 million pounds) algal oil, expandable to 100,000 MT/year (220 million pounds). Solazyme also has a joint venture with Bunge Global Innovation LLC that produces commercial scale algal oil in a purpose built facility in Brazil with nameplate capacity of 100,000 MT, expandable to 300,000 MT/year. Both production facilities may be used to produce a variety of Solazyme's oils depending on the microalgae strain used, ranging from high oleic algal oil to high myristic or based on customer demand. American Natural Processors has agreed to handle product distribution from the Clinton IA facility (Anon 2013b). Goulston Technologies has agreed to purchase Tailored™ high oleic algal oil beginning in 2014 to support production of high performance textile fiber lubricant products (de Guzman 2013). Future availability of high stability high oleic algal oil will depend on constraints such as production capacity, current obligations, and efficiency improvements.

2.4 WHAT ABOUT INTEGRATION AND MARKET TRANSITION TO HIGH STABILITY SOYBEAN OIL?

The development of high-oleic soybean varieties is facilitated by substantial breakthroughs in genomic and genome editing technologies (Wilson 2012). SoyBase, a bioinformatic resource developed by the USDA Agricultural Research Service, is the official portal to *Glyma1*, the "Williams 82 version 1.01" genome assembly (Schmutz et al. 2010), and the main repository for data sets and tools for translational genetics (Grant 2010). Examination of soybean genome structure has revealed a complex network of genes that regulate oleic acid concentration in soybean oil. Oleic acid concentration is mediated by a gene family that encodes ω-6 desaturase enzymes (Table 2.3) which catalyze synthesis of linoleic acid from oleic acid. *Glyma1* reveals at least 22 different members of this family in soybean (Chi et al. 2011). Critical structural variations in FAD2-1 gene sequences compromise linoleic acid synthesis, resulting in higher than normal oleic concentrations in seed oil. Critical structural variations in FAD2-2 and FAD6 genes tend to impact plant growth and development through effects on oleic acid levels in membrane lipids, but also are present in seed. Genotypes having one recessive FAD2-1A and one specific recessive FAD2-1B allele exhibit about 80% oleic acid in seed oil (Gillman and Bilyeu 2012; Pham 2010, 2011). Hence, the soybean genome sequence presents a critical roadmap for pinpointing appropriate targets among copies of a given gene (FAD2 or FAD6 in this case) for genetic modification.

Further advances in genetic technology reduce genomic information to useful practice. The process of breeding agronomic high oleic soybean varieties may be accelerated through application of high

Table 2.3 Chromosomal Location of Known FAD2 (Omega 6 Fatty Acid Desaturase) Gene Sequences in Soybean

Gene symbol	Gene locus tag	Chromosome
GmFAD2-1A	Glyma 10g42470.1	10
GmFAD2-1B	Glyma 20g24530.1	20
"	Glyma 20g24530.2	20
"	Glyma 20g24530.3	20
"	Glyma 20g24530.4	20
"	Glyma 20g24530.5	20
GmFAD2-2A	Glyma 19g32940.1	19
GmFAD2-2B	Glyma 19g32930.1	19
GmFAD2-2C	Glyma 15g23200.1	15
GmFAD2-2D	Glyma 03g30070.1	3
	Glyma 03g30070.2	3
GmFAD2-2	Glyma 03g30050.1	3
GmFAD2-2	Glyma 03g30060.1	3
GmFAD2-2	Glyma 06g38430.1	6
GmFAD2-2	Glyma 09g14360.1	9
GmFAD2-2	Glyma 10g20450.1	10
GmFAD6A	Glyma 02g36460.1	2
GmFAD6B	Glyma 09g17170.1	9
GmFAD6	Glyma 12g13970.1	12
GmFAD6	Glyma 13g27910.1	13
GmFAD6	Glyma 15g20600.1	15
GmFAD6	Glyma 17g08220.1	17

FAD2/FAD6, omega 6 fatty acid desaturases.
Gene locus tag from *Glyma1* from www.soybase.org; Chi X, et al. 2011. *Plant Mol Biol Rep* 29:769–783

throughput resequencing of the genomes of individual progeny in a breeding population. This technology can detect structural differences; single nucleotide polymorphisms (SNPs) are most common, in and around the DNA sequences associated with the models for FAD2 genes in a given inbred hybrid. Ability to distinguish the genotypes of hybrids through genome wide association studies (GWAS) helps breeders choose early generation lines with the most advantageous combination of FAD2-1 gene mutations without having to wait for field validation of the expressed phenotype; another term for this approach is "genotype by sequencing" (Heger 2013).

Genomic roadmaps also help guide the targeting of specific genes for modification, insertion or deletion by genetic engineering. These maps also facilitate quality control measures to ensure appropriate chromosomal positioning and presence of intact functional constructs of the transgenic event. These principles have been stringently applied in the development of varieties that now establish markets for high stability soybean oils. The current varieties in commercial production are (Anon 2013c; Wilson 2012):

- Monsanto MON87705 (Vistive Gold™ with RoundUp Ready-2™ herbicide tolerance)
- Pioneer DP305423 (Plenish™ with sulfourea and RoundUp Ready-1™ herbicide tolerances).

Regulatory approvals for cultivation, food, and/or feed use of these soybean cultivars have been granted from countries that purchase 84% of US soybean exports (Anon 2013d; USDA FAS 2014). The quality of these oils is exceptionally high. OSI value for high stability soybean oil with 75% oleic acid is 50 hours compared to 7 hours for commodity RBD soybean oil with 23% oleic acid with or without low linolenic acid (Mermelstein 2010). The OSI of high stability soybean oil also compares favorably with other modified trait oils (Table 2.4). Projected supplies of high stability soybean oil should reach 9 billion pounds by 2023 (Watson 2013b), and pending preemptive intervention by the FDA should fill the void in supply created by the planned industry phase-out of trans fats in food products in a timely manner (Figure 2.3).

Table 2.4 Comparative Oxidative Stability of Trait-Modified Oils

Oil	% Oleic acid	OSI (hours @ 110°C)
High oleic algae	88	40
High oleic soybean	75	50
High oleic sunflower	82	25
High oleic canola	75	21
High oleic safflower	75	14
Mid oleic sunflower	56	9
Low linolenic soybean	23	8
Soybean	23	7

OSI, Oxidative Stability Index – neat oil without antioxidants.

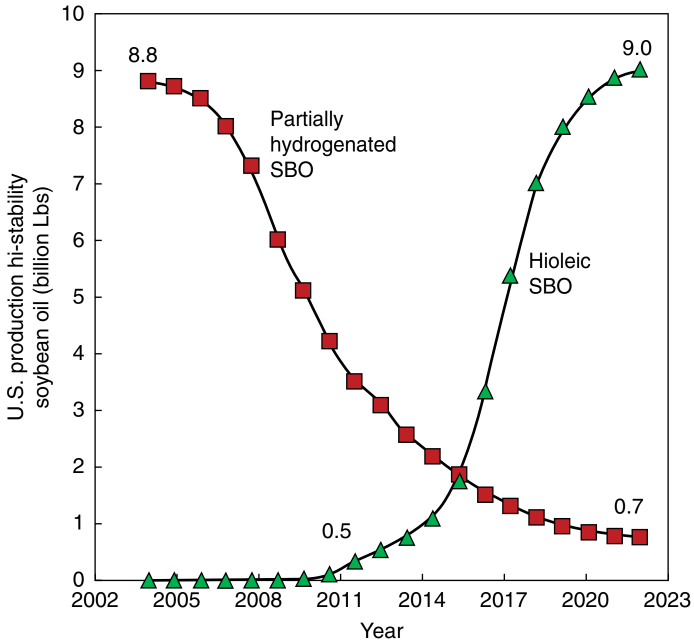

Figure 2.3 Trends in North American supply of partially hydrogenated and trait-modified soybean oils.

2.5 WHAT IS THE MARKET OUTLOOK FOR HIGH STABILITY TRAIT-MODIFIED VEGETABLE OILS?

Industry efforts to remove trans fats from all applications while meeting escalating North American consumer demand for high quality food products is far from a trivial endeavor. Nevertheless, the US oilseed industry is actively engaged in a deliberate and timely process for the replacement of sources of dietary trans fat with high stability oils. About 6 billion pounds of PHSBO has been eliminated from North American diets in the past 5 years, and the remainder should be replaced as much as possible by 2025. The proposed FDA action to deny GRAS status to partially hydrogenated oils may be an attempt to accelerate this process, but may also result in a number of unintended consequences that are counter to the intended public good (Watson 2014). Such governmental intervention at this time would impact about 3 billion pounds of PHSBO and other hydrogenated oils that are currently available, without facilitating

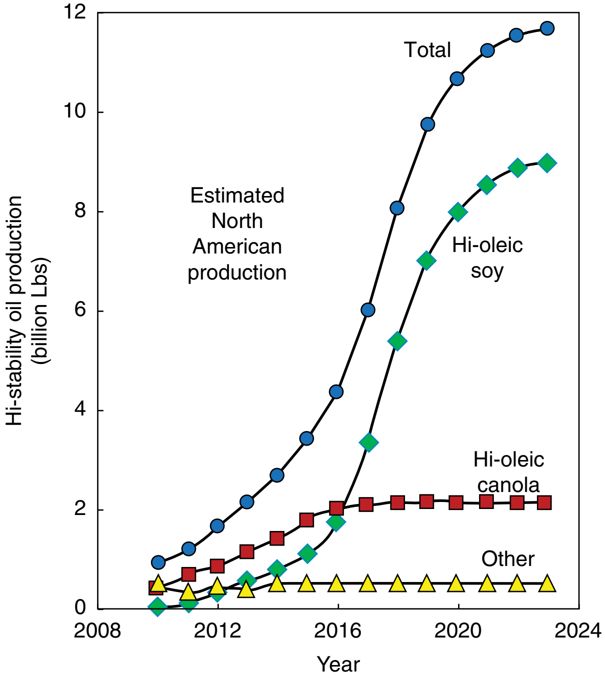

Figure 2.4 Projected trends in North American production of high stability vegetable oils.

alternatives to ensure adequate supply of nutritionally acceptable oils to meet rising consumer demand for high quality food products. It may be assumed that high stability oils will provide that alternative. Estimates of North American supply project the availability of nearly 12 billion pounds of high stability vegetable oils by 2025 (Figure 2.4). However, commercial production of high stability canola, sunflower, and soybean oils in North America is in an early stage of market integration, and future sources (cottonseed, peanut, safflower, algae) will be constrained by product cost and/or low availability. Time is also needed to develop or optimize oil processing technologies such as interesterification to help expand the utility of high stability oils in baking and other applications. As these processes are allowed to develop in a responsible manner, high stability trait-modified oils will grow to commodity status and play a dominant role in meeting future consumer demand for high quality and nutritionally enhanced food products.

2.6 ACKNOWLEDGMENT

This review was prepared in part with financial support from United Soybean Board project 1430-612-6224.

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3 A Survey of the Composition and Functional Characteristics of Trait-Modified Oils

Gary R. List[1] and Frank T. Orthoefer[2]

[1] *USDA ARS NCAUR (Retired), Peoria, IL, USA*
[2] *FTO Foods, Knoxville, TN, USA*

Trait modification usually implies changing the fatty acid composition of a fat or oil, through either plant breeding and/or genetic manipulation (Loh 1999; Lui 1999). Much of the early work was aimed at reducing the linolenic acid content of soybean oil as a means to improve flavor and oxidative stability (Evans et al. 1965; Hammond 1984; Hammond et al. 1972; Mounts et al. 1988). Other researchers aimed at breeding out the erucic acid from rapeseed oil (Daun 1986), resulting in the introduction of canola oil. In the early 1990s, USDA researchers (Miller et al. 1987) introduced sunflower oil with reduced linoleic acid content and thus NuSun or mid oleic sunflower was introduced to the marketplace (Gupta 1998). Low linolenic acid soybean oil and high oleic sunflower oil became commercial realities in the early 1990s but were not entirely successful because of higher costs compared to commodity oil (Erickson and Frey 1994; Krawczyk 1999). However, in view of trans fat labeling, which became effective January 1 2006, many food manufacturers turned to trait-modified oils including low linolenic soybean, high/mid oleic canola, and mid oleic sunflower (NuSun). Currently, a number of trait-modified oils are nearing commercialization. They include mid

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Trait-Modified Oils in Foods, First Edition. Edited by Frank T. Orthoefer and Gary R. List.

oleic soybean, high oleic soybean, and high stearic acid soybean. This chapter will review the properties, oxidative stability, functionality, and food uses of trait-modified oils.

3.1 AN OVERVIEW OF TRAIT-MODIFIED OILS

3.1.1 Soybean Oils

The fatty acid composition of trait-modified soybean oils is given in Table 3.1 with commodity oil included for comparison. Low linolenic soy shows a linolenic acid content of about 3% compared to 7–8% for commodity oil. Mid and high oleic soybean oils typically have oleic acid contents of 55–60% and 75–80% respectively. Low linolenic acid soy production amounted to over 1 billion pounds in 2009. Ultra low linolenic soy (1% linolenic soy) was commercialized in 2005 but has since been discontinued. The mid and high oleic acid soybean oils are now commercialized. Low linolenic soybean oil has been reviewed by Wilkes (2008). High stearic acid soybean oils contain up to 33% stearic acid compared to about 4% for commodity oil (List et al. 1996). These oils are still under development and expect to find uses where increased solid fats are needed such as margarine/spread oils, baking shortenings, and frying fats. The reader is directed to a number of articles on high saturate soybean oils (Chrysam and Pelloso 2000; Fehr and Hammond 1996, 1998; Graef et al. 1985; Kok et al. 1999; List et al. 2000b).

3.1.2 Canola Oil

Currently, high oleic and low linolenic canola oils are commercially available. Low linolenic canola is characterized by a lowered linolenic acid content of about 4% compared to 8–10% for commodity canola and oleic acid from about 22% in commodity oil to about 74% in high oleic canola. Both trait-modified oils are commercially available in the food service arena. The low linolenic oil contains high levels of linoleic acid (65%) which is desirable as a source of polyunsaturates for use in margarine/spreads where nutritional issues are important but is a disadvantage in

Table 3.1 Estimated Fatty Acid Composition of Trait-Modified Soybean Oil and Commercially Available Vegetable Oils

Oil	16:0	18:0	18:1	18:2	18:3	Sats	18:4
High oleic oils							
Canola							
High oleic	–	–	74	14	3	<7	–
Low linolenic	–	–	65	22	4	7	–
Commodity	–	–	60	20	10	7	–
Sunflower							
High oleic	–	–	82	10	<1	8	–
Mid oleic	–	–	56	33	<1	9	–
Commodity	–	–	20	65	<1	10	–
Others							
High oleic safflower	–	–	75	14	<1	7	–
High oleic soybean	–	–	83	2	3	12	–
Olive	–	–	75	8	<1	14	–
Lauric oils							
Coconut	–	–	6	2	–	92	–
Palm kernel	–	–	15	3	–	82	–
Commodity oils							
Cotton	–	–	17	56	–	27	–
Soybean	–	–	23	51	7	15	–
Corn	–	–	26	60	1	13	–
Palm	–	–	39	10	<1	50	–
Soybean oils							
Commodity	11	4	24	52	7	–	–
Low linolenic[1,2]	11	4	24	57	2.5	–	–
Ultra low linolenic[3]	11	5	25	58	1	–	–
Mid oleic/ultra low linolenic[3]	10	1	53	32	1	–	–
Mid oleic[1]	6	5	80	2	3	–	–
Mid oleic/low saturate[2]	3	3	75	15	2.5	–	–
High stearate[2]	9	18	23	43	3	–	–
High oleic/high stearate[1]	6	20	61	4	4	–	–
Stearidonic acid[2]	11	4	20	24	10	–	20

Suppliers: [1] Dupont, [2] Monsanto, [3] Asoyia.
Source: Wilkes (2008). Reproduced with permission of Wiley-Blackwell.

frying operations where polymerization occurs. The reader is referred to a number of patents on canola oil. (Debonte et al. 1999, 2001; Fan 2001). The effects of genetic modification on the minor constituents of canola have been reported by Abidi et al. (1999). The oxidative stability of canola oil was reported by Broadbent and Pike (2003).

3.1.3 Sunflower Oil

Conventional sunflower oil contains about 70% linoleic acid which is both an advantage and a disadvantage, as discussed above. The mid and high oleic oils typically contain 50–80% oleic acid (Warner et al. 2010). Both are available commercially and have consumption in the 800 million pounds per year range.

3.1.4 Other Oils

High oleic safflower (Fuller et al. 1985) and peanut oils contain 77% oleic acid and are available commercially. They are low in saturated acids (7%). Typically, these oils have excellent stability (Active Oxygen Method [AOM] 40 hours). High oleic peanut oil has been studied in the laboratory (Okeefe et al. 1993), as has high oleic corn oil (Warner and Knowlton 1997).

3.2 OXIDATIVE STABILITY OF TRAIT-MODIFIED OILS

The oxidative stability of edible oils is extremely important in food manufacture, particularly when a long storage life is needed (Tiffany 2007). Examples include snack foods, salty snacks, and cookies. Oxidative stability is also a prime consideration in choosing a deep fat frying oil where the oil is heated at high temperatures for extended periods. Several tests have been employed to assess oxidative stability. They include the Active Oxygen Method, the Schall Oven Test (Anon 1997; Joyner and Mcintyre 1938) and the Oxidative Stability Index (OSI). The AOM test is largely obsolete and equipment is no longer being manufactured. However, much of the older literature makes reference to AOM values. The AOM test involves bubbling moist air through the sample at about 98°C and the value is the number of hours under these conditions to reach a peroxide value of 100 meq/kg fat (Deman and Deman 1984; King et al. 1933; Mehlenbaher 1942). The OSI or Metrohm Rancimat test was introduced in the early 1980s and has been studied by several investigators. The test involves bubbling air through the oil at 110°C. As the oil oxidizes, volatile organic acids are collected in distilled water in a cell. The instrument measures the conductivity and the endpoint occurs when the conductivity begins to rise rapidly (Farroosh 2007; Gordon and Mursi 1994; Hassenhuettl and Wan 1992; Jebe et al. 1993; Matthäus 1996). The OSI test is dependent on temperature and results should be reported at 110°C. Equations for converting OSI values to AOM numbers have been published by Jebe et al. (1993).

The AOM and OSI data for a number of commodity and trait-modified oils are given in Table 3.2. The common commodity oils, including soybean, corn, sunflower, canola, and cottonseed, show AOM values in the 12–16 hour range with OSI values ranging from 5 to 17 hours. The conversion from OSI to AOM is about a factor of 2.

Improvements in stability for trait-modified oils are shown by comparison to the commodity oils. Low linolenic acid soy shows little improvement over commodity soy. However, the mid and high oleic oils show about 2–6 times improvement (Knowlton 1999). As would be expected, high oleic (80% oleic) soy shows the most improvement (45 hours versus about 7 hours). High oleic sunflower, high oleic canola, and high oleic corn oils show varying improvement over commodity

Table 3.2 Tocopherol Content of Vegetable Oils

Oil	Tocopherol (ppm)					AOM (hours)
	α	β	γ	δ	Total	
Soybean	100	23	842	363	1328	12
Cotton	355	502	8	0	865	16
Peanut	211	20	239	11	481	25
Corn	152	12	1276	61	1501	19
Sunflower	690	26	5	0	721	11
NuSun						30
HoSun	262	2	1	0	265	40
Canola	233	421	13	0	667	18
Olive	103	8		0	111	22
Palm	172	30	26	13	241	54
Coconut	49		6	0	55	150
Lard	172	30	26	13	241	54
Safflower	445	10	8	0	463	2
High oleic safflower						40

AOM, Active Oxygen Method.
Source: O'Brien (2009). Reproduced with permission of Elsevier.

oils. High and mid oleic sunflower improve from about 5 hours to about 19 hours while high oleic canola improves slightly from 17 to about 19 hours. The effects of blending high oleic sunflower oil with less stable oils have been reported by Frankel and Haung (1994). Marked improvements in oxidative stability were observed when the high oleic oil was blended with canola, corn or soybean oil.

The oxidative stability of a fat or oil is dependent on several factors, including fatty acid content, trigylceride structure, total unsaturation (iodine value), and tocopherol content (Gupta et al. 2004; Warner et al. 1997). Typically highly saturated fats, including coconut, palm, and palm kernel, are more stable than liquid oils because they contain low levels of polyunsaturated acids. The major unsaturated acid in these fats is oleic containing one double bond and is about 10 times as stable as many common oils which contain high levels of polyunsaturates. For example, palm oil (iodine value 45–50) typically contains about 50% saturated acids and has an AOM value of 54 and an OSI of about 17 hours. Coconut oil (iodine value 7–11) contains about 85% saturated acids with AOM and OSI values of 150 and 50 hours respectively. Both palm and coconut oils are low in tocopherols (O'Brien 2009). On the other hand, liquid commodity oils like corn, cottonseed, soybean, sunflower, and canola (iodine values 111–130) are highly unsaturated but contain higher levels of tocopherols (see Table 3.2).

O'Brien (2009) points out that the rate of oxidation in a triglyceride oil is dependent on the number of double bonds and the number of active methylene groups. For example, oleic, with zero active methylene groups, has a relative oxidation rate of 10 and, for each additional active methylene group, the rate doubles. Thus, linoleic has a rate of 20, linolenic 40, etc. Multiplying the oxidation rate of each fatty acid by its concentration in a fat or oil gives an inherent oxidative stability value. Results for 18 oils and fats are given in Table 3.3 along with AOM data. As shown in Figure 3.1, a plot of iodine value versus AOM yields a good correlation.

The effect of fatty acid composition on AOM stability is further shown in Figure 3.2 where the linoleic acid content of safflower and sunflower oil is plotted against AOM hours. As linoleic acid is decreased, significant improvements in oxidative stability result (Purdy 1985). The same effect occurs in trait-modified oils where linoleic acid decreases and oleic acid increases.

Table 3.3a Fats and Oils Oxidative Stability Ratings

Rating	Fat and oils source	Inherent		Calculated	
		oxidative stability	PUFA oxidizability	iodine value	AOM (hours)
Worst	Menhaden oil	32.9	148.5	176.2	1
	Safflower oil	8.0	78.5	146.1	2
	Sunflower oil	7.1	69.1	135.3	11
	Soybean oil	7.1	68.9	133.0	12
	Corn oil	6.5	62.0	128.4	19
	Cottonseed oil	5.8	55.8	112.6	16
	Canola oil	4.5	38.6	113.0	18
	Peanut oil	3.7	32.0	97.1	25
	NuSun oil	3.7	30.6	104.9	30
	High oleic sunflower oil	1.7	9.0	85.6	40
	Olive oil	1.6	7.7	82.4	22
	High oleic safflower oil	1.6	7.4	83.3	40
	Palm oil	1.5	10.9	52.4	54
	Lard	1.5	10.3	59.3	54
	Tallow	0.8	3.7	48.4	16
	Milk fat	0.7	4.0	34.0	42
	Palm kernel oil	0.4	2.3	17.2	100
Best	Coconut oil	0.2	1.6	8.1	150

AOM, Active Oxygen Method. PUFA, polyunsaturated fatty acid.
Source: O'Brien (2009). Reproduced with permission of Elsevier.

Table 3.3b Comparison of AOM and OSI Values in Trait-Modified Oils

Oil	AOM (hours)	OSI (hours) 110°C
Low linolenic soybean	7	6.9
Mid oleic soybean		13.7
High oleic soybean	45	150.0
Low linolenic canola	18.8	4.3
High oleic canola	40	20.9
Mid oleic sunflower	30	8.5
High oleic sunflower	40	12.0
High oleic safflower	40	14.3

AOM, Active Oxygen Method; OSI, Oxidative Stability Index.

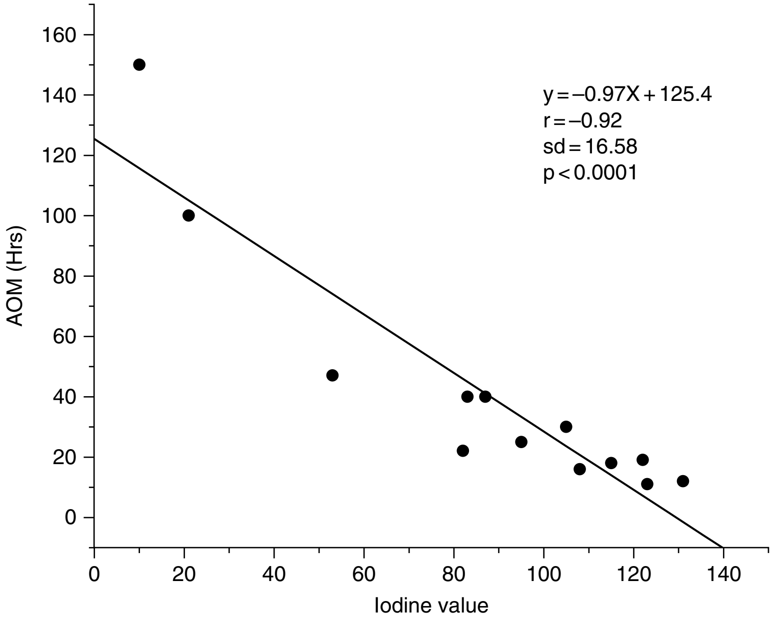

Figure 3.1 Comparison of oxidative stability with iodine value of various oils. AOM, Active Oxygen Method.

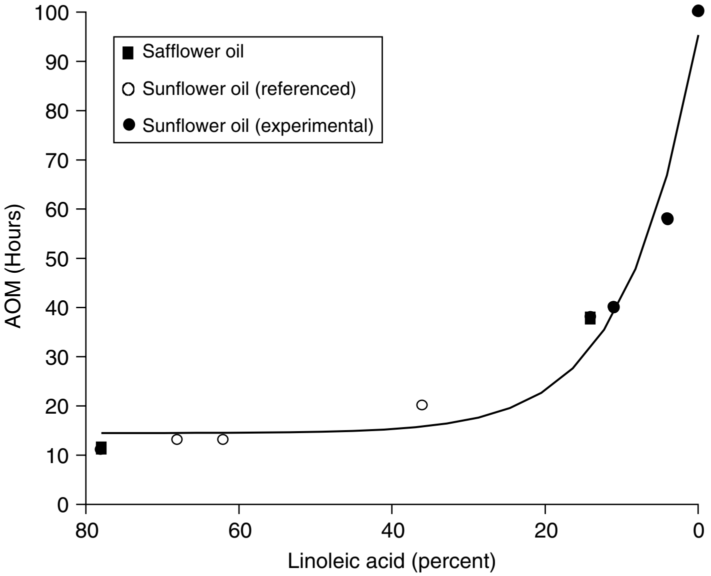

Figure 3.2 The effect of linoleic acid concentration on AOM stability of safflower and sunflower oils. AOM, Active Oxygen Method. Source: Purdy (1985). Reproduced with permission of AOCS Press.

The oxidative stability of trait-modified oils can be improved through the addition of tocopherols to high oleic oils (Carrick and Yodice 1993). Figure 3.3 shows the AOM values of high oleic sunflower oil as a function of oleic acid content (part A) and the percentage increase after the addition of 2000 ppm tocopherol (part B). The results indicate that γ-tocopherol is more effective than α-tocopherol in stabilizing the oil against oxidation and levels of γ-tocopherol at levels of 500 ppm (part C).

The effects of antioxidants in conventional and high oleic oils have been studied by Merrill et al. (2008). Tocopherols (200 ppm), rosemary extract (1000 ppm), ascorbyl palmitate (1000 ppm) and tert-butylhydroquinone (TBHQ) (200 ppm), either alone or in various combinations, were added to high oleic canola, high oleic safflower, and high oleic sunflower oil. The effect of these additives on oxidative stability as measured by OSI are shown in Table 3.4. The results show that TBHQ at concentrations of 200 ppm is an excellent antioxidant and yields nearly equal to others in combination. TBHQ is approved for food use and is commonly used to stabilize fats and oils against oxidative deterioration.

Warner and Moser (2009) studied the stability of mid oleic sunflower oil having been first stripped of tocopherols followed by the addition of pure α, δ, and γ isomers. Tortilla chips were fried in the oils and the loss of tocopherols in the frying oils and chips was determined after 1, 3, and 6 hours of frying. γ-Tocopherol showed the lowest retention in both the frying oil and oils extracted from chips stored for up to 4 months at 25°C.

Sunflower oil with increased content has been achieved through plant breeding techniques (Warner et al. 2008). Mid oleic oils were developed with 300–700 ppm of γ-tocopherol compared to 20 ppm in traditional lines. A mid oleic oil containing 470 ppm γ, 100 δ, and 300 ppm α had the best oxidative stability.

The effects of α-tocopherol on the oxidative stability and phytosterol oxidation in conventional and high oleic oils have been reported (Tabee et al. 2008). α-Tocopherol was shown to be effective in olive oil, but had little effect in high oleic rapeseed (canola). However, α-tocopherol was effective in reducing the phytosterol oxidation products (POP) in rapeseed oil.

The optimal tocopherol content needed to inhibit oxidation in soybean oil was reported by Evans et al. (2002). Typically, refined, bleached and deodorized oil contains 800–1000 ppm of α, γ and δ isomers, whereas

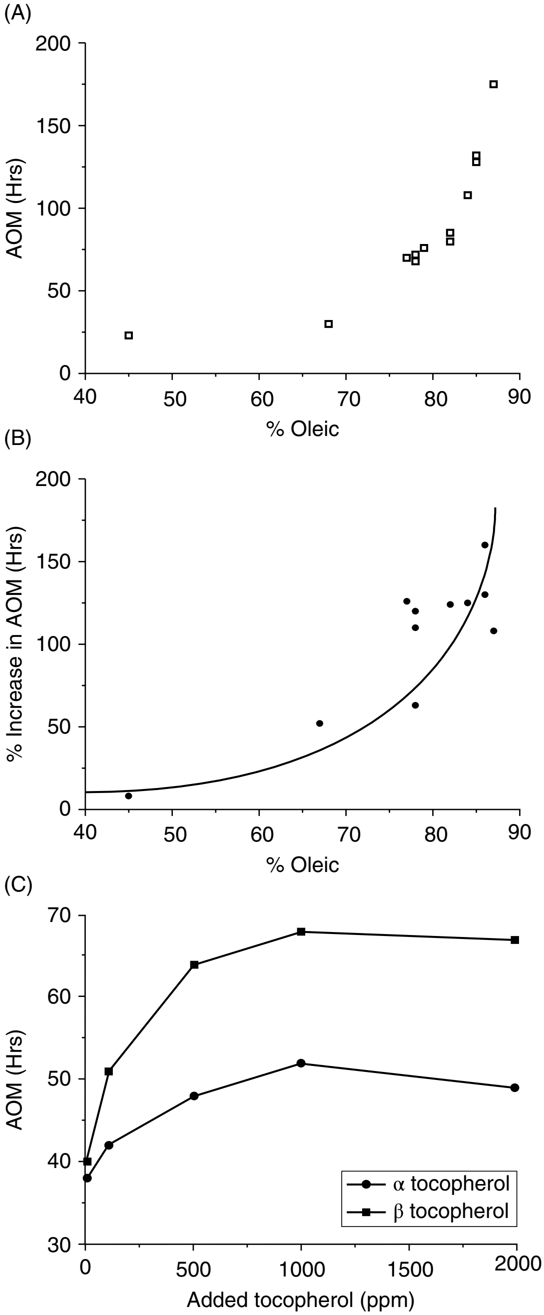

Figure 3.3 Effects of oleic acid content (A) on AOM stability, tocopherol addition (B), and individual tocopherols (C) on the oxidative stability of high oleic oils. AOM, Active Oxygen Method. Source: Carrick and Yodice (1993). Reproduced with permission of the authors.

Table 3.4 Effect of Addition of Rosemary Extract (RM; 1000 ppm), Ascorbyl Palmitate (AP; 1000 ppm), Tert-Butylhydroquinone (TBHQ; 200 ppm), and Mixed Tocopherols (TOC; 200 ppm) on Oxidative Stability of High Oleic Canola (HOCAN), Very High Oleic Canola (VHOCAN), High Oleic Sunflower (HOSUN), and Safflower (SAF) Vegetable Oils

	OSI 110°C (hours)			
Antioxidant addition	**HOCAN**	**VHOCAN**	**HOSUN**	**SAF**
Control – no antioxidants	11.9 ± 0.18	16.9 ± 0.00	12.2 ± 0.11	13.8 ± 0.57
TOC	12.1 ± 0.00	17.4 ± 0.07	17.3 ± 2.12	19.6 ± 0.04
RM	15.7 ± 0.14	21.2 ± 0.25	16.7 ± 0.18	19.3 ± 0.32
AP	17.3 ± 0.18	24.4 ± 0.35	15.8 ± 0.42	19.7 ± 0.64
TBHQ	36.0 ± 0.85	46.9 ± 1.87	41.0 ± 0.32	49.6 ± 0.92
TOC-RM	16.0 ± 0.67	21.0 ± 0.64	20.5 ± 0.11	24.7 ± 0.04
TOC-AP	18.0 ± 0.18	23.6 ± 0.81	20.2 ± 1.31	26.0 ± 0.04
RM-AP	20.0 ± 1.63	27.2 ± 1.38	20.7 ± 0.85	25.5 ± 0.35
TBHQ-RM	35.2 ± 0.67	43.4 ± 2.51	39.1 ± 2.02	20.3 ± 0.11
TBHQ-AP	37.9 ± 1.06	47.9 ± 0.85	44.5 ± 0.21	21.8 ± 0.04
TBHQ-TOC	37.4 ± 0.00	46.3 ± 1.03	45.0 ± 0.07	54.3 ± 0.49
TOC-RM-AP	19.7 ± 0.95	26.5 ± 0.42	24.4 ± 2.19	29.9 ± 2.23
TBHQ-TOC-RM	35.3 ± 0.14	42.7 ± 0.07	43.6 ± 2.23	53.9 ± 0.11
TBHQ-RMAP	39.1 ± 0.71	45.0 ± 1.84	47.3 ± 2.40	50.8 ± 1.13
TBHQ-TOCAP	40.9 ± 0.04	47.8 ± 1.41	48.8 ± 0.78	55.7 ± 4.24
TBHQ-TOC-RM-AP	37.6 ± 0.85	48.5 ± 2.40	46.1 ± 2.97	53.2 ± 2.23

Source: Tabee et al. (2008). Reproduced with permission of AOCS Press.

optimum stability was found to be 340–660 ppm. α-Tocopherol was 3–5 times more potent than γ and 16–32 times more potent than δ. These findings are in agreement with early work by Frankel et al. (1959) who found that soybean oil contains more tocopherols than needed for optimal oxidative stability.

3.3 FATTY ACID COMPOSITIONS OF TRAIT-MODIFIED OILS

The fatty acid compositions of trait-modified oils, up until 2000, have been reported by Hazebroek (2000) along with data on oil content, triacylgylcerol characterization, minor and unusual fatty acids. Extensive data on the composition of canola and other oils can be found in Gunstone (2004, 2005). Warner et al. (2010) have reported on the fatty acid composition of sunflower oils. The reader is also directed to a book aimed at the snack food/food service industry which provides much useful information on the composition and properties of trait-modified oils for use in deep fat frying and snack food preparation (Dellaporta 2008).

3.4 TRAIT-MODIFIED OILS AS TRANS FAT REPLACEMENTS

Trans fat labeling became federal law in July 2003 (Anon 2003). Key provisions include that, by January 1 2006, trans fats had to be included on nutrition labels but foods containing less than 0.5 g trans fat/serving may be declared as zero. Many food companies began testing and reformulation to low/zero trans well before the 2006 deadline and the number of foods increased from about 200 in 2003 to well over 1900 by 2007. These results are shown in Figure 3.4. An excellent review of existing fats and oils used in low trans products is Tarrago-Trani et al. (2006). Trans fat labeling has had a pronounced effect on edible oil consumption patterns in the US. While total consumption of fats and oils has remained fairly static over the past decade, a shift from heavily hydrogenated baking/frying fats has occurred towards the use of liquid or lightly

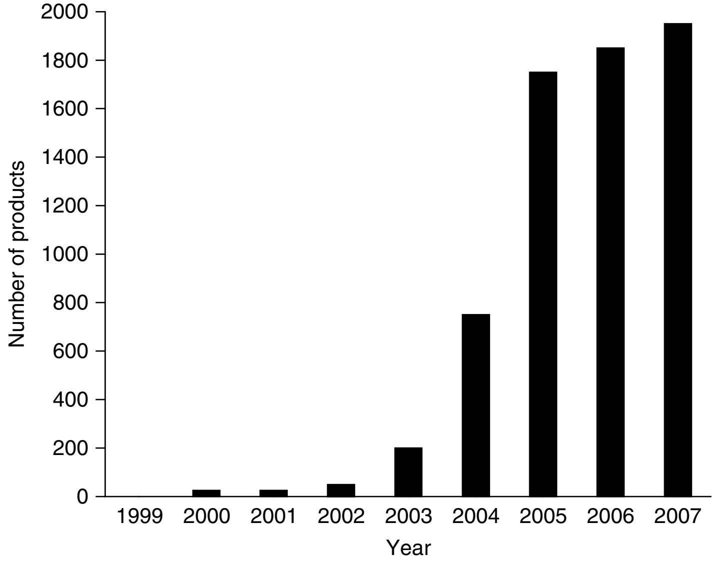

Figure 3.4 Number of products claiming zero (or low) trans fats.

Table 3.5 Fats and Oils Usage in the United States

		Baking/frying		Margarine		Salad/cooking	
Year	Total	Million pounds	%	Million pounds	%	Million pounds	%
2001	21,364	9388	44.0	1392	6.5	10,167	47.6
2002	22,310	9687	43.4	1292	5.8	10,928	49.0
2003	21,500	9237	42.7	1207	5.6	10,670	49.6
2004	21,416	8934	41.7	1262	5.9	10,784	50.3
2005	22,994	8999	39.7	916	4.0	12,598	54.8
2006	22,866	7930	34.7	1056	4.6	13,368	58.4
2007	22,590	6227	29.3	977	4.3	14,473	64.1
2008	22,884	5680	25.5	891	4.0	15,264	68.5

2005 – Year prior to trans fat labeling.
2006 – Year trans fat labeling effective.
2007 – Year after trans fat labeling.

hydrogenated oils for salad/cooking. Trans fat labeling has accelerated this trend. See Table 3.5.

The food industry has a number of options for trans fat replacement (Kodali and List 2005; List 2004; List et al. 2007). These include

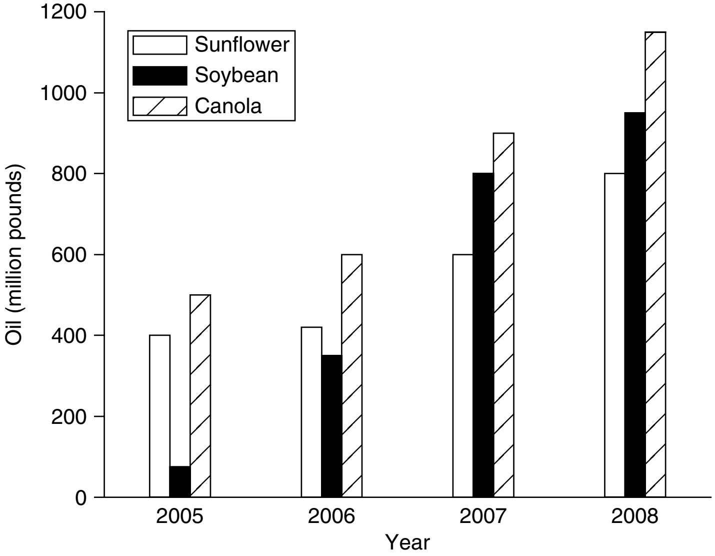

Figure 3.5 Growth of naturally stable oils category.

interesterification (chemical/enzymatic), use of tropical oils, fractionation, use of naturally stable commodity oils like cottonseed, corn and sunflower, modified hydrogenation technologies/catalysts and trait-modified oils. Figure 3.5 shows the usage of naturally stable and trait-modified oils. Over the period 2005–2008, about 3 billion pounds of trans free oils were produced, amounting to about 12% of total food oil production. It is estimated that 750 million pounds of trans fat and 120 million pounds of saturated fats were removed from the diet (Heintz 2009).

3.5 PROCESSING AND QUALITY OF TRAIT-MODIFIED OILS

The processing of trait-modified oils (soybean, canola, sunflower) is much the same as for commodity oils and consists of seed preparation, extraction, degumming, caustic refining, adsorbent bleaching, and deodorization. For detailed descriptions of these processes, the reader is referred to a number of extensive reviews (Grampone 2005; Hammond et al. 2005; Przybylski et al. 2005).

Soybean oil is generally extracted from the seed with hexane while canola and sunflower are considered high oil crops and are processed by a combination of pressing and solvent extraction. Soybean and canola oils are essentially free of waxes which cause clouding at refrigerator temperatures while sunflower oil requires a dewaxing step (Grampone 2005). Modern refineries are designed to protect the oils from oxidation at all stages of processing. Key design features include the sparging of oil with nitrogen as it leaves the deodorizer and storage under a nitrogen blanket. As a result, trait-modified oils are bland in taste with no off flavors, have a peroxide value of zero, and are light in color. Typically trait-modified oils have a Lovibond red color in the 1–1.5 range. All major suppliers furnish technical data sheets for their products and include fatty acid composition, iodine value, color, taste, free fatty acid, peroxide value, and AOM/OSI values.

3.6 FUNCTIONAL AND PHYSICAL PROPERTIES OF TRAIT-MODIFIED OILS

Trait-modified oils, including low linolenic, mid and high oleic soy, high oleic canola, and mid oleic sunflower, are composed of triglycerides with low melting points and, as such, remain liquid at low temperatures well below refrigerator temperatures (8–10°C) and remain clear without clouding or deposition of solids. As a result, trait-modified oils are easily pumped, poured and handled in food service operations. In addition, trait-modified oils can be conveniently packaged in drums or in 35 pound jugs whereas solid shortenings are often packaged in cubes with a plastic liner to protect the product. The liner must be disposed of and can fall into a deep fat fryer which is a problem for the operator in that the oil becomes contaminated and must be replaced.

3.7 FOOD USES OF TRAIT-MODIFIED OILS

The food service industry is a major outlet for trait-modified oils. Several large companies have switched to low linolenic soybean oil, including Kentucky Fried Chicken and Kellogg. Frito Lay is a major user of mid oleic sunflower oil to prepare snack foods. Canola oil has found widespread acceptance in the food service industry and is readily available in chain stores catering to the food service industry and household consumers. Typically, these products are packaged in 35 lb jugs and sell for $25–40.

Trait-modified oils have been investigated in numerous frying studies in the laboratory. They include high oleic corn oil (Warner and Knowlton 1997), low and ultralow soybean (Erickson and Frey 1994; Gerde et al. 2007; Warner and Gupta 2003), high oleic sunflower (Normand et al. 2006), mid oleic sunflower (Warner and Moser 2009), high oleic soybean (Warner and Gupta 2005), and high oleic canola (Matthäus et al. 2009). An extensive study comparing the performance of a number of trait-modified oils with that of a high trans hydrogenated shortening has been reported (www.frytest.com). The general conclusion from these studies is that trait-modified oils perform well in heavy duty frying operations. High stability oils are needed in numerous food applications including those where a long shelf-life is needed. Traditionally these oils have been prepared by a combination of hydrogenation and fractionation and as a result are high in trans acids (Gooding 1972; Lampert 1999;).

Applications and functions of trait-modified oils where high stability is needed are shown in Table 3.6. Applications include nut roasting where the oil serves as a heat transfer medium and gloss enhancement, and extends the shelf-life of the product. Oils can also serve as a carrier for minor components including flavors, colors, vitamins, spices, and nutraceuticals. Other applications and functions include acting as a moisture barrier in foods (dried fruits, croutons, cereals, pizza crusts, crackers). Oil prevents either wanted moisture from leaving or unwanted moisture from entering the food. Oils also function as lubricating/releasing agents in baking operations without viscosity increases, polymerization or off flavor development. Oils also serve as antidusting/anticaking agents in dried mixes and fruits. As discussed previously, high stability oils function well in products where a long shelf-life is needed, i.e., the military and export market, as well as low volume, high margin specialty foods.

Erickson and Frey (1994) reported studies on the use of trait-modified oils as spray oils for snack crackers. High oleic sunflower and low linolenic soybean oils were compared against hydrogenated canola and

Table 3.6 High Stability Oil Functionality Requirements Per Application

Application	Function(s)
Nut roasting (premium nutmeats)	Heat transfer, gloss enhancement and shelf-life extension because some oil enters the nutmeat during roasting
Carrier of flavors, colors, fragrances, vitamins, spices, and pharmaceuticals	Mixes with fat soluble ingredients, remains neutral for long periods of time and, in many cases, enhances natural flavors
Moisture barrier for foods such as dried fruits, croutons, confections, RTE cereals, frozen pizza crust, and crackers	Prevents wanted moisture from leaving or unwanted moisture from entering foods. For example, keeps cereals crisp in milk
Viscosity modifier for candy centers and coatings	Compatible with other fats and oils, allowing for improved and consistent yields and extended shelf-life
Gloss enhancer for foods such as nuts, fruits, confections, licorice, and gummies	Adheres to food surfaces in a thin layer for improved appearance, adhesion, and protection
Lubricating/releasing agent for pan and mold release. Convenient form for easy dosing	Lubricates without viscosity increase, polymerization or off flavor development. Can improve line efficiencies
Antidusting/anticaking agent for seasonings, spices, mixes, and dried fruits	Controls dust, prevents clumping and sticking of particulates, especially those with surface sugars
Frying of products requiring extended shelf-life	Extreme stability for military use, export and low volume, high margin specialty foods

Source: Lampert (1999). Reproduced with permission of AOCS Press.

soybean oils. After 5 months storage at 72°F and 95°F, the trait-modified oils held up in sensory tests as well as the hydrogenated oils or, in some cases, were superior. Similar results were obtained in tests where French fries were evaluated. Fry lives of the trait-modified oils were comparable to the hydrogenated oils and the French fries were of good quality. Erickson and Frey also reported that high oleic sunflower oil containing mono- and diglycerides perform well in nondairy creamer applications where, typically, these products need a long shelf-life.

Warner and Fehr (2008) have described studies on the use of mid oleic/ultra low linolenic acid soybean oils as a frying medium for tortilla chips and were compared to hydrogenated soybean oil, ultra low linolenic acid soybean oil, and soybean oil. Their results indicated that the mid oleic/ultra low linolenic acid oil had superior fry life and the tortilla chips were oxidatively more stable than with the control oils.

Trait-modified oils perform well in baking applications/recipes calling for vegetable oil which typically include muffins, biscuits, cookies, and buns. When blended with emulsifiers, trait-modified oils would be an excellent choice for bread shortening or for pizza dough. Household cake and brownie mixes provide other baking applications for trait-modified oils.

Pan and griddle frying are popular food preparation methods in the home, in restaurants, and in food service operations. Factors to be considered in choosing a fat or oil for these uses include trans/saturated fat, cholesterol, physical properties (liquid or solid), flavor, operational factors, cost, oxidative stability, and availability. Traditionally, commodity oils, palm oil, and meat fats have been used in these applications. All have disadvantages, with trans and saturated fats most prominent. The introduction of trait-modified oils represents a new approach to alleviate many of these drawbacks. Limited published data suggest that trait-modified oils provide a new approach to many food service applications. Since all are trans and cholesterol free and the canola and sunflower oils offer a low saturated acid option, they are particularly attractive. A major issue is that of higher costs and availability. Kiatsrichart et al. (2003) compared the stability of NuSun (mid oleic sunflower oil) with canola oil in the pan frying of hash brown potatoes and concluded there was little difference in fried food flavor or oxidative stability between the two oils.

Snack foods including potato chips, corn chips, tortilla chips, extruded snacks, popcorn, and roasted nuts have high oil content (24–40%) and as such must be stable for a long shelf-life. Traditionally, these products have been prepared with commodity oils which may or may not be hydrogenated. (Dellaporta 2008). Trait-modified oils (canola, sunflower) have been shown to be excellent alternatives because they are trans free, low in saturated fat and have excellent oxidative stability and flavor profiles (Warner and Gupta 2005). Baked snack crackers have been reformulated with unhydrogenated liquid commodity soybean oil. Thus, trait-modified oils should be superior in these products (Klemann 2005).

Liquid, pourable, creamy shortenings have been popular for many years and are made by blending liquid oil with completely hydrogenated oil to form a beta stable suspension. The liquid oil may or may not be hydrogenated (Andre and Going 1957; Herzig 1996; Holman and Quimby 1950; Mitchell 1950; Widlak 2001).

Fluid shortenings with a hydrogenated base contain up to 30% trans acids. However, by substituting a trait-modified oil, a trans free solution is provided.

3.8 FOOD USES OF HIGH SATURATE SOYBEAN OILS

Soybean oils high in stearic acid have been in development for a number of years (Graef et al. 1985; Kridl 2007). Compared to commodity soybean oil containing about 4% stearic acid, the high stearic acid lines may contain up to 33% (List et al. 1996). Other lines have been developed with both high palmitic and stearic acids (Fehr and Hammond 1996, 1998). The triglyceride structure of these oils includes the symmetrical types where the saturated acids, palmitic and stearic, occupy the outer 1, 3 positions and the unsaturated acids, oleic, linoleic and linolenic, occupy the middle or 2 position in the molecule. As such, the melting points of these oils are too low for use in margarine/spreads and shortenings. In order to utilize the high saturate oils in these applications, hardstock (i.e., completely hydrogenated soybean or cottonseed oil) can be added to give solid fat and melting point requirements. Other components serving this purpose include palm oil, an interesterified palm/hardstock blend, or soybean oil/hardstock blends. Several laboratory studies have shown that chemical interesterification of high stearic or high palmitic raises the melting points and solid fat levels for use in soft margarines and spreads (Kok et al. 1999; List et al. 1996, 1997, 2000a, 2001).

Chrysam and Pelloso (2000) describe in detail other potential food uses for high saturate soybean oils. They include edible emulsions high in fat such as spreads, leavened baked goods, dairy products, and cheeses. Other uses include frozen desserts (ice cream, sherbets, milk shakes), peanut butter, salad dressings, and mayonnaise. High saturate oils may find uses in baked goods (cakes, bread, rolls, pastries, cookies, and biscuits). These authors point out that high stearic oils may be useful in flavor, nutrient, drug or functional additive delivery systems.

3.9 TRAIT-MODIFIED OILS IN ZERO TRANS SPREADS AND SHORTENINGS

Margarines, spreads, and shortenings contain liquid oil (50–70%) as a component (List et al. 2000b). The most common oils include commodity oils like soybean, corn, cottonseed, olive, canola, and sunflower. Recent trends in the margarine/spread market include heart healthy formulations with low trans and saturated acid contents as well as the addition of plant sterols (List et al. 2007). Many all purpose household as well as food service baking shortenings have been reformulated to zero trans and reduced saturated fat contents. Trait-modified oils offer opportunities to meet enhanced nutritional needs in these products. The high oleic canola and mid/high oleic sunflower as well as a high oleic low saturate soybean oil, which are now commercialized (Wilkes 2008), are particularly well suited for low trans/saturated fat products (Orthoefer 2005).

3.10 CONCLUSION

Although trait-modified oils supply only about 12% of US consumption, health and nutrition issues will increase the supply and demand for these oils. Many of the trait-modified crops are grown under contract with farmers who receive a premium (40–50 cents/bushel) over commodity crops. In addition, costs are incurred with identity preservation in grain handling and processing facilities. As a result, trait-modified oils command a higher price in the marketplace than commodity oils. Retail prices for these oils often are in the 80–90 cents per pound range compared to 50–60 cents for commodity oils. Typically, 3–4 years are required to increase production from 100 million pounds/year to 1 billion pounds/year. However, as previously discussed, the use of trait-modified soybean, canola, and sunflower oils has grown over the period 2005–2014, much of which has been driven by trans fat labeling regulations and the trend away from heavily hydrogenated frying oils to liquid oils. Thus, a bright future exists for trait-modified oils and their growth will provide consumers with a wide variety of edible oils and foods.

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4 Development of Trait-Modified Soybean Oil

Joseph W. Burton

USDA ARS NCSU (Retired), Raleigh, NC, USA

Oil produced from soybean (*Glycine max* L. merr.) has a long history of use in various industrial products and in food preparation. As its use as an edible oil increased in the mid-20th century, problems with stability in storage and extended usage led to research which implicated autooxidation of polyunsaturated fatty acids, linoleic and linolenic acids as the primary source of poor flavors (Kalbrener et al. 1974). Early investigations into the genetic control of oil biosynthesis in soybean seeds led to conclusions that fatty acid composition in soybean was quantitatively inherited, i.e., determined by the action of many genes with small effects (Howell et al. 1972; White et al. 1961). In addition, Wilson et al. (1976) determined that oleic acid concentration was inversely related to linolenic acid concentration in soybean seeds. Given these findings, it was concluded that plant breeding methodology could be used to genetically reduce linolenic acid in soybean seeds.

C.A. Brim began a program of recurrent selection for increased oleic acid in a soybean population. He began with two plant introductions, PI90406 and PI92567, as his genetic source of improved oil quality genes. Both had above average oleic acid and below average linolenic

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acid. He used indirect selection for low linolenic acid by selecting directly for higher oleic acid (Wilson et al. 1981). This seemed the best approach at the time because there appeared to be more genetic variation for oleic acid concentration in his breeding materials. The method was successful. After four cycles of selection, oleic acid had increased from 24.8% to 33% in the selection population and linolenic acid had decreased from 7.8% to 6.3%. Successful reverse selection after cycle 6 showed that significant genetic variation remained in the population and after nine cycles of selection, oleic acid had increased to 41.6% and linolenic acid had decreased to 5.9% (Carver et al. 1986). Two genotypes, N78-2245 and N79-2077, generated in that selection experiment were of particular importance. N78-2245 had 51.0% oleic acid and 4.2% linolenic acid (Wilson et al. 1981), and N79-2077 had a reduced palmitic acid concentration of 6.1% (Burton et al. 1994).

4.1 DEVELOPMENT OF LOW LINOLENIC SOYBEANS

Research over the past 35 years has resulted in the development of soybean varieties that have less than 3% linolenic acid. These include Monsanto's VISTIVE varieties, Pioneer brand low linolenic soybeans and Iowa State University's ultra low (less than 1%) linolenic soybeans (United Soybean Board). These are being used by the oil processing industry to produce soybean oils that are more stable in extended frying applications and that have a longer shelf-life.

The genesis of these current varieties began with the early soybean lines, N78-2245, developed through genetic recombination and selection (Wilson et al. 1981), A5 (Hammond and Fehr 1983) and C1640 (Wilcox et al. 1984) developed by mutagenesis with ethyl methane sulfanate (EMS). The linolenic concentration of these materials ranged from 3.2% to 5.1% of the oil. Then a fourth source of low linolenic acid was discovered in the USDA germplasm collection, PI361,088B, with 3.8% linolenic acid (Rennie et al. 1988). Later, Rahman et al. (1994), using x-ray mutagenesis, produced M-5, a line with 5.1% linolenic acid.

Most of the above were inherited as single gene mutations. Occasionally mating them with other low linolenic mutants, PI123440

(Wilson and Burton 1986) and A23 (Fehr et al. 1992), resulted in soybeans that had lower linolenic acid than either parent: N85-1726 with 3.5% (Burton et al. 1989) and A16 with 2.2% (Fehr et al. 1992). This suggested that at least two genes were involved in reduced linolenic acid. Another reduced linolenic, A89-144003, germplasm developed by EMS mutagenesis, produced a 1% linolenic acid soybean, A29, when combined with the other two genes from A5 and A23 (Ross et al. 2000).

Molecular analysis has determined that at least three of the genes involved in the above low linolenic soybeans are homologs of the omega 3 fatty acid desaturase gene (FAD3), first found in Arabidopsis (Bilyeu et al. 2003). In soybean, three independent FAD3 loci, GmFAD3A, GmFAD3B, and GmFAD3C, have been identified. Deleterious mutations of these three genes have been derived through EMS mutagenesis, e.g., A5, A23, and A89-144003 (Bilyeu et al. 2005). Other deleterious FAD3 mutants have been identified in the USDA soybean germplasm collection using modern genomic analysis and are presumably natural mutations, e.g., PI123,440 and PI361,088B. Combinations of two FAD3 mutant alleles produce low linolenic (<3% 18:3) soybean varieties and combinations of all three FAD3 mutant alleles produce ultra low linolenic soybeans (1% 18:3) (Bilyeu et al. 2005). The ultra low linolenic type of soybean has also been produced by molecular gene silencing techniques that suppress the activities of all FAD3 genes in the genome (Flores et al. 2008; Kinney 1995). The ultra low linolenic trait produced by siRNA gene silencing is stable and heritable (Flores et al. 2008).

Trait stability over environments is a difficulty that often plagues soybean varieties with altered seed composition. Linolenic acid has been shown to decline in high temperature environments and increase in low temperature environments (Wolf et al. 1982). Of the unsaturated fatty acids, linolenic acid appears to be more environmentally stable than either oleic or linoleic acid. Carver et al. (1986) found linoleic acid to be more stable than oleic acid over 2 years and four locations each year, and the lower linolenic materials appeared to be more stable than the higher oleic materials. Schnebly and Fehr (1993) showed that production year significantly affected the linolenic concentration but not differences in planting date and the difference among years for the soybeans with less than 3% linolenic acid was only 0.3 percentage points.

More recently, the ultra low linolenic soybeans have been found to be even more stable over environments. Thus farm production of low linolenic soybeans can proceed with little concern that the trait will be lost by the time the crop is harvested.

4.2 DEVELOPMENT OF HIGH POLYUNSATURATE SOYBEANS

Increasing levels of polyunsaturated fatty acids in soybean oil can improve the oil's usefulness for industrial applications, e.g., inks, lubricants, and drying oils. Omega 3 (n-3) fatty acids, which are made in the human body from linolenic acid (18:3 n-3), are believed to reduce the risk for cardiovascular disease (Damude and Kinney 2008). Thus, increasing linolenic acid in soybean oil would make it a healthier oil in human diets. The instability of such an oil might make soybeans with that trait more desirable for soy foods, such as tofu (Burton et al. 2004) or as an "additive to fortify traditional oils" (United Soybean Board).

A mutant with increased linolenic acid, B739, was produced in Japan by x-ray mutagenesis of the cultivar "Bay" (Rahman et al. 1994). A single recessive gene mutation was found to increase linolenic acid from 9% in Bay to 13% in B739. Another genetic source of increased linolenic acid was identified in *Glycine soja*, the wild soybean (Pantalone et al. 1997). This genotype, designated PI424031, has 15% linolenic acid and was shown to produce useful genetic variation for breeding when hybridized with *G. max* (Rebetzke et al. 1997).

All of the above are in very early stages of development in soybean. There are currently no high linolenic soybean cultivars in farm production in the USA.

4.3 DEVELOPMENT OF HIGH MONOUNSATURATED SOYBEANS

Increasing the monounsaturated oleic acid concentration along with a decrease in linolenic acid provides an additional increase in the oxidative stability of soybean oil. Linoleic acid is derived from oleic acid by a desaturation reaction catalyzed by a membrane associated omega 6 desaturase. In soybean, there are two genes that encode this desaturase, FAD2-1 and FAD2-2 (Heppard et al. 1996). FAD2-1 is specifically expressed in seeds and there are two isoforms of this FAD2-1 in the soybean genome, FAD2-1A and FAD2-1B (Tang et al. 2005). Silencing these genes results in seed oil with 85% oleic acid (Kinney 1997). Soybean cultivars with FAD2-1 genes silenced and high oleic acid (>80%)are now available. Continued selection and genetic recombination of higher oleic materials developed by recurrent selection (Carver et al. 1986) led to the development of a soybean line, N98-4445A, with 56% oleic acid (Burton et al. 2006). Subsequent breeding with this line and a sister line, N00-3350, has shown the high oleic trait to be quantitatively inherited with at least six genes involved (Monteros et al. 2008). A mapping study of gene loci associated with this trait found mutations in FAD2-1A, FAD2-1B, and FAD2-2B genes not to be involved in producing increased oleic acid in the N98-4445A soybean (Bachlava et al. 2008).

A mutant, M23, developed by x-ray irradiation of the cultivar Bay has 50% oleic acid (Takagi and Rahman 1996). It is now known that the elevated oleic acid is due to a chromosome deletion that includes the FAD2-1A gene (Anai et al. 2008). Loss of the FAD2-1A function resulted in reduced omega 6 desaturase activity, less lenoleic biosynthesis, and a surplus of oleic acid. Mutations in both FAD2-1A and FAD2-1B have now been discovered (Kristin Bilyeu, Research geneticist, USDA ARS, personal communication), and combining the two in a soybean line produces high oleic acid (>70%) (Grover Shannon, Professor of Plant Sciences, University of Missouri). Molecular markers for these two mutants have also been developed which will expedite transfer of these mutants to high yielding soybean cultivars. The two FAD2-1 mutant alleles along with one or more of the FAD3 mutant alleles will provide high oleic, low linolenic soybeans that are not transgenic.

Until now, a problem with farm production of elevated oleic soybeans has been environmental stability. While oleic acid of M23 was more environmentally stable than N98-4445A, the oleic levels of both were dependent on where the two were grown (Lee et al. 2009). Over 16 environments, M23 ranged from 43% to 58% and N98-4445A ranged from 38% to 69%. It is believed that the FAD2-1A, FAD2-1B double mutant soybeans will be more environmentally stable, but this will not be known until they are grown over an array of environments. It is known that high temperatures affect the gene expression of FAD2-1A, making it less stable than FAD2-1B (Tang et al. 2005). This may affect the ultimate level of oleic acid in the seeds. But if the range of environmental instability is at levels greater than 70%, then soybean oil produced from these materials should remain at the quality needed for frying and other food uses.

4.4 LOW SATURATES

Of the two saturated fatty acids in soybean lipids, palmitic and stearic, palmitic has received the most attention. An EMS induced mutant line, C1726, derived from the cultivar "Century," reduced palmitic acid from 11.0% to 8.6% (Erickson et al. 1988; Wilcox and Cavins 1990). Another mutant line, N79-2077-12, discovered in a recurrent selection population, reduced palmitic acid to 6.0% (Burton et al. 1994). The mutant genes in these two breeding lines were independent and when combined through breeding, worked additively to reduce palmitic to 4.4% (Wilcox et al. 1994). Another germplasm developed by mutagenesis with N-nitrose amine N-methyl urea has approximately 7.0% palmitic acid and when combined with C1726, produces progeny with 4% palmitic acid (Fehr et al. 1991). Molecular genetic research has shown that palmitic acid can be reduced in soybean by silencing GmFATB genes that encode the palmitoyl-ACP thiosterase (Kinney 1997). This is an enzyme in the biosynthesis pathway of palmitic acid that esterifies 16:0 ACP to 16:0 CoA after it is released from plastids into the cytoplasm. It is now known that N79-2077-12 and A22 carry FATB mutant genes. There are four FATB genes expressed in soybean. The gene designated GmFAB1a is deleted in N70-2077-12 and defective in A22 (Cardinal et al. 2007). The genetic change in C1726 that lowers palmitic acid is not known at this time.

When palmitic acid is reduced through breeding with either of the above lines, lower palmitic materials have reduced yields (Cardinal et al. 2008; Ndzana et al. 1994; Rebetzke et al. 1998a). This may be due to deleterious genes that are linked to the FATB1a gene locus, or it may be that decreasing saturated fatty acids can change the plant's physiology in a negative way, perhaps by affecting cell membrane lipids and membrane permeability. It is also known that there are gene modifiers which are heritable and can affect the concentration of palmitic acid in seed oil (Rebetzke et al. 1998b).

Palmitic acid content in soybean seeds is affected by the environment in which the seeds develop. This effect is thought to be primarily due to temperature. Warmer temperatures during the seed filling period tend to increase palmitic acid in seed oil (Rebetzke et al. 2001).

4.5 HIGH SATURATES

Both stearic and palmitic acids can be elevated through breeding. Germplasms with increased stearic and/or increased palmitic acid are available. But medical research indicates that unlike palmitic acid, stearic acid is not associated with elevated cholesterol and increased risk for coronary heart disease (United Soybean Board). Thus, high stearic soybean oil may be a good alternative to partially hydrogenated oil for products that require saturated fat, e.g., margarine and shortening.

There are several sources of elevated stearic acid in soybean. Four of these range in stearic acid concentration from 9% to 30% (Wilson et al. 2002). Three of these were derived by chemical mutagenesis and one is naturally occurring. All are mutants at a gene locus designated FAS, and are presumably allelic to each other. Two other genotypes, M25 (21% stearic) and KK-2 (7% stearic), were derived by seed irradiation of the cultivar Bay. When these two mutants are combined in a single line, the stearic acid content is 25% (Rahman et al. 1997). This is evidence that the two mutants are at two different gene loci.

A stearoyl-acyl carrier protein desaturase is known to be important in the biosynthesis of stearic acid. Genes that encode these enzymes are designated SCAPD (Zhang et al. 2008). There are at least three SCAPD genes in soybean. Two, SCAPD-A and SCAPD-B, have not been found to be associated with elevated stearic acid (Byfield et al. 2006). Sequence variations in the third gene, SCAPD-C, have been found in elevated stearic soybeans (Zhang et al. 2008). Thus, FAS and SCAPD-C are identical.

Several soybean lines have been developed with elevated palmitic acid using chemical mutagenesis. One of these, C1727, has 17% palmitic acid (Wilcox and Cavins 1990). A mutation in the gene that encodes a 3-β-acyl-ACP synthase II, designated KASII, has been identified as the probable source of elevated palmitic acid. Aghoram et al. (2006) identified two KASII genes, GmKASIIA and GmKASIIB, in soybean. The gene sequence for KASIIB was found to be identical in both C1727 and a normal palmitic variety. But KASIIA had a single amino acid substitution in C1727 which prevented translation of that gene. A molecular marker specific for this gene has been developed which could aid in breeding with C1727. Other elevated palmitic soybean lines, A21, A24, and A27, have between 17% and 15% palmitic acid (Wilson et al. 2002). Specifically, how these affect the biosynthesis of palmitic acid is not known. But it is known that mutant genes in A22 and A24 are independent of each other and the KASIIB gene in C1727 (Schnebly et al. 1994). Breeding experiments with A21 and A24 showed elevated palmitic acid to be associated with lower yields and lower seed protein and oil concentrations (Hartmann et al. 1996). This will likely make it difficult to breed a high yielding cultivar with increased palmitic acid.

4.6 CONCLUSION

Soybean oil, as a commodity, will remain plentiful as long as demand for soy protein remains high. Thus the possibility of developing soybean varieties that have the above oil compositions should increase the versatility of soybean oil. If yield potential of these soybean varieties is equivalent to the yields of standard varieties, there should be no impediment to farm production. So far, the oil type that appears to be the most difficult for yield increase is low palmitic acid but additional research and new genetics may solve that problem. Of course, identity preservation of a variety with a particular altered oil would be an issue but that is a problem that has been addressed in other commodities and is already being managed with low linolenic soybeans.

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5 Applications of Trait Enhanced Soybean Oils

Richard S. Wilkes[1] and Neal A. Bringe[2]

[1] Wilkes Food Technology Consulting, Township of Washington, NJ, USA
[2] White Wave Foods, Bloomfield, CO, USA

Trait enhanced soybean oils are valued for their improvements in functionality, enrichment in healthful and sustainable long chain omega 3 fatty acids or for their enrichment in oleic acid and reduction in polyunsaturated fatty acids that resists oxidation. Heat and oxidative stability are required by the food service and processed food industries for a range of applications including frying (e.g., potatoes, meat and poultry), snack foods (e.g., potato chips, corn chips), baked goods including donuts and in other applications where the use of oils that resist oxidation is required (e.g., spray oils on crackers and snack foods). With the mandatory labeling of trans fats on all processed food in the United States beginning in January 2005, and subsequent bans on the use of trans fats in food service products sold in several states and municipalities, the food industry has rapidly adopted nutritionally improved oils that provide the required functional properties. Despite the use of several technologies to meet the initial needs, food companies, ingredient companies, and oil processors continue to desire additional trait enhanced oils to meet ongoing food company needs. This chapter

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focuses on the application of emerging trait enhanced oils that provide enhanced functional and nutritional benefits.

5.1 TRANS FAT REPLACEMENT OILS

In the past, animal fats such as beef tallow were used (49.8% saturated fat, 109 mg cholesterol/100 g; USDA). However, concerns about cholesterol (oxides) in foods fried in animal based fats created a market for high stability vegetable oils (Haumann 1987). Hydrogenated vegetable oils filled this need until concerns about trans fat levels created a demand for alternatives (Skeaff 2009). The need to transition away from hydrogenated oils was anticipated in the 1990s (Erickson and Frey 1994; Miller 1993). The generation of trans fats in many foods was a result of the partial hydrogenation of oils, including soybean oil, to provide required resistance to oxidation, fry stability and solid fat functionality for a range of foods, including baking. In considering trans fat replacements, food companies have had to evaluate options against a range of criteria including functionality, performance in actual restaurant or food processing operations, availability, and cost. Several oils used initially included liquid oils from canola, corn, and soybean, but these oils often do not provide the same level of oxidative stability as partially hydrogenated soybean oil. Another product launched at the time of mandatory trans fat labeling was a trait-modified soybean oil in which the linolenic (18:3n3) content was reduced from 8% to 3%.

Although these oils showed some improvement in oxidative stability, they did not match the stability of partially hydrogenated oil. As a result, there has been an increase in blending oils to provide needed properties, or the inclusion of a small amount of fully hydrogenated oil to provide both oxidative and solid fat functionality.

Another approach has been the incorporation of palm oil (rich in 44% palmitic acid). Palmitic acid is associated with impairing satiety (Maljaars et al. 2009), decreasing insulin sensitivity (Benoit et al. 2009; Xiao et al. 2006), enhancing fat accumulation in muscle tissue (Crunkhorn et al. 2007; Garcia-Escobar et al. 2008), and raising low density lipoprotein (LDL) cholesterol (Mensink et al. 2003). It is in the best interest of food providers to use healthful fats to maintain the popularity of tasty and convenient foods.

After several years of tests and considerations by the soybean industry, the leading fatty acid targets were summarized by the United Soybean Board (sixth edition of Soybean Oil Innovations, 2009) as follows:

- reduced saturates (maximum of 7%)
- reduced linolenic acid (maximum of 3%)
- increased oleic acid (minimum of 50%).

Recognizing that many replacement oils were not ideal, plant breeders and molecular biologists worked together with food scientists to create new oilseeds having improved compositions for a range of applications, including frying and baking. High oleic soybean oils are entering the market to meet this need (Wilkes 2008).

5.2 HIGH OLEIC OILS

A range of oils with increased levels of oleic acid have been introduced in the last 5 years or are in final development prior to commercialization. They offer food processors several benefits including increased oxidative stability, operational efficiency, and reduced levels of saturated fat. These are primarily from canola, sunflower, and soybean seeds. Depending on the seed developer, they can vary in levels of oleic acid. High oleic canola, for instance, can range from 65% to over 80%. Table 5.1 provides a comparison of the estimated fatty acid compositions of several of these oils.

5.2.1 High Oleic Oils: Impact on Fry Stability and Shelf-Life

The use of high oleic oils should improve fry stability and shelf-life of foods fried in these oils due to the reduction in highly oxidative polyunsaturated fatty acids. In an experiment described by Wilkes and Jurado (2010), the impact of several modified soybean and canola oils on the

Table 5.1 Estimated Fatty Acid Compositions of Trait-Modified Soybean Oil and Commodity Available Vegetable Oils

Oil	16:0	18:0	18:1	18:2	18:3	Sats	MUFA	PUFA
Canola[1]								
High oleic	3.4	2.5	77.8	9.8	2.6	7.7	79.9	12.4
Commodity	3.6	1.5	61.6	21.7	9.6	6.3	62.4	31.3
Soybean								
High oleic[2]	6.0	5.0	80.0	2.0	3.0	1.0	80.0	5.0
High oleic low saturate[3]	3.0	3.0	74.0	15.0	3.0	6.0	74.0	18.0
Commodity[1]	11.0	4.0	23.0	53.0	8.0	15.0	23.0	61.0
Sunflower								
Mid oleic[4]	4.4	3.7	58.0	32.0	0.2	8.1	58.0	32.2
High oleic[5]	2.9	3.9	89.1	3.7	0.0	6.8	89.1	3.7
Commodity[1]	6.8	4.7	18.6	68.2	0.5	11.5	18.6	68.7

Adapted from:

[1] Gunstone (2002)

[2] DuPont Pioneer

[3] Monsanto

[4] Kiatsrichart et al. (2003)

[5] Warner and Knowlton (1997).

MUFA, monounsaturated fatty acid; PUFA, polyunsaturated fatty acid; Sats, saturates.

fry life of French fries was reviewed. In this experiment, low linolenic soybean oil, partially hydrogenated soybean oil, high oleic canola oil, and low saturated fat/high oleic soybean oil were tested using commercial scale fry equipment to evaluate the impact of each oil on fry life using French fries as the vehicle. Oil was heated to 350°F and held for 8 hours per day. For six of those hours, French fries, obtained through a local food service distributor, were continuously fried. The frying lasted a total of 15 days or 120 hours of continuous frying. The fryers and oils were cooled down each night during the duration of testing. Each morning, the oil was filtered and topped up with fresh oil if needed. In order to determine fry life, an EBRO food oil meter was used to determine the amount of total polar material (TPM) in the oil. TPM is a measurement of the breakdown of the oil and can indicate the required time replenishment of the oil. A target of 24% TPM was used to determine the end of the fry life for each oil evaluated. This is consistent with the maximum level of TPM allowed in fry oil for several European countries. Figure 5.1 shows the results, demonstrating increased stability for both high oleic canola oil and low saturate/high oleic soybean oil being more similar to partially hydrogenated soybean oil which was extensively used prior to mandatory trans fat labeling. No differences in oil replenishment, both daily and cumulative, were observed. Total fat content of the French fries also showed no differences.

In a follow-up study, Wilkes and Jurado (2012) also reported the impact of low saturate/high oleic soybean oil on the fry stability and shelf-life of tortilla chips. Tortilla chips were fried continuously for 8 hours per day at 350°F for a total continuous frying time of over

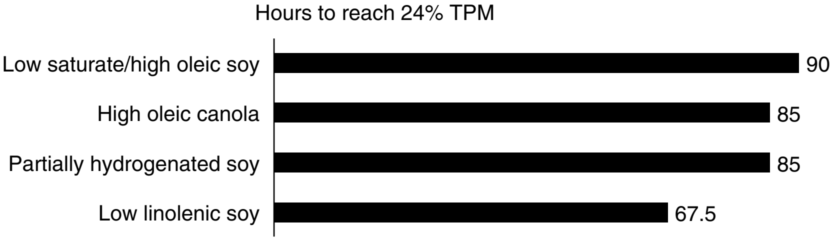

Figure 5.1 Fry life results demonstrating hours of use prior to reaching 24% total polar material (TPM). Source: Wilkes and Jurado (2010).

170 hours. Each batch of tortilla chips was fried for 1 minute 15 seconds to reach the desired color and texture. During the first day of frying, tortilla chips were sampled and packaged in metallized pouches and vacuum sealed for use in a shelf-life study. All samples were held at ambient temperature (72°F) and stored for 4 months for analytical and sensory evaluation. Oils tested in this study included a control oil comprising 85% corn oil, 10% mid oleic sunflower oil and 5% high oleic canola oil (corn oil blend); low saturate/high oleic soybean oil, and another low saturate/high oleic soybean oil that contained 190 ppm tert-butylhydroquinone (TBHQ), a common antioxidant used in fry oils. Fry life results indicating the hours to reach 24% TPM as measured by the EBRO food oil meter are shown in Figure 5.2. The results show that the low saturate/high oleic soybean oil exhibited significantly improved fry life compared to the corn oil blend. The incorporation of TBHQ had minimal impact on fry life in this study.

To assess the impact of the fry oils on shelf-life, the tortilla chips were analyzed for hexanal content and TOTOX (2 x Peroxide Value + Anisidine Value) monthly throughout the storage study. Figure 5.3 shows the hexanal analysis results. Figure 5.4 shows the TOTOX results. Hexanal can be an indicator of off flavor in oils (Warner et al. 1978) and in food (Chitsamphandhvej et al. 2008). Both analyses had good agreement and show that throughout the study, the low saturate/high oleic soybean oil samples exhibited low development of off flavors and oxidation. At 3 months, the off flavors and oxidation in the corn oil

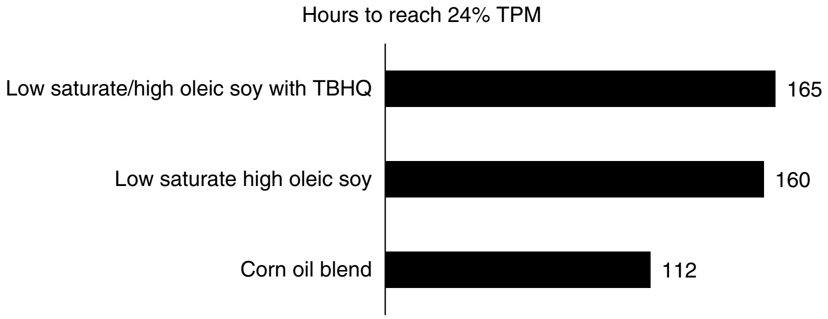

Figure 5.2 Fry life results demonstrating hours to reach 24% total polar material (TPM) for tortilla chip frying. TBHQ, tert-butylhydroquinone. Source: Wilkes and Jurado (2012).

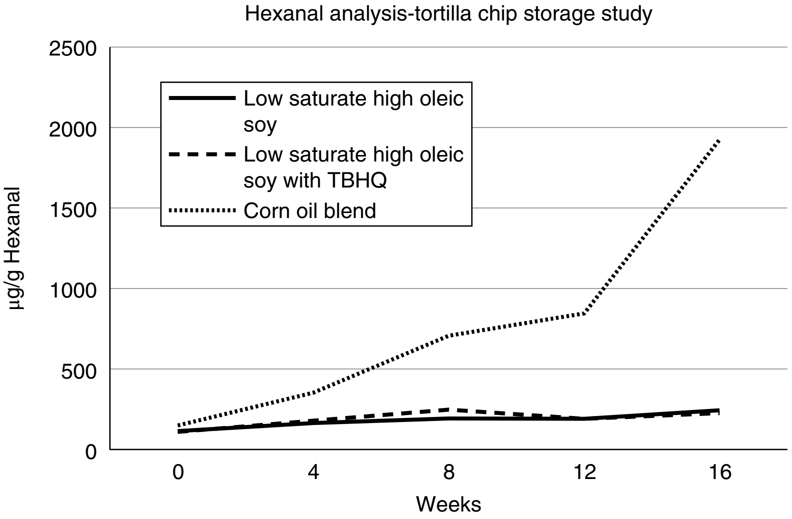

Figure 5.3 Results of hexanal analysis of tortilla chips throughout shelf-life. TBHQ, tert-butylhydroquinone. Source: Wilkes and Jurado (2012).

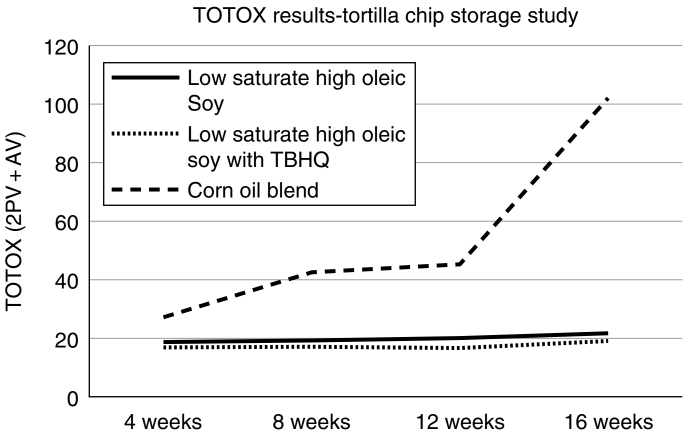

Figure 5.4 Results of TOTOX analysis of tortilla chips throughout shelf-life. TBHQ, tert-butylhydroquinone. Source: Wilkes and Jurado (2012).

blend sample significantly increased whereas the levels in both low saturate/high oleic soybean oil samples remained stable. Using a typical 3 month shelf-life for packaged tortilla chips, use of low saturate/high oleic soybean oil could provide for an extended shelf-life compared to corn oil blends used today.

5.2.2 Flavor Benefits of High Oleic Oils

Much effort was made to understand the basis for fried flavors, especially fried potato flavor, that can be used to create modified oils with optimum properties. While sulfur amino acids of potato proteins create boiled potato notes by producing methanethiol (Wagner and Grosch 1997), oxidation products of linoleic acid such as 2,4 decadienal are the primary volatile compounds responsible for fried flavor (Choe and Min 2007; Wagner and Grosch 1997; Warner et al. 2001). Competing negative odors were identified as fruity (nonanal) and plastic ((E)-2-undecenal) notes derived from oxidation of oleic acid (Neff et al. 2000; Warner et al. 2001); crayon-like odors derived from hydrogenated fat; stale odors derived from oxidation of linoleic acid (e.g., hexanal, pentanal); and fishy odors derived from oxidation of linolenic acid (Warner and Mounts 1993). The intensity of fried flavor was high when fried in oil with 63% linoleic for a short time, as expected, because linoleic is a source of fried food flavor. However, after 17 hours of frying, negative odors counterbalanced positive odors from fries produced in the high linoleic oil reducing the level of fried flavor. This issue was resolved by using trait enhanced oil (23% linoleic) where the fried flavor was improved over the same frying time (Warner and Knowlton 1997).

One can also go too far in lowering the linoleic acid content of frying oils. Some high stability oils (>80% oleic, <6% linoleic) are expected to produce only low levels of deep fried potato taste (Warner et al. 2001). This expectation is consistent with the finding that 78% oleic oil with 12% linoleic acid produced lower intensity fried food flavor and lower overall flavor quality compared to 68% oleic oil containing 23% linoleic acid when potato chips were fried in 12-hour oil and aged 6 months and when French fries were fried in 30-hour oil (Warner et al. 1997). Any issues with low linoleic oils can be resolved by blending or by using a high oleic oil with more linoleic acid. Blending high oleic soybean oil with only 1.3% linoleic with low linolenic soybean oil (55% linoleic) improved flavor quality of potato chips significantly from an hedonic score of 4 to a score of 6 on a scale of 1 (bad) to 10 (excellent) after 5 weeks of storage (Warner and Gupta 2005).

5.2.3 Fried Food Quality

To assess the impact on quality of fried foods, French fries have been selected as an example. Potatoes are a popular vegetable, with consumption in the US of 126 lbs/capita in 2007 (USDA 2012). Where consumption is high, they make an important dietary contribution of carbohydrate, phenolic compounds, ascorbic acid, and potassium (Camire 2009). Boiling potatoes results in greater losses of vitamins and potassium than baking, roasting, and frying (Camire 2009). French fries have a significantly lower glycemic response than boiled potatoes possibly from the formation of amylose-lipid complexes (Leeman et al. 2008). Whether fried on a grill, in a skillet, or in a deep fat fryer, the formation of crisp textures and fried tastes in potatoes improves the eating experience. The kind of oil used influences the quality of fried potatoes.

The uptake of too much oil in French fries can make them less appealing because they are less firm and crisp and contain high fat levels. An increase in oil uptake occurs with an increase in oxidative degradation because the higher viscosity of deteriorated oil makes it more difficult to drain from the food (Bouchon 2009; Dana and Saguy 2006; Tseng 1996). A trend of increased uptake of fresh liquid vegetable oils with increased viscosity is caused by lower levels of unsaturation in their fatty acid structure (Kim et al. 2010; Kita et al. 2007). Oil viscosity increases with decreased levels of polyunsaturated fatty acids and increased levels of oleic acid (Kim et al. 2010). Logically, the viscosity raising and firmness lowering effect of increasing oleic acid composition of oil on fries can be controlled by lowering the saturated fatty acids in a trait enhanced soybean oil, resulting in an oil with limited viscosity that is more stable to increases in viscosity during frying. A less desirable alternative is to use highly saturated frying fats where solid fat contributes to product firmness (Kita et al. 2005).

5.2.4 Nutrition Benefits of High Oleic Oils

Most frying and cracker applications benefit from the stability of high oleic oils which eliminate requirement for the solid fat of palm oil which is rich in palmitic acid (44% of total fatty acids).

The fatty acid compositions of high stability oils influence their potentially beneficial effect on LDL cholesterol (Figure 5.5) and triglycerides (Figure 5.6) as a replacement for partially hydrogenated soybean oil (Mensink et al. 2003). The 75% oleic canola and 74% oleic

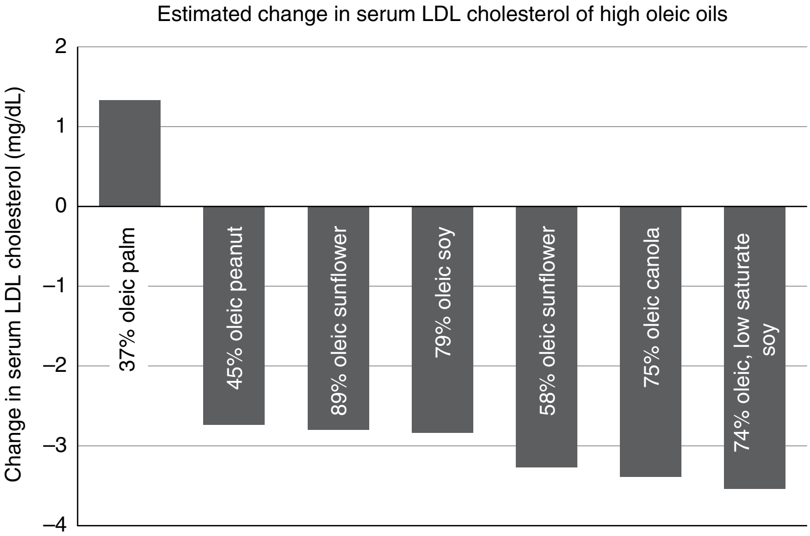

Figure 5.5 Change in serum LDL cholesterol for several high oleic oils. Adapted from Mensink et al. (2003). Reproduced with permission of the American Journal of Clinical Nutrition.

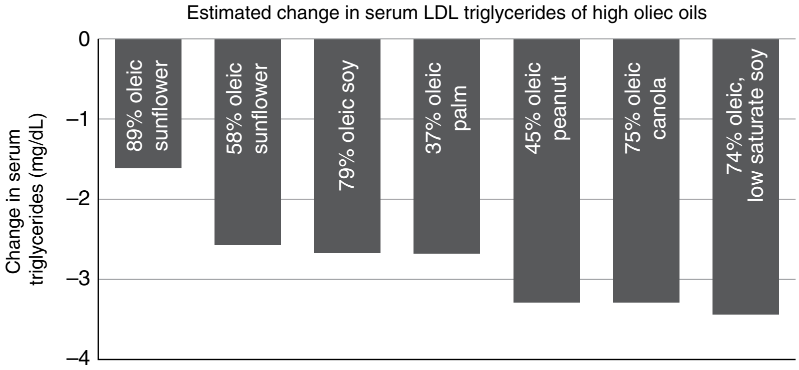

Figure 5.6 Change in serum triglyceride levels for several high oleic oils. Adapted from Mensink et al. (2003). Reproduced with permission of the American Journal of Clinical Nutrition.

soybean oils are good replacements and 37% oleic palm oil is a poor replacement to produce an improved effect on serum lipids. The level of essential linoleic acid contributes to the healthful compositions of the high oleic oils and is also important for fried potato taste. These factors were considered in creating trait enhanced soybeans.

Another benefit of the replacement of partially hydrogenated soybean oil with trait enhanced and unmodifed vegetable oil in foods is that they can provide significantly reduced cardiovascular risk factors (Mozaffarian and Clarke 2009). The healthfulness of fried potatoes has been improved in recent years by removing hydrogenated fat. There are additional components of fried potatoes that are formed during frying that counterbalance the healthful properties of potato nutrients. These reaction products are called advanced glycation (or glycoxidation) endproducts (AGEs) and the one that has received most attention is acrylamide. Fried potato products are a significant source of AGEs in the diet, with commercial potato chips having 865 kU/serving compared with, for example, only 40 kU/serving for popcorn with butter (Goldberg et al. 2004). French fries and potato chips are among the top contributors of acrylamide in the US diet (Federal Register, August 26, 2009). The potential significance of consuming fried potatoes was shown in a pilot clinical study where chronic ingestion of potato chips caused significant increases in oxidized LDL and C-reactive protein, indicating an overall proinflammatory state in humans (Naruszewicz et al. 2009).

Overall, there are compelling data that AGEs are a source of dietary oxidants contributing to aging (Vlassara et al. 2009). Among the strategies for reducing the formation of AGEs and acrylamide is limiting the exposure of foods to oxidized oil (Arribas-Lorenzo et al. 2009; Chuang et al. 2005). Thus the oxidative instability of highly polyunsaturated oils that contributes to AGE formation in fried potato applications can be reduced by using high oleic soybean oils. The long frying life of high oleic soybean oils and improved value as biodiesel raw material (Bringe 2005; Graef et al. 2009) may enable food service operations to discard frying oil at a lower TPM value, facilitating fried potatoes with lower AGEs.

A dietary intake assessment was conducted where replacement of current oils by low saturate high oleic soybean oil for current oils in quick service restaurants was modeled for saturated fat intake by average quick service restaurant (QSR) consumers. In this model, an

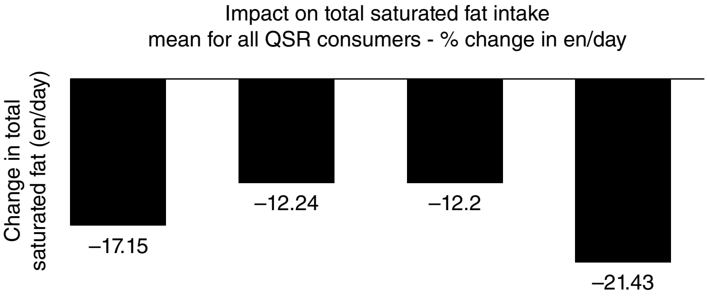

Figure 5.7 Impact of substitution of low saturate high oleic soybean oil on the diet of quick service restaurant (QSR) consumers. Source: Wilkes and Jurado (2012).

oil blend containing 70% soybean oil, 9% canola oil, 4% partially hydrogenated cottonseed oil, 12% corn oil, and 4% olive oil was used as the current blend based on publicly disclosed oil blends, industry displacement data, and consumption patterns based on the National Health and Nutrition Examination Study (NHANES). The results in Figure 5.7 demonstrate the potential to reduce the intake of saturated fat among average QSR customers if the oil is replaced with a low saturate high oleic soybean oil. This change is driven primarily by the reduction in palmitic acid (Wilkes and Jurado 2012).

5.3 LONG CHAIN OMEGA 3 BENEFITS AND CONSUMPTION

The health benefits of long chain omega 3 polyunsaturated fats, also known as omega 3 fatty acids, have been widely reported in the scientific literature (Albert et al. 2002; GISSI-Provenzione Investigators 1999; Leaf et al. 2003). Consumers have developed increased awareness of the benefits of omega 3 fatty acids which has translated into increased consumption, resulting in the growth of dietary supplements in addition to other sources of omega 3 fatty acids. US NHANES data, however, continue to demonstrate that most Americans do not meet the recommended intake of long chain fatty acids (National Center for Health Statistics 2011). Several health focused organizations, including the American Heart Association and the Academy for Nutrition and

Dietetics, have recommended increased consumption of long chain omega 3 fatty acids. Today, most sources of long chain omega 3 fatty acids are from fatty fish (e.g., mackerel, herring, salmon) or supplements. The use of fish oil in formulated food products has met with mixed success due to flavor and shelf-life concerns. The 2010 Dietary Guidelines for Americans Committee report concluded that consumption of two 4 oz servings of fatty fish per week, contributing 250 mg/day of long chain omega 3 fatty acids, is associated with reduced cardiac mortality from coronary heart disease or sudden death in persons with or without cardiovascular disease (USDA HHS 2010). The Committee also reported that there is little ALA (the omega 3 most commonly found in plant sources including soybean and canola) conversion to more desirable eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), reinforcing the need to increase seafood sources of EPA and DHA into the diet, unless plant derived sources of EPA and DHA can be developed.

5.3.1 Modified Plant Sources of Long Chain Omega 3

Stearidonic acid (18:4n3) (SDA) is an intermediate product in the conversion of ALA to EPA and is the desaturation product of ALA. The conversion from ALA to SDA occurs via the rate limiting enzymatic activity of Δ6 desaturase. However, most ALA appears to undergo oxidation before conversion to SDA can take place (Whelan 2009). When SDA enters the metabolic pathway, no conversion via Δ6 desaturase is needed, essentially acting as a "pro-EPA" fatty acid that is rapidly converted to EPA (Whelan 2009). SDA has better oxidative stability than the more highly saturated omega 3 fatty acids, EPA and DHA, due to a lower number of double bonds. Soybeans have been successfully modified to produce SDA, which can be found in other sources including echium and primrose. These soybeans may contain 18–30% SDA.

One advantage of modifying soybeans to contain SDA is that soybeans have inherent antioxidant protection systems such as encapsulated oil bodies, inherent antioxidants and control of prooxidative metals that can protect fatty acids from oxidation. Lipids in oilseeds are often packaged in physical structures known as oil bodies, which are naturally antioxidative. Gray et al. (2010) found that the oxidative stability of oil bodies

Table 5.2 Estimated Fatty Acid Composition of Stearidonic Enhanced Soybean Oil

Fatty acid	Weight %
Palmitic	12.2
Stearic	4.2
Oleic	15.9
Linoleic	24.5
γ-Linolenic (n-6)	7.2
α-Linolenic (n-3)	10.8
Stearidonic (n-3)	23.7

Source: Vazquez et al. (2012). Reproduced with permission of Springer.

was much greater over time than extracted oil and emulsified oil. Based on analysis, oil from SDA enhanced soybeans contained 1100 µg/g of total tocopherols, a natural antioxidant. In comparison, primrose, flaxseed, and menhaden oils contained 341, 150, and 48 µg/g total tocopherols (Akoh and Vazquez 2011, unpublished data). The estimated fatty acid composition of SDA soybean oil is listed in Table 5.2. In addition to SDA, it has been reported that work continues on a modified canola seed enhanced with both EPA and DHA that may be commercialized at the end of the current decade (Watson 2011).

5.3.2 Nutrition Benefits of SDA Soybeans

The nutritional benefits of consuming SDA soybean oil have been reported. Harris et al. (2008) and Lemke et al. (2010) demonstrated the beneficial impact of consuming SDA soybean oil as part of a diet. These studies demonstrated significant increases in red blood cell EPA content and an increase in the omega 3 index, an emerging marker for coronary heart disease risk. Lemke et al. (2010) published the results of a large scale randomized, placebo controlled, double blind multicenter clinical study in which a total of 252 overweight subjects were randomly assigned to one of three treatments for a total of 12 weeks: 1 g/d encapsulated soybean oil plus 14.7 g/d liquid soybean oil to be mixed in food (control group); 1 g/d encapsulated EPA plus 14.7 g/d liquid soybean oil (EPA group); and 1 g/d encapsulated soybean oil plus 14.7 g/d liquid SDA enriched soybean oil (20% SDA content) providing 4.2 g/d SDA

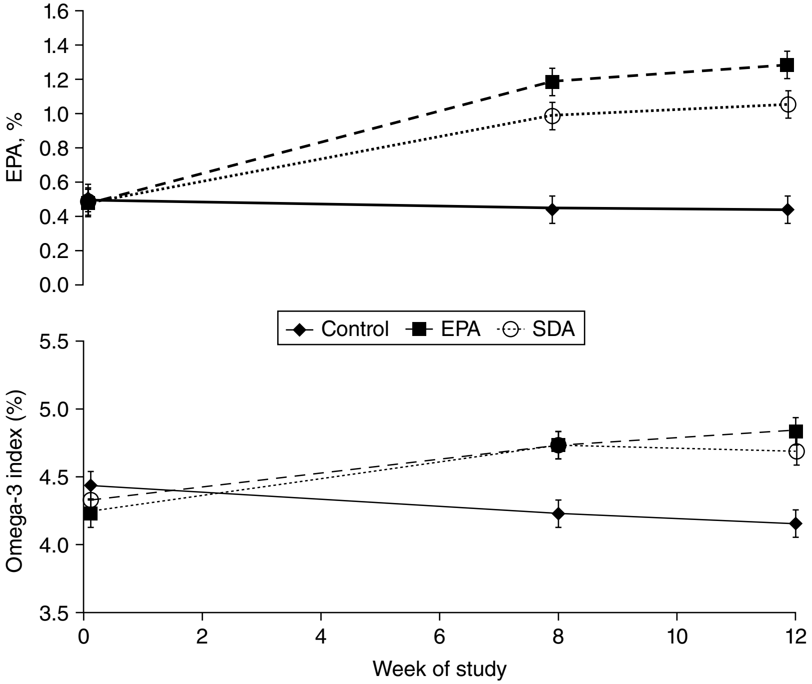

Figure 5.8 (Mean ± SE) omega 3 index and percentage of eicosapentaenoic acid (EPA) in red blood cell membranes measured at weeks 0, 8, and 12 for subjects in the completer population. SDA, stearidonic acid. Source: Lemke et al. (2010). Reproduced with permission of the American Journal of Clinical Nutrition.

(SDA group). All subjects were instructed to replace current oil in their diet with that provided in the study. Despite the baseline omega 3 index (which measures the combination of EPA and DHA) being similar for all treatment groups, after 12 weeks both the omega 3 index and EPA levels in red blood cells significantly increased for both the EPA and SDA groups, whereas there was no change with the control group. As a result, SDA enriched soybean oil increased the omega 3 index by raising erythrocyte EPA concentration. Figure 5.8 shows the results on EPA concentration in red blood cells for this study.

Krul et al. (2012) also evaluated the effect of treatment and dosage of EPA and SDA on red blood cell EPA content. The researchers found that SDA increased the percentage of EPA in red blood cells in a dosage and time dependent manner at intakes as low as 1.3 g/day. The authors also found that the SDA:EPA equivalence ratio was from 2.4 to 6.0

dependent on dose and is consistent with the estimated conversion of SDA to EPA from previously published studies.

5.3.3 Applications of SDA in Food

With improved oxidative stability and flavor, SDA enhanced soybean oil has the potential to be added to a range of foods and maintain flavor and shelf-life, offering more consumers a choice of increasing omega 3 in their diet. Decker et al. (2012) reviewed work in which a range of food prototypes have been developed containing SDA soybean oil and evaluated for shelf-life and consumer acceptance. Based on recommended intakes of long chain polyunsaturated fatty acids and observed conversion rates of SDA to EPA, a target of 375 mg SDA/serving for an individual food product was selected. The range of food prototypes includes cream soups, strawberry flavored dairy beverage, frankfurters, bagels, strawberry yogurt, mixed berry yogurt drink, fruit and nut granola bars, margarine type spreads, and mayonnaise. For each prototype, both a control containing soybean oil and the test prototype containing SDA soybean oil were prepared. In addition to descriptive analysis to determine impact on shelf-life, hedonic testing was conducted to determine consumer acceptance at a point in time when consumers would typically consume each product. Thirty to 60 panelists were recruited and evaluated each control and test prototype using a nine point hedonic scale for overall liking, flavor liking, aroma liking, and texture liking. Each product was presented to the untrained panelists using a sequential monadic protocol. Results were statistically analyzed and demonstrated no difference in hedonic scores between the control and prototypes made with SDA soybean oil. Results for overall liking are presented in Figure 5.9.

Whittinghill and Welsby (2010) also reported the successful incorporation of SDA soybean oil in a range of bakery applications, either directly into the formulation or through formulation of a shortening. In one example, apple cinnamon baked cereal bars were prepared contining 6% SDA soybean oil and manufactured using a standard industrial process. Consumer acceptance testing demonstrated no significant differences.

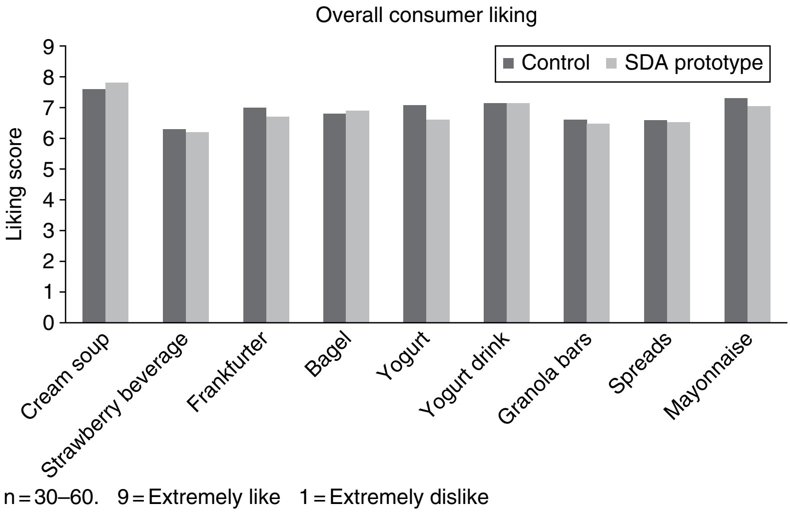

Figure 5.9 Summary of overall consumer acceptance testing of stearidonic acid (SDA) soybean oil in a range of food products. Each product was evaluated on a hedonic scale from 9 = extremely like to 1 = extremely dislike. Source: Decker et al. (2012). Reproduced with permission of the American Journal of Clinical Nutrition.

5.4 FUTURE RESEARCH NEEDS FOR TRAIT-MODIFIED OILS

There is a need for more published research on the use of high oleic soybean oils for frying (e.g., chicken and fish), in spray applications (crackers) and in blends for spreads and bakery products where benefits are expected. There is a growing amount of research on the health properties of fried foods. Some significant benefits of frying over other methods of cooking were discovered, such as reduced levels of heterocyclic amines (HCAs) in cooked chicken (Liao et al. 2010). More research is needed to evaluate the value of foods in the context of the other foods consumed at the same time (e.g., bean dip, humus, salsa, and cheese consumed with snacks and the fruits, vegetables and beverages consumed with main meal items). Not only does fat and fat-containing food improve the palatability of a meal, but fat also can have positive effects on meal nutrition and vice versa. For example, fats and fat-containing foods improve the bioavailability of nutrients in vegetables such as carotenoids (Brown et al. 2004; Unlu et al. 2005);

marinades reduce the formation of HCAs in fried meat and fish (Gibis 2007; Iwasaki 2010); flavonoid-rich foods protect lipids from oxidation in the stomach (Kanner 2007) and LDL from glycation reactions in the blood (Wu et al. 2009); and the fat component of food can positively impact the effect of food on beneficial gut microflora (Mandalari et al. 2008). This type of research can promote practical perspectives that ultimately help people gain the most benefits from foods and meals prepared with trait enhanced soybean oils.

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6 Canola Oil: New Versions

Thomas G. Patterson

Dow AgroSciences LLC, Zionsville Rd Indianapolis, IN, USA

Determining what is "new" about canola oil left the author with a bit of discomfort. First, new is a constantly changing attribute, and what may be perceived as new today (or at least from the author's viewpoint) may be "routine" to someone else, or outdated within a few years. Canola as it will be defined in this chapter is already a relatively new crop and commodity when compared to more traditional oilseeds or grain crops that have been cultivated by humans for thousands of years. It is the belief of this author that what makes canola new is a unique intersection of technology with a crop species. Canola owes its existence to developments in analytical chemistry, and some of the new and exciting developments arise from the application of molecular biology. Rapid changes in molecular genetics and plant breeding, supported by new analytical technology, have made what was once considered novel almost routine practice. With that mindset, we will examine some of the new developments in canola, canola oil, and the impact of modern science on their continued development.

Trait-Modified Oils in Foods, First Edition. Edited by Frank T. Orthoefer and Gary R. List.

6.1 WHAT IS CANOLA?

The name “canola” is an interesting example of how a trademark becomes synonymous with a product: a crawler tractor is a “Cat,” a paper copy is a “Xerox,” and an internet search is a “Google.” Rather than having any botanical significance, the name “canola” derives from a trademark registered to the Canola Council of Canada, and is an contraction of *Can*adian and “ola” (www.canolacouncil.org/ind_overview.aspx). Canola oil is more accurately described as a low erucic acid rapeseed oil, sometimes abbreviated as LEAR. In Canada, canola is described both by the LEAR trait and a reduced glucosinolate level of <30 μmoles per gram. Combined, a low erucic acid, low glucosinolate rapeseed is also described as “double zero” or “00” rapeseed.

6.2 BOTANICAL ORIGINS OF CANOLA

Rapeseed actually describes several species of Brassica that can be grown for oil production. *Brassica juncea*, or Indian mustard, is produced both as a confectionary mustard crop as well as an oilseed crop. *Brassica rapa* (also known as *Brassica campestris*), or turnip rape, is adapted to colder climates with short growing seasons. *Brassica carinata*, or Ethiopian mustard, is a highly drought tolerant species that can be grown as either a leafy vegetable or an oilseed crop. *Brassica napus*, or Swede rape, is the species that is now described as canola. The Brassica species are related to each other genetically due to interspecific hybridization, with genomes being shared between some of the species. Table 6.1 shows the genetic relationship between the oilseed Brassica species.

Confusion can quickly arise as to what is canola and what is a “canola quality” Brassica. Historically, both *B. rapa* and *B. napus* were used to produce canola oil, although currently the acreage of *B. rapa* in production is in decline. Advances in *B. juncea* breeding have given rise to varieties that also meet the specifications for canola oil. Hence, canola oil should be defined as a Brassica derived oil with an erucic acid content of <2%, and a grain glucosinolate content of <30 μmole/g whole seed. For convenience sake, from this point forward the term

Table 6.1 Comparative Genetic Relationships of the Major Oilseed Brassica Species

Species	Genome	Chromosome number
B. rapa	AA	2n = 20
B. carinata	BBCC	2n = 34
B. juncea	AABB[1]	2n = 36
B. napus	AACC[2]	2n = 38

[1] B genome from *B. nigra*, 2n = 16.
[2] C genome from *B. oleracea* 2n = 18.

"canola" will encompass all low erucic acid, low glucosinolate Brassica oilseeds and the oil produced from them.

To examine new versions of canola oil, it is worth understanding the history and development of what is now modern canola oil, and to provide a context for how it may change with future developments. The history of the development of what is now canola oil is well documented in other sources (Booth and Gunstone 2004; Busch et al. 1994). In studying this fascinating story, a very novel aspect readily becomes apparent, i.e., the development of modern canola into a crop parallels the development of new analytical technologies that made this development possible. Advances in canola breeding were and continue to be dependent on sophisticated chemical analytical technology and, more recently, the new tools of molecular biology. Unlike other major crops such as corn and to some extent soybeans, advancements in canola development likely might not have occurred had new advances in analytical chemistry not been coincident with the plant breeding efforts.

Although canola oil is a 20th century development, rapeseed with erucic acid content of >2% has been cultivated for centuries. Rapeseed was grown as a vegetable crop, and developed as an oilseed crop for both lamp oil and consumption (Booth and Gunstone 2004). Rapeseed oil also found use as an industrial lubricant, which drove the production of this crop in Canada during World War II. After World War II, the market for rapeseed oil collapsed in Canada. A government effort to find a replacement oilseed led to collaborative efforts between Keith Downey, a breeder for Agriculture Canada, and Burton Craig, a biochemist with the National Research Council. Craig acquired a very primitive gas chromatograph, a technology that had only been invented

Table 6.2 World Production of Rapeseed, 2008 (Tonnes)

Region	Grain	Oil
Africa	112,221	38,446
Americas	13,674,235	2,835,844
Asia	19,113,636	7,862,707
Europe	23,339,066	7,234,519
Oceania	1,617,000	200,000

Source: FAO Stat (http://faostat3.fao.org).

in the early 1950s. By synthesizing some new polymers, he developed a liquid phase coating for the solid phase GC packing material that would efficiently separate individual fatty acid methyl esters. Downey developed a technique known as half-seed analysis, where one cotyledon of the canola seed was surgically removed for fatty acid analysis. Craig scaled down the assay for the gas chromatograph to effectively analyze the fatty acid composition of the single half seeds. Through their collaborative efforts, rapid plant breeding progress became possible and the first true breeding LEAR rapeseed lines were produced.

Since the early release of canola varieties, worldwide production has expanded. Table 6.2 shows the geographical distribution of rapeseed production worldwide in 2008. Although some of this production is likely high erucic acid rapeseed, production in the Americas and Europe is almost exclusively low erucic acid lines.

6.3 EXTRACTION AND REFINING OF CANOLA OIL

As with any oilseed crop, the oil must be extracted and refined to remove impurities. Detailed reviews of all aspects of canola oil extraction and refining can be found elsewhere (Booth 2004). A generalized process for oil extraction is shown in the flowchart in Figure 6.1.

Although there can be a number of specific modifications to the general process as outlined, most commercially produced canola oil is manufactured following this scheme. Hexane is the most common solvent utilized in commercial oil extraction, although other organic solvents have been evaluated. In some cases, additional treatments are

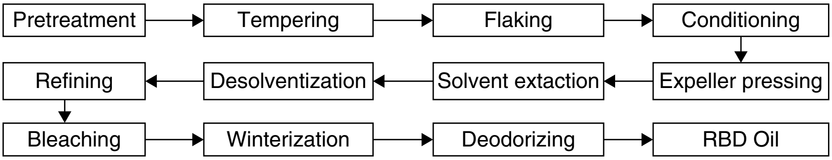

Figure 6.1 Generalized flow chart of canola oil extraction and refining. RBD, refined, bleached, and deodorized.

added such as dehulling prior to expeller pressing. A variant of the production of refined canola oil involves the elimination of the solvent extraction step. These processes can utilize single or double pressing to extract the oil from the presscake. Other variants involve careful temperature regulation of the expeller press to <50°C, producing what is called cold pressed oil. Nonhexane extracted oils are refined and sold as premium oils in some markets.

While the traditional expeller pressing/solvent extraction process accounts for the majority of canola oil produced today, alternative technologies are being explored. Supercritical carbon dioxide has been demonstrated to be an excellent solvent for triglycerides. A combination expeller press with carbon dioxide assisted extraction has been developed and patented (Homann et al. 2006). This technology has been commercialized by Crown Iron Works (www.crowniron.com). A novel process based on the use of a refrigerant based solvent has recently been commercialized (www.foodprocessing-technology.com/projects/bioexxcanolaoilseeda/; Wilde et al. 2002) and is reported to produce both a high quality crude oil and an improved quality oilseed meal. Currently, there is no differentiation in the marketplace between traditionally extracted canola oil and that using the BioExx process.

Other variations in refining processes have been reviewed by Dijkstra (2009). Processes such as enzymatic degumming using phospholipase treatment have been suggested as replacements for traditional alkaline refining methods.

Deodorization by a combination of vacuum-steam stripping at elevated temperatures is critical to the production of high quality, refined, bleached, and deodorized (RBD) canola oil. The deodorization process is critical to producing bland oil with good organoleptic properties by removing free fatty acids, volatile compounds, and other contaminants.

However, studies on the influence of deodorization conditions (Ceriani and Meirelles 2007; Hénon et al. 2001; Lambelet et al. 2003) clearly demonstrate the undesirable formation of trans fatty acids with increasing temperature. Refinery operators need to be aware of the potential for trans fat formation, and the need to carefully control deodorization conditions to maximize oil purity but minimize undesirable trans- at accumulation.

6.4 COMPOSITION OF CANOLA OIL

Describing the composition of any crop of grain immediately runs into several problems. Well known to all plant breeders and production agronomists is the fact that the composition of any seed crop will be influenced by the growing conditions. Weather conditions influence crop quality, which in turn can impact processing conditions at the crushing plant and refinery. An early frost prior to the grain reaching full maturity results in high seed chlorophyll content, which will extract with the oil during crushing and requires modifications to normal processing conditions to remove. Drought, soil fertility, and temperature stress will impact the complex biochemical pathways involved in seed development and oil biosynthesis, resulting in variation in oil composition. While this is well understood and routinely accommodated in the oilseed breeding, production, and processing industry, it complicates the definition of a "typical" canola oil composition. The author once approached a plant breeding colleague with a request for an average grain sample, to which the plant breeder replied "If I ever see one I'll be sure to let you know."

Further complicating this task is the fact that there are now market classes of canola based on different modifications to the standard fatty acid profiles. These have been achieved by traditional plant breeding and selection, mutation breeding, and more recently by transgenic modifications. Finally, within any canola population resides a wealth of genetic variability for compositional factors and minor components in the oils. Unless these are specifically part of a selection process in a breeding population, this variability may carry

Table 6.3 Composition of Grade #1 Canola produced Western Canada in 2009

	% Oil[1]	**% Protein**[2]	**Chlorophyll content (mg/kg)**	**Glucosinolates**[1]
Mean	44.5	19.9	15.4	9.59
Min	37.6	14.7	0.3	5.0
Max	52.5	27.6	57.1	17.6
n	1355			

[1] 8.5% moisture basis.
[2] % N x 6.25, 8.5% moisture basis.
Compiled from Barthet (2009).

through to the final released variety. Thus, while a specific fatty acid profile may be fixed, variation may exist for components like tocopherols and phytosterols.

Focusing on the most recently available production data, the composition of canola grain produced in Western Canada in 2009 is shown in Table 6.3 (Barthet 2009). These data, compiled by the Canadian Grain Commission, show the range of proximate compositions for a crop within a growing season over multiple geographies and canola varieties. The ranges in composition represent the contribution of genetics, geography, and climate to the development of the canola grain and the resulting components.

Table 6.4 shows the average fatty acid composition of regular grade #1 canola produced in Western Canada in 2009. This fatty acid profile represents the current average composition of "regular" canola as of the 2009 growing season. The predominant fatty acids are oleic (62.25%), linoleic (18.81%), and linolenic (10%), with the C18 fatty acids representing 92.82% of the total fatty acid profile.

Specialty canola, while representing increasing market shares of the Canadian grain market, is not tracked as a specific canola class in Canada. The fatty acid profiles of some of the major specialty canola types are shown in Table 6.5. These lines have all been developed by the incorporation of mutant genes in the fatty acid pathway, resulting in reduction in linolenic acid or increases in oleic acid. Since different genes are involved in the formation of linolenic acid and oleic acid, it is possible to combine both types of mutations together to yield the high oleic low linolenic (HOLL) oil profile.

Table 6.4 Average Fatty Acid Profile of Western Canada Grade #1 Canola in 2009

	Fatty acid composition (%)												
	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C20:2	C22:0	C22:1	C24:0	Total saturates
Mean	3.9	0.26	1.76	62.25	18.81	10	0.62	1.24	0.07	0.3	0.01	0.2	6.9

Compiled from Barthet (2009).

Table 6.5 Fatty Acid Compositions of Some Specialty Canola Varieties

				Fatty acid composition (%)											
				C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C20:2	C22:0	C22:1	C24:0	24.1
Low linolenic					1.9	62.1	25.5	2.5	0.7	1.3	0.1	0.4	0.1	0.2	0.2
High oleic					1.8	80.5	7.4	3.4	0.7	1.7	0.1	0.4	0.1	0.3	0.2
High oleic low linolenic	nd	0.1	3.3	0.2	1.7	73.8	15.3	2.6	0.6	1.5	0.1	0.3	0.1	0.2	0.1

Data from Ratnayake and Daun (2006).
nd, not detected; nr, not reported.

Genetically modified oils are actively being researched with the goal of modifying oil properties in novel ways by directed manipulation of the biochemical pathways of oil synthesis. While these approaches are considered novel, at the writing of this chapter they would not be considered "new." The first genetically modified canola oil was reported in 1997 (Neff et al. 1997). Both transgenically produced high stearate (28% C18:0) and high laurate (31.3% C12:0) oil was produced from canola through genetic modifications to the fatty acid biosynthetic pathway (Table 6.6). Knutzon (1999) reported the production of elevated γ-linolenic acid and stearidonic acid (C18:4) in canola half seeds (Table 6.7). Modification of fatty acid pathways to produce the very long chain fatty acids docosahexaenoic acid (DHA, C22:6) and eicosapentaenoic acid (EPA, C20:5) has been discussed by multiple authors as a desirable goal (Damude and Kinney 2007, 2008; Ursin 2003). Although not specifically reported in canola, the production of EPA and DHA has been demonstrated in Arabidopsis (Metz 2007), which is a relative of the Brassica family.

Finally, although not a transgenic line, the development of a canola quality *B. juncea* has been reported by Wijesundera et al. (2008). The fatty acid profile of the canola quality *B. juncea* is shown in Table 6.8, which closely reflects the profile of regular canola (see Table 6.4).

Other than the early high laurate transgenic canola lines, no genetically modified organism (GMO) output traits exist on the market at the time of writing. However, various commercial and academic institutions are actively working on the development of altered oil profiles through genetic engineering. These products will be subject to a regulatory approval process prior to their release into the commercial grain channel, like that for existing herbicide tolerance traits in canola. Although refined oil is thought to be quite "pure" and likely not to be contaminated with either DNA or substantial amounts of protein, Ramazzotti et al. (2008) did demonstrate that residual protein could be detected in refined oils, albeit at very low concentrations. This raises the possibility that a potential allergen could survive the oil refining process and present a potential health concern, however slight. Whether any specific transgenic protein survives the oil refining process will have to be examined on a case by case basis, and be subjected to regulatory scrutiny.

Table 6.6 Representative Fatty Acid Profile of High Stearate and High Laurate Canola

	Fatty acid composition (%)													
	C12:0	**C14:0**	**C16:0**	**C16:1**	**C18:0**	**C18:1**	**C18:2**	**C18:3**	**C20:0**	**C20:1**	**C20:2**	**C22:0**	**C22:1**	**C24:0**
High stearate	0	0.21	3.6	0.2	28	28.8	18.4	17.4	2.2	0.4	nr	0.4	nr	0.4
High laurate	31.3	4.2	3.3	0.2	1.1	35.1	14.6	8.8	0.3	0.7	nr	0.2	nr	0

Data from Neff et al. (1997)
nr, not reported.

Table 6.7 Representative Fatty Acid Profiles from Stearidonic Acid Producing Canola Seeds

	Fatty acid composition (%)												
	C16:0	**C16:1**	**C18:0**	**C18:1**	**C18:2c6,9**	**C18:2c9,12**	**C18:3c6,9,12**	**C18:3c9,12,15**	**C18:4**	**C20:0**	**C20:1**	**C20:2**	**C22:0**
Line 1	6.35	0.84	1.9	4.7	0	14.81	56.73	3.78	6.29	2.12	0.66	0.59	1.04
Line 2	8.92	0.96	1.64	14.61	0	18.69	36.98	7.44	7.43	1.01	0.49	0.49	0.95

Data from Knutzon (1999).

Table 6.8 Average Fatty Acid Profile of Canola Quality *Brassica juncea*

	Fatty acid composition (%)											
	C16:0	**C16:1**	**C18:0**	**C18:1**	**C18:2**	**C18:3**	**C20:0**	**C20:1**	**C20:2**	**C22:0**	**C22:1**	**C24:0**
B. juncea	3.3	nr	2.3	65.2	14.7	12.3	0.7	1.4	nr	0.3	nr	nr

Data from Wijesundera et al. (2008).
nr, not reported.

6.5 MINOR COMPONENTS

In addition to the major triglyceride components of canola oil, a number of important minor compounds are present in refined oil. Tocopherols and phytosterols are two important classes of compounds that contribute to the functionality of the oil.

Tocopherols exist in four different forms. α-Tocopherol is the biologically active form of vitamin E. Three other forms of tocopherol are β-, δ-, and γ-tocopherols. In a study of the genotypic and environmental variability of tocopherols in *B. napus* and *B. juncea*, Richards et al. (2008) found that across the *B. napus* genotypes, total tocopherol content ranged from a high of 820 μg/g oil to a low of 389 μg/g oil. Three tocopherols were detected; α, β, and γ, with β present only at relatively low levels. A wider range of concentrations was measured in the *B. juncea* germplasm, with total tocopherol contents ranging from a high of 928 μg/g oil to a low of 256 μg/g oil. As with *B. napus*, α- and γ-tocopherols were the dominant forms, with low levels of β-tocopherol.

Phytosterols in oils are related to cholesterol that is typical in mammals. However, phytosterols have been shown to have positive health benefits in humans. From that standpoint, the potential of phytosterols as a nutraceutical in oils should be considered. Amar et al. (2008) studied the variation and inheritance of phytosterols in winter rapeseed. Four major phytosterols were determined in this study: sitosterol, campesterol, brassicasterol, and avenasterol. Total phytosterol contents ranged from 2.57 g/kg to 4.15 g/kg. Although not specifically measured in this study, the authors noted that phytosterols exist in both free and esterified forms in the oil. They determined that the variation in phytosterol content in the lines studied was highly heritable, and could be altered through a selected breeding effort.

Crude canola oil contains a complex mixture of chemicals prior to refining. The majority of these compounds are removed during processing. However, some of the compounds potentially have a functional benefits which, if they could be retained in the oil, might have value. One such novel compound was identified by Wakamatsu et al. (2005), and given the common name canolol. The compound, 4-vinyl-2,6-dimethoxyphenol, was shown to be a highly active free radical scavenger, with a strong activity towards alkylhydroperoxides. While very active in the crude oil fraction, this compound was removed during the standard refining process and was not detectable in the deodorized oil. Other novel compounds likely exist in crude canola oil extracts, some of which might have positive benefits from either a functional or nutraceutical perspective. However, alternative oil refining procedures would likely be required to exploit the potential benefits of these compounds.

6.6 OXIDATIVE STABILITY OF CANOLA OIL

The oxidative stability of oils is a primary functional property that greatly impacts the applications of the oil. Oil that is highly susceptible to oxidation may quickly go rancid, generating foul odors or flavors. The susceptibility to oxidation is a complex function of the influences of the fatty acid composition, structure of the triglycerides, and the mixture of minor components in the oil. Further complicating this is the impact of contaminants such as metal ions which can promote oxidation reactions. Similarly, photooxidation can occur due to exposure to light which can in turn catalyze the oxidation reactions.

Choe and Min (2006) discuss in detail the chemistry of oil oxidation reactions and their mechanisms. While this is a complex topic, at the fundamental level oxidation is driven by the exposure of oil to atmospheric oxygen, and catalyzed by heat as well as reactive species such as metal ions. The basic mechanism of autooxidation of oils is described in the following steps.

$$\begin{array}{lll}
\text{Initiation} & RH & \rightarrow R^{\cdot} + H^{\cdot} \\
\text{Propagation} & R^{\cdot} + {}^{3}O_2 & \rightarrow ROO^{\cdot} \\
 & ROO^{\cdot} + RH & \rightarrow ROOH + R^{\cdot} \\
\text{Termination} & ROO^{\cdot} + R^{\cdot} & \rightarrow ROOR \\
 & R^{\cdot} + R^{\cdot} & \rightarrow RR
\end{array}$$

In addition to the formation of lipid hydroperoxides, chain cleavage can occur with oxidation, leading to the formation of short chain aldehydes, carboxylic acids, alcohols, and hydrocarbons.

The relative stability of different fatty acids is a function of the number of double bonds in the fatty acid chain. A fully saturated fatty acid is very resistant to oxidation, while susceptibility to oxidation increases with increasing degrees of unsaturation. In general, the relative susceptibility of the 18 carbon fatty acids to oxidation is C18:0 > C18:2 > C18:3. Although not reported in the literature, one would anticipate a C18:4 fatty acid to be less stable than C18:3. Likewise, long chain polyunsaturated fatty acids (C20:5, C21:6) are well known to be very susceptible to oxidation.

Neff et al. (1997) conducted a detailed analysis of the factors affecting the oxidation of regular canola oil as well as genetically modified high stearic and high lauric oils. They were able to attribute increases in oxidative stability to three factors:

- a reduction in the more susceptible linoleic and linolenic fatty acids with a concomitant increase in the more stable oleic, stearic, and lauric acids
- replacement of linoleic acid at the sn-2 position of the glycerol backbone with oleic acid
- a reduction in the proportion of triglycerides containing linoleic and linolenic acids and an increase in those containing stearic and/or lauric acid with oleic acid.

Comparisons between regular and low linolenic canola oils were performed by Przybylski et al. (1993) and Vaisey-Genser et al. (1994) utilizing accelerated storage conditions combined with chemical and sensory evaluations. Using Schaal oven test methodology with accelerated aging in open containers at 60°C, they were able to show that low linolenic acid canola (2.5% linolenic acid) oil was more stable to oxidation than regular canola oil (12.5% linolenic acid). Total volatile and carbonyl formation was higher from the regular canola oil than from the low linolenic canola oil.

Normand et al. (2001) studied different canola oils and the impact of tocopherols on frying stability using French fries as a test food product. In a direct comparison of regular, low linolenic, high oleic, and high oleic low linolenic canola oils, they determined that while there was no statistically significant difference in the rate of free fatty acid formation between the oils, regular and high oleic low linolenic produced lower overall levels of free fatty acids. Similarly, the accumulation of total polar compounds over the 72 hours frying experiment was higher in the low linolenic and high oleic oils than in the regular and high oleic low linolenic oils. There were differences in total tocopherol contents between the four oils, with the low linolenic oil having 468 µg/g total tocopherol and levels of 565, 601, and 893 µg/g for the regular, high oleic, and high oleic low linolenic oils, respectively. The rate of depletion of tocopherols was faster for the low linolenic and high oleic oils, but slower for the regular and high oleic low linolenic oils. The higher stability of regular canola oil in this study is unexpected, and likely indicated the complex nature of the breakdown of oils due to oxidation as well as the nature of the experimental condition, i.e., frying in this particular study.

The evolution of volatile oxidation products from oils can provide information about the breakdown of oils with heating. Fullana et al. (2004) compared commercial canola oil with olive oils in a study of the evolution of volatile compounds with heating at 240°C and 180°C respectively. In this study, the authors measured significantly higher levels of volatile emission from the canola oil relative to the regular and extra virgin olive oils. They attributed this to the higher levels of linoleic acid in the canola oil relative to olive oil, as well as higher levels of oleic acid in the olive oils. Unfortunately, they did not include a detailed fatty acid profile in this study, and relied on commercial bottled oils for the study.

Studies of the oxidative stability of canola quality *B. juncea* were conducted by Richards et al. (2005) and Wijesundera et al. (2008). Using headspace analysis, the authors compared oils prepared from *B. juncea* and *B. napus* experimental lines. They determined that the oil from *B. juncea* was more stable to oxidation than the equivalent oil extracted from *B. napus*. However, these studies relied on crude hexane extracted oil that was unrefined. Since crude oils may contain other compounds that have significant impact on oxidative stability, it is not known if the differences they measured would be reflected in the final, refined oil produced from the same oils.

An extensive study of conventional and high oleic oils with combinations of antioxidants was undertaken by Merrill et al. (2008). Using the

Oxidative Stability Index (OSI), a series of different commercial oils were studied and the four with the highest OSI 110°C values (high oleic canola, very high oleic canola, safflower, and high oleic sunflower) selected for further study. In this particular study, the authors listed high oleic canola oil as 59.1% oleic acid and 3.5% linolenic acid contents, and very high oleic acid canola oil as 71.3% oleic acid, with 3.9% linolenic acid content. Various combinations of four different antioxidants were evaluated: mixed tocopherols at 200 ppm, rosemary extract at 1000 ppm, ascorbyl palmitate at 1000 ppm, and tert-butylhydroquinone (TBHQ) at 200 ppm. In general, TBHQ had the largest effect on OSI as a single additive for very high oleic canola oil, with only incremental increases in concert with the other antioxidants. Interestingly, TBHQ in conjunction with rosemary extract actually showed a slight reduction in the OSI relative to the effect of TBHQ alone. While this is an interesting model study using the OSI technique, the influence of antioxidants in a more complex frying system could yield different results.

Blending canola oils with other oils is another way to alter the oxidative stability properties of an oil. Farhoosh et al. (2009) studied blends of regular canola oil with palm olein (38.2% palmitic acid, 42.1% oleic acid, and 10.6% linolenic acid), olive oil, and corn oil in binary or tertiary blends. The total polar content of canola oil alone was higher than blended oils, and the lowest with blends of the more highly saturated oils. The OSI was most stable with a blend of canola, palm olein, and olive oils (75:15:10). While blended oils may be useful to achieve improved stability of regular canola oil, they may not represent a significant improvement over more stable versions of canola oil (high oleic low linolenic). Additionally, blending with high saturate oils has the disadvantage of increasing the saturated fat content of foods cooked in these oils.

The stability of the phytosterols in canola oil was studied by Kmiecik et al. (2009). As listed by these authors, canola (rapeseed) is second only to corn oil in phytosterol content. Heating can cause the oxidation of beneficial phytosterols to oxysterols which do not have the beneficial effects of phytosterols, and may actually have negative effects. In this study, BHT, green tea extract, and rosemary extract were examined for their effect on phytosterol oxidation in both a Rancimat® and Oxidograph® oxidation system. Rosemary extract had the strongest impact in reducing the oxidation of phytosterols in this test system. The stability of phytosterols has not been evaluated in other canola oils systems using modified canola oils. This would be a worthwhile future study.

6.7 PERFORMANCE OF CANOLA OIL IN FOOD APPLICATIONS

A benefit of modified canola oils is the gain in stability without the need for partial hydrogenation. As discussed by Orthoefer (2005), high oleic low linolenic canola oil has a number of applications including frying, blended shortenings, spray oil coatings, nutritional bars, and sauces and dressings. The improved oxidative stability of modified canola oils makes them attractive for applications requiring longer shelf-life or improved oxidative stability. Similarly, the ability to offer superior performance without the addition of higher levels of saturated fats is a significant health advantage.

Matthäus (2006) conducted an extensive potato frying study comparing high oleic low linoleic rapeseed oil, partially hydrogenated rapeseed oil, palm olein, and high oleic sunflower oil. Sensory evaluation of the French fries produced in this study indicated that after 60 hours, the fries cooked in partially hydrogenated rapeseed oil and palm olein were unacceptable, while a similar endpoint was reached for high oleic low linolenic rapeseed oils and high oleic sunflower oils after 72 hours. The relative change in oxidative stability of the oils as measured by OSI at 120°C was similar in high oleic sunflower, palm olein and partially hydrogenated rapeseed oil (95.9–98.7% reduction) but only 70.9% in high oleic low linolenic rapeseed oil. When comparing all the results from this study, the high oleic low linolenic rapeseed oil and high oleic sunflower oils had the best overall scores, although not significantly different from partially hydrogenated rapeseed oil. The author concluded that the high oleic low linolenic rapeseed oil had some advantages relative to the overall sensory evaluation of the product, as well as the advantage of being free of trans fatty acids.

The use of high oleic rapeseed oil as a basestock for transesterified fats was examined by Gitlesen et al. (1995). A high oleic (74.4%)

rapeseed oil was transesterified using lipase enzyme treatments to form modified triglycerides. From the initial stearic acid content of 1.9% in the high oleic oil, lipase catalyzed trans esterification with ethyl stearate increased the final concentration to almost 50%. Farmani et al. (2009) studied trans esterified blends of canola oil (61.3% oleic, 7.6% linolenic) with palm olein or fully hydrogenated soybean oils produced by sodium methoxide or lipase catalyzed reactions. They noted that the properties of the final blends differed depending on the method of trans esterification. Producing trans fat free vegetable shortenings clearly can be accomplished using trans fat free solid fat sources and canola oil as a base liquid oil.

6.8 CONCLUSION

Canola oil continues to change with constant advances in plant breeding, genetic engineering technology, and analytical sciences. Next generation oils enriched in long chain omega 3 fatty acids are on the horizon. Other nutritionally desirable traits such as reduced saturated fatty acids and elevated nutraceutical components may also be envisioned for the future. The benefits of modified canola oils are very much a function of the specific end-use application. Oils with elevated long chain omega 3 fatty acids may be desirable in lower temperature applications such as spreads, sauces and bottled oils, but might be too unstable for frying or baking applications. Detailed comparisons of all versions of modern canola oils are difficult to find, so the studies cited here likely do not represent the final authoritative comparison of all oils in all possible applications. Indeed, when entering the realm of blended oils and shortenings, an almost unlimited number of permutations and combinations is possible. Additionally, the increased use of canola/rapeseed oils for biodiesel and biofuel applications raises the possibility that additional variants will be developed for industrial feedstock application. The diversity of oil types and applications for an oilseed crop that only came into existence in the 1950s is a tribute to all the efforts of development scientists who aggressively sought to improve this relatively new crop, and who have succeeded admirably in elevating its status to a major oilseed grown worldwide.

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7 Sunflower Oil: From Mid Oleic, High Oleic, High Stearic to Low Saturate Versions

Larry W. Kleingartner

National Sunflower Association (Retired), Mandan, ND, USA

Historically, sunflower has been known and prized for its high linoleic acid (C18:2) content, largely due to European experience with sunflower oil. In the 1960s vegetable oil was replacing animal fat as a cooking medium in Europe. Medical research identified linoleic acid as one of the primary fatty acids responsible for cholesterol reduction. With that information, the Western European market for high linoleic content oils grew quickly. The best and most available source of high linoleic oil at that time was sunflower oil. Most of the oil was initially imported from Russia (former Soviet Union) and Eastern Europe. Sunflower oil has been considered a "premium" oil in the world market since that time.

The US sunflower industry was born out of this European demand when farmers in the former Soviet Union were not able to consistently supply Western Europe's growing demand. The vast majority of US sunflower production from 1975 to 1983 was exported to Europe. The high linoleic sunflower oil was used in food preparation at home as well as for industrial use in margarine production. The strong European demand for US sunflower seed declined sharply when European oilseed

Trait-Modified Oils in Foods, First Edition. Edited by Frank T. Orthoefer and Gary R. List.

production incentives promoted the production of oilseeds like sunflower in Europe.

Sunflower oil never really got a foothold in the US market as there was already sufficient tonnage of oils with linoleic acid content. Soybean, cotton, and corn oils had a long history of production and availability in the US market. In addition, hydrogenation made all oils equal for frying and industrial food applications. Corn, cotton, and soybean oils were a by-product of other industries and by-products tend to be cheap. Sunflower oil could not compete in this environment.

The major use of high linoleic sunflower oil in the US was for home use and as an ingredient in food products such as margarine. Its limitation was the short shelf-life due to the high linoleic acid content. It was also used as an ingredient in some upscale pet foods and in some cosmetics. Small amounts of linoleic acid in the diet of dogs and cats is reputed to promote glossy fur.

But the oil was not used in frying applications. For that purpose sunflower oil would need to be hydrogenated and soybean oil already dominated that market. Palm oil was also competitive in the frying market as a nonhydrogenated alternative. There simply was not room for another oil. Thus, the majority of US sunflower oil production depended on export markets in Mexico, North Africa, and the Middle East until 2004.

7.1 OLEIC DEVELOPMENTS

Sunflower was likely the first major oilseed to be trait-modified. Genetic work in the former Soviet Union on modifying traditional sunflower oil to high oleic acid (C18:1) dates back to the early 1970s. Russian genetic work resulted in a near “one to one” exchange of linoleic to oleic acid. Total saturates were incidentally lowered by three to four points as well. The market for high oleic sunflower oil in the former Soviet Union did not develop. There was no market incentive at that time to differentiate vegetable oils, much less an oil with an altered fatty acid structure. Another factor may be that high oleic sunflower open pollinated plants did not perform as well agronomically as the traditional high linoleic types.

Work on high oleic sunflower in the US began in the early 1980s. A US patent was issued in 1985 for the high oleic genetic trait and the resulting high oleic oil. Genetic researchers used traditional breeding means to accomplish this work. The commercial introduction of high oleic sunflower oil occurred in the mid to late 1980s.

The genesis of high oleic sunflower opened a new chapter for vegetable oil use and product development in the US. However, high oleic sunflower oil was literally ahead of its time. There was little incentive for a food company to switch from the utility of inexpensive and highly functional partially hydrogenated soybean oil. Nor was the food industry interested in purchasing from a single supplier whose product was under patent. In general, high oleic sunflower oil was used in some baby food formulas and other niche food products. The oil was also used in some industrial applications as a lubricant. In some cases excess oil was exported as sunflower oil to places like Europe and Mexico. It was not unusual for buyers to call their US exporter to question them about this sunflower oil with an unusual fatty acid composition. In a unique case, it was reported that high oleic sunflower oil was blended with olive oil in Europe to extend the volume of more expensive olive oil. This practice was reportedly short-lived even though the mixture was not readily apparent without extended fatty acid analysis.

The production of high oleic sunflower was conducted on a contract basis with farmers, processors, and the end user. The grower contract specified the hybrid seed to be planted, the delivery schedule, and the price. The price was placed at a premium to traditional linoleic sunflower to entice farmers to sign production contracts. Initially, high oleic hybrids were not competitive agronomically. That changed over time and today high oleic sunflower hybrids yield competitively with other sunflower hybrids. The seed and oil were identity preserved throughout the marketing/transportation system. However, demand was relatively small and total acreage did not exceed an estimated 80,000 hectares or 45,000 metric tons of oil production annually.

The high oleic patent provided an early precedent. The patent was challenged in court and upheld. The ruling opened a new arena for patenting genetic events. The vast majority of the genetic events making up modified oils today are patented.

The development of mid oleic sunflower oil occurred with the recommendation of representatives of Frito Lay and Archer Daniels Midland (ADM). They pointed to increased negative public health concerns surrounding trans fats. This development, they reported, could provide excellent market opportunities for naturally stable oils. They further emphasized the limitations of traditional high linoleic sunflower oil in the domestic market. The US sunflower industry recognized the opportunity to use high oleic genetics for this possible development. Additionally, the industry was eager to shift from its heavy dependence on oil exports to a more stable domestic market.

Mid oleic sunflower was developed through conventional breeding practices beginning in 1995. In simple terms, it required the genetic crossing of a high oleic parent line with a high linoleic parent. To differentiate this new mid oleic sunflower from traditional and high oleic, the industry termed it NuSun®.

In 1996 Frito Lay tested sunflower oil that was approximately 70% oleic acid. The oil was used in Frito Lay's test kitchens to produce potato chips and met their initial requirements as a suitable frying oil. A laboratory test of the first experimental hybrid cross was made in 1997. This oil had an oleic level of 61%. Potato cubes were used and comparisons were made with commercially available frying mediums such as partially hydrogenated soybean oil, peanut oil, canola oil, soybean oil, and low linolenic canola oil. A roundtable sensory panel was used. Conclusions are summarized in Table 7.1.

These frying data, early in mid oleic sunflower development, were an important element in convincing the US sunflower hybrid seed industry to continue to invest in this new endeavor. It also provided opportunities to begin discussing the commercialization of this oil with the US food industry.

Limited commercial supplies were available by 2000. Market segregation was necessary from the farm to the processor to the end user. By 2005 a significant shift of acres to mid oleic sunflower had occurred. By 2009 the acreage of traditional high linoleic sunflower was very small. Since mid oleic is now the predominant type of sunflower produced, it no longer requires the same intense identity preservation.

In the 2014 crop year, a high stearic (C18:0) sunflower will be produced in the US and the oil will be available to the US food market

Table 7.1 Frying Stability and Taste Comparisons Between Mid Oleic Sunflower Oil (MOSO), Partially Hydrogenated Soybean Oil (PHSO), Soybean Oil, Canola Oil, Peanut Oil and Low Linolenic Canola Oil (LLCO)

Test comparison	MOSO frying stability	Sensory analysis	Comments
MOSO compared to PHSO	Similar frying stability and heat stability	MOSO more pleasing fried food flavor	MOSO less than 10% saturates compared to PHSO with 17% saturates and 15% trans
MOSO compared to soybean, canola and peanut oil	Superior to soybean and canola oil, equal to peanut oil	MOSO more pleasing food flavor compared to the other three oils	Saturated fats less than peanut and soybean oils
MOSO compared to LLCO	Similar heat and frying stability	MOSO more pleasing fried food flavor	MOSO less darkening in later frying stages

Source: Campbell et al. (1998).

(Ismail and Arafat 2014). The seed was developed in a conventional manner (non-GMO) by the National Council of Scientific Research of Spain and the international seed company Advanta. The planting seed is under US patent. The high stearic/high oleic sunflower will also be grown under contract. The production of seed and oil will be identity preserved throughout the marketing system.

A low saturated sunflower is now available in the US market. This genetic discovery was made by Dow AgroSciences and is patented in the US. This production will also be identity preserved throughout the production and marketing systems.

7.2 FATTY ACID COMPARISONS

Traditional high linoleic sunflower is the most common sunflower type grown around the world. Linoleic values vary between 50% and 70%. Oleic acid levels will decrease or increase depending on the linoleic levels. The linoleic variance is directly related to geography; the more northern latitudes produce the highest linoleic values while the central production regions in Kansas and Colorado produce the lower level.

Table 7.2 Fatty Acid Composition of Five Types of Sunflower Oil

Fatty acid	16:0	18:0	18:1	18:2	18:3	Misc*
Traditional	7.0	4.5	18.7	67.5	0.8	1.5
Mid oleic	4.6	4.2	63	26	0.6	1.6
High oleic	3.5	5.2	82	9.0		0.3
High stearic/high oleic	4	18	70	4		4.0
Low saturate	1.9	0.7	94	2	0.2	1.2

* Misc may contain less than 0.5% of a combination of other fatty acids.

The variance can also be affected by temperature during the late part of the growing season. Table 7.2 summarizes the average fatty acids in five types of sunflower oil.

High oleic sunflower oil can vary in oleic acid from 82% to 94%. However, oleic level variance is more hybrid specific as opposed to environmental factors such as air temperature and latitudes. Most hybrid seed companies have several high oleic hybrids for growers to select from. Grower contracts may have minimum oleic levels. The oleic level in sunflower hybrids has been increasing. A common average oleic level is 82–85%. Most of the high oleic hybrids are agronomically competitive in yield and oil content with other sunflower hybrids. Most high oleic hybrids also have the latest genetics for disease resistance and herbicide tolerance.

Levels of oleic acid in mid oleic sunflower hybrids range from 55% to 75%. The oleic level is directly related to a hybrid's genetic background and is also stable from region to region and year to year. Farmers can choose from nearly 100 different mid oleic hybrids when selecting their planting seed.

Since the transition from high linoleic to mid oleic is complete, farmers do not need to consider the oleic level of a hybrid. The National Sunflower Association has a verification system that seed companies must meet in order for the company to use a NuSun verification logo on the seed bag. Farmers now select the hybrid that has an excellent yield history, high oil content and disease and herbicide resistance. The variation in oleic level from numerous hybrids and fields has resulted in an overall commercial oleic level of 62–64%.

High stearic/high oleic sunflower hybrids have been tested in wide geographic regions including North and South America, India, and

Spain. The fatty acid structure of the hybrid seed remains consistent throughout these diverse producing regions. A stearic acid level of 18% combined with an oleic acid level of 70% makes this oil unique.

The fatty acids in low saturated sunflower hybrids are also stable when grown in different regions. Total saturates under 4% combined with 93–94% oleic acid make this oil unique among vegetable oils.

7.3 UTILIZATION

High oleic sunflower oil has been available since the late 1980s and therefore is the veteran among modified oils. The clear advantage of high oleic sunflower oil is its high stability. The oil can be used in a broad range of food products. Production of snack foods is a common use. Stability in the fryer and on the store shelf are key factors when using high oleic sunflower oil. A snack food company that eliminated hydrogenated oil from their product line well before the trans labeling requirement found that only high oleic sunflower oil provided the necessary shelf-life in their chips. Intense heat during the summer months in the delivery trucks alone was a significant component in reduced shelf-life when using oils with high levels of either linoleic or linolenic acid.

A major customer in Canada is using high oleic sunflower oil in its chain of fast food restaurants. New York Fries has about 200 Canadian outlets and a dozen international outlets. The company is best known for its use of fresh potatoes sliced only on demand and immediately fried in high oleic sunflower oil. The company says that the process "… seals in flavor and nutrients and delivers crispy, lightly golden French fries made fresh for each customer" (Boyce 2009). New York Fries made the switch from hydrogenated oil to high oleic sunflower oil in 2004. The company needed oil that could withstand hours of continuous and intense heat and yet maintain its frying quality and provide neutral flavor. High oleic sunflower oil was able to meet that challenging requirement. It has a bland taste profile not overwhelming the natural taste of the potato and other food products.

High oleic sunflower oil is used as an ingredient in numerous confectionery products and nondairy creamers, as spray oil on dried fruit, crackers and cereals, and as liquid oil for flavors and seasonings. Again, its excellent stability provides real advantages for food manufacturers. Its neutral taste is perfect as a spray oil.

High oleic sunflower oil is used sparingly as bottled oil. It is found only in high end niche markets domestically and overseas. Industrial use is in machinery requiring high heat lubrication. There are uses in the cosmetics industry as well.

NuSun or mid oleic sunflower oil is synonymous with potatoes. The first test of a small volume of mid oleic sunflower oil was conducted by Frito Lay in 1996 in frying potato chips. The experimental test was an overwhelming success. The first production of commercial mid oleic sunflower oil in 2000 was used by Barrel O'Fun®, a regional potato chip company located in Minnesota. Another early user was the manufacturer of Pringles® Chips. These two pioneering customers found the oil to be excellent for frying with a pleasing taste profile. David Chang of Procter & Gamble reported in 2001 that mid oleic sunflower oil had low polar compounds (2.3%). He ventured that this may be the reason why chips fried with mid oleic sunflower oil have a cleaner taste; "It will help easier flavor display in seasoning brands".

The demand was strong for mid oleic sunflower oil as more supplies became commercially available. The makers of Crisco® shortening developed a labeled product free of trans fats using mid oleic sunflower oil as one of the primary ingredients.

The Food and Drug Administration (FDA) announced its intention to require food companies to label trans fatty acids in 2003. That spurred food companies to look for alternatives prior to the labeling requirement becoming law in 2006. Frito Lay was very aggressive in eliminating trans fats from ingredient panels of its many product lines, and made a significant commitment by announcing in May 2006 that it would be switching all of its key potato chip brands to mid oleic sunflower oil. The company had already shifted away from hydrogenated oils several years before. The use of mid oleic sunflower oil, in place of cotton oil, allowed the company to dramatically lower the saturated fat level in such key product lines as Lays® and Ruffles® potato chip brands. The market response sent mid oleic sunflower oil prices sharply higher and a key weather event lowered production. Frito Lay later added corn oil, in addition to sunflower, to the label of Lays and Ruffles. Frito Lay continues to be an important mid oleic sunflower oil customer, using the oil exclusively in its SunChips® line, Natural line of snack products, and Kettle Cooked lines, among others.

Most if not all of the regional potato chip manufacturers have one or more of their product lines using mid oleic sunflower oil exclusively. Others have it listed as an ingredient with another oil choice. The oil is very popular as an ingredient in the production of kettle chips. For example, Old Dutch Foods has a kettle cooked product line called Dutch Crunch™. Its website describes why it uses mid oleic sunflower oil: "We insist on sunflower oil because it has no cholesterol, which is good, and it cooks the chips to a perfect crisp, with no oily taste, which is great" (www.olddutchfoods.com/).

Mid oleic sunflower oil is used as an ingredient in a host of other food products such as a spray oil on dried fruit and cereal. It is an ingredient in instant and frozen potato products. The oil is used in those applications where stability, good shelf-life, and neutral flavor are necessary.

There is no nationally distributed bottled oil brand containing mid oleic sunflower oil. However, there are a number of regionally marketed mid oleic sunflower bottled oils. Although the consumer is often asking for sunflower oil, the bottled oil market has been reluctant to compete directly with the snack food market for supplies.

The restaurant and institutional use of sunflower oil is also small but growing. Research by Tom Tiffany of ADM gave the oil high marks for food service use. "Laboratory frying data suggests that NuSun sunflower oil can be successfully used as a foodservice frying medium, offering good frying stability, while producing fried food products with good taste and good nutritional characteristics" (Tiffany 2001). The oil's high smoke point of 230°C is another positive feature for the food service industry. Restaurants using an oleic type sunflower oil report extended use in their fryers compared to other oils. Chefs also report that the oleic sunflower oils maintain their bland or neutral taste despite repeated use with a variety of foods from fish to potatoes. This was confirmed by work done by Dr Edward Perkins at the University of Illinois comparing mid oleic sunflower oil to creamy liquid frying shortening (104 IV PHSBO) in side by side dining hall fryers. The frying protocol was 24 hours for 8 consecutive days preparing typical dining hall fare. Dr Perkins summarized that mid oleic sunflower oil exhibited less color formation when compared to the shortening. This is an important aspect since many restaurateurs use the oil's color as a deciding point for discarding. Flavor stability and a more pleasing fried food flavor were identified in food prepared in mid oleic sunflower oil. Finally, Dr Perkins noted the vastly superior nutritional profile of mid oleic sunflower oil compared to the partially hydrogenated soybean oil (Perkins 1999).

Another early food service test of mid oleic sunflower oil was conducted in 2002 at Brigham and Women's Hospital which is the Harvard teaching hospital located in Boston, Massachusetts. The mid oleic oil was tested in the hospital's food service kitchens as a possible replacement for partially hydrogenated oil that had a trans content of 15–20%. The kitchen staff were wary about shifting away from a recognized proven oil but the pressure was mounting in the health community that trans fats were a health hazard and institutions such as hospitals must provide an example of pursuing good health.

The National Sunflower Association staff conducted a seminar with kitchen staff and food service leaders at the hospital. The critical taste test passed easily. "They fast realized that this oil could satisfy their food service needs, along with helping the hospital meet recommended health guidelines" (Isaak and Kearny 2002). Brigham and Women's Hospital continued to use the oil in an extended trial. The key piece of information gained by the National Sunflower Association in this test was that mid oleic sunflower oil has significant market potential in a broad range of uses. The oil meets the criteria of a clean and pleasant taste, comparable in frying performance with hydrogenated oil and is competitive in price.

Several major cities have now outlawed the use of hydrogenated oils in restaurants. Market opportunities for mid oleic or high oleic sunflower oils in these venues are very good. The smoke point of sunflower oil is 230°C and the taste is considered to be "clean" or bland, thus allowing the natural taste of the food product to be enjoyed by the consumer. Extending the fry life of either oil can lower overall costs, including the cost of disposal. Traditionally, sunflower oil was not readily available in 35 pound containers for institutional use. That has now changed with the elimination of hydrogenated oils and the sunflower industry switch to more stable oleic sunflower oils.

There are differences in the use of high oleic and mid oleic sunflower oil. Food companies who choose high oleic are looking for enhanced stability and longer shelf-life. Although it also provides good stability, mid oleic sunflower oil has a slight advantage in taste profile. It contains a greater amount of linoleic acid which provides a more pleasing taste and mouth feel. This is the summary of work completed by Dr Kathleen Warner of the USDA ARS National Center for Agricultural Utilization Research. She states (Warner 2006):

> "Therefore, oil with a very high level of oleic acid will be oxidatively stable, but the flavors (waxy and plastic) produced will not be desirable in a fried food. Although linoleic acid does break down, it should not be reduced to extremely low levels in an oil. Some of the decomposition products from linoleic acid such as the dienals contribute to the deep fried flavor. Linoleic acid should be present in the composition at least at the 20% level in order for the decomposition of this fatty acid to produce compounds responsible for the deep fried flavor."

For potato chips and other fried snack items, taste is paramount. Thus, mid oleic sunflower oil with a linoleic level in the high 20s is a preferred oil for the fried snack industry.

High stearic/high oleic sunflower oil has a unique fatty acid structure that will provide food companies with additional stability. The oil will be best adapted for bakery products, chocolates and chocolate fillings, shortenings, margarines, ice cream and in frying situations where very high stability is required. The frying stability index at 110°C is 36 hours for the high stearic/high oleic sunflower compared to 6 hours for the traditional high linoleic sunflower oil (http://nutrisunoil.com). High stearic/high oleic sunflower oil will be an excellent replacement for hydrogenated oil and oils that are highly saturated with palmitic acid. The high stearic sunflower oil will provide companies with a "clean" ingredient label who otherwise might be using hydrogenated oils or tropical oils such as palm, palm kernel or coconut oil.

The low saturated sunflower oil with total saturates under 4% presents many new opportunities to the food industry. The oil can be labeled as "saturated fat free" or having "zero grams of saturated fat" per serving based on US FDA food labeling guidelines. The high oleic content of this oil will provide good stability and will fit well into any of the high oleic uses. It will also make this oil an excellent oleic acid feedstock. This oil will have good consumer appeal as a bottled oil because of the very low level of saturates.

There has been interest in sunflower oil for biodiesel use. This is largely due to the high oil content of sunflower seeds. Oil content in sunflower seed can vary from 38% to 50% depending on weather during the growing season and hybrid genetics. A yield of .897 to 1.12 metric tons of oil per hectare is achievable. All types of sunflower oil are adaptable to biodiesel use but large scale commercial development has not taken place. This is largely due to strong commercial demand from food companies for sunflower oil. The price relationship of sunflower oil compared to conventional soybean is likely to keep sunflower oil out of the energy market. A small processing plant has been constructed with the goal of producing sunflower biodiesel. However, economics have forced that plant's sunflower oil production into the commercial food market. There are a few very small on-farm facilities for producing sunflower oil biodiesel to meet that farm's energy needs. The amount of product going into that use is estimated to be extremely small.

7.4 TOCOPHEROL

The various types of sunflower oil are good sources of vitamin E or α-tocopherol. This is an important nutritional factor recognized in sunflower oil. It is also an important antioxidant providing additional shelf stability. The natural tocopherols were found to keep sunflower oil and stripped soybean oil (natural tocopherols stripped and sunflower tocopherol added) from deteriorating when they were held in lighted storage conditions (Warner 2005). Table 7.3 identifies the tocopherol levels in three types of crude sunflower oil.

The variation in tocopherol levels may be due to geographical variation in the production region which stretches from Manitoba to southern Texas. A tocopherol analysis of refined, bleached, and deodorized mid oleic sunflower oil averaged: α 590 mg/kg; β 30 mg/kg; γ 17.2 mg/kg; and δ 2.28 mg/kg (Warner et al. 2003).

Table 7.3 Range of Tocopherol Levels in Crude Sunflower Oil, NuSun Oil and High Oleic Sunflower Oil

Tocopherols	Traditional sunflower oil (mg/kg)	Mid oleic (NuSun) sunflower oil (mg/kg)	High oleic sunflower oil (mg/kg)
α-Tocopherol	403–935	488–688	400–1090
β-Tocopherol	nd 45	19–52	10.0–35
γ-Tocopherol	nd 34	2.3–19.0	3.0–30
δ-Tocopherol	nd 7	nd 1.6	nd 17
α-Tocotrienol	nd	nd	nd
γ-Tocotrienol	nd	nd	nd
δ-Tocotrienol	nd	nd	nd
Total	440–1520	509–741	450–1120

Source: Warner et al. (2003).
nd, not detectable.

7.5 HEALTH RESEARCH

The role of fatty acids in the diet has long been researched and discussed. Of considerable interest has been heart health and cholesterol reduction. Polyunsaturated fatty acids continue to be associated with cardiovascular health.

Researchers at Penn State University conducted a study to look at possible cholesterol reduction in 31 adults with slightly elevated cholesterol levels. Researchers evaluated the outcomes of healthful diets with either mid oleic sunflower oil or olive oil compared to the average American diet. The olive and sunflower oil diets consisted of total fat at 30% with saturated fat representing 8%. Cholesterol was less than 300 mg. The average American diet contained 34% total fat, 11.2% saturated fat, 14.9% monounsaturated fatty acid, 7.8% polyunsaturated fatty acid and 300 mg cholesterol. Each participant followed each of the three diets for 4 weeks.

The study results showed that the mid oleic sunflower oil diet reduced low density lipoprotein (LDL) cholesterol more than olive oil compared to the average American diet. By comparison, the olive oil diet did not result in significant cholesterol lowering.

The authors pointed out two likely reasons why the mid oleic sunflower oil performed better than olive oil in LDL reduction: (1) the higher level of linoleic acid in the mid oleic sunflower at 32% compared to olive at 14%; and (2) the lower level of saturated fatty acids in mid oleic sunflower oil of 9.6% compared to 14.3% in olive oil (Binkoski et al. 2005).

7.6 CONCLUSION

Sunflower has been manipulated through traditional genetic means to create high oleic, mid oleic, high stearic/high oleic and low saturate sunflower oils. These oils were developed to meet consumer demand which requires greater stability than traditional high linoleic sunflower oil can provide. All of these oils are an excellent substitute for partially hydrogenated oils.

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8 Performance Trials Using Trait-Modified Oils

Roman Przybylski

University of Lethbridge, Department of Chemistry and Biochemistry, University Drive, Lethbridge, Alberta, CA

A variety of modified oils have been created using conventional and transgenic plant breeding methods to replace oils containing trans fatty acids and to lower amounts of saturated fats. The oils usually contain elevated levels of oleic acid and lower amounts of linoleic and linolenic acids. Oils with this composition of fatty acids and lower contribution of polyunsaturated fatty acids (PUFA) offer improved oxidative stability during storage and frying, eliminating hydrogenation. Many new oils are characterized by low contribution of saturated fatty acids, with canola/rapeseed at the lowest level. As frying oils, many provide an extended fry life and produce the desirable flavor of fried products. The oils are also good replacements for the trans containing fats used for baking and margarine applications.

Oils and fats have to offer properties defined by the final application, marketing, and consumer expectations. Nutritional quality is currently attracting the most attention due to the connection of consumed lipids with Western civilization health problems. Research over the past 20 years has shown that consumption of trans and saturated fatty acids raises levels of low density lipoprotein (LDL), the “bad cholesterol” in

Trait-Modified Oils in Foods, First Edition. Edited by Frank T. Orthoefer and Gary R. List.

human blood, and lowers high density lipoprotein (HDL), the "good cholesterol." Consumption of trans and saturated fats has been directly linked to the increased risk of cardiovascular diseases (CVD) and obesity development (Mensink et al. 1992; Mozaffarian et al. 2006). As the media began covering nutritional studies related to lipids involvement in disease development, consumers began paying attention, and the trend toward eating healthier fats progressed.

In January 2006, the Food and Drug Administration in the USA and Health Canada mandated food manufacturers to list the trans fat content separately on the nutrition facts label, mandatory on all packaged food products. This change allows consumers to identify the amount of trans fat in a serving of food. Label regulation allows trans fat content to be declared as "zero" for products containing less than 0.5 g of trans fat per serving. This option offers the food industry good marketing and advertising tools, but it is limited by the availability of trans free fat replacements. This regulation added an additional criterion for fats/oils selection for food applications and was mandated by other jurisdictions around the world.

The physical and chemical properties of lipids are important mainly in food preparation and formulation, including fried products, spreads, cooking and baking fats, frying oils, creams, etc. Chemical traits are important for both nutritional quality and utilization and include:

- fatty acid composition which includes levels of saturated acids, cis and trans monoenes, essential fatty acids, long chain PUFA, and defines the make-up of triacylglycerol molecular species
- the presence and levels of desirable minor constituents such as carotenes, tocopherols, sterols, etc.
- oxidative stability.

Crucial physical properties are the most commonly associated with the composition and structure of triacylglycerols, crystallization, crystal type, melting behavior, and oxidative stability. Frying oils are evaluated and selected by food services on the following criteria: flavor; texture; mouthfeel; stability (i.e., fry life of the oil/fat); cost; availability; and minimizing the content of trans fatty acids (TFA) (Matthäus et al. 2009; Tiffany 2007).

For spreads, shortenings and margarines it is desirable that the solids are in the β'-crystal form and remain in this form until used. These crystal structures are relatively small and can incorporate large volumes of liquid oil, offering a product with a glossy surface, a smooth luster and good lubricity. Initially small β'-crystals have a tendency to grow into needle-like agglomerates that incorporate lower amounts of liquid oil and change to a grainy texture. Commodity oils usually contain mainly C16 and C18 fatty acids which are more likely to be in the β'-crystalline form whilst mono- and polyunsaturated C18 acids are known to crystallize mainly in β-form, which have larger crystals and a grainy texture (Gunstone 1998).

The main source of trans fatty acids in our foods are hydrogenated oils, and partial hydrogenation provides widespread isomerization due to poor control of this process. As alternatives to trans containing fats, oils available on the market offer good natural oxidative stability. Most of these oils contain high amounts of oleic and low amounts of linolenic acid derived from canola/rapeseed, soybean, and sunflower oils naturally low in PUFA such as cottonseed, palm, and peanut. Among these oils, high oleic, low linolenic canola oil (HOLLCO) has received the most attention because of its general availability, functionality, and competitive pricing (Dzisiak 2004). This oil produces excellent quality fried food and offers an extended fry life, and products made with HOLLCO have an improved shelf-life. This oil is easily blended or interesterified to produce basestock to formulate shortenings, margarines, and spreads that meet the specification of fried food producers, food service operators, baker's margarine and shortenings, and is also usable for spreads formulators (Orthoefer 2005).

Implementation of label regulation forced the food industry to adopted trans fat free alternatives of food products utilizing already existing fats and oils. The need for food reformulation often causes an increase in the cost of goods and some processors adopted less than optimal alternatives that impacted negatively on sensory and physical properties, and lowered the nutritional value of their products. There is continued interest in improving the quality of food products by replacement of trans fats with functional fats and oils which improve nutritional properties and create better marketing opportunities.

8.1 FRYING TRAIT OILS/FATS

Frying is one of the oldest methods used for preparing foods and deep fat frying is affected by the most complex degradation process. Today's consumers are becoming more educated about the healthfulness of the food they consume but are unlikely to eliminate fried products from their diets.

The food service industry has always selected frying media based on the criteria discussed above, in which concern about TFA is included. The TFA criterion is in response to health concerns and the fact that many jurisdictions are limiting trans fats in fried products. Frying oil/fat has become a very important aspect of fried food as perceived by customers and operators of frying facilities. During frying, most foods take up considerable amounts of oil which usually determines the quality of the food (Table 8.1). The fatty acid composition of fried food is closer to the composition of the oil used for frying than to the original product (Sanchez-Muniz et al. 1992). Further, degradation products formed in frying oil are transferred to fried food and many of them have negative effects on the human digestive tract (Billek 2000). Therefore, the oxidative stability of frying oil should be one of the main selection criteria to provide fried food with proper nutritional quality.

Table 8.1 The Amount of Lipids in Raw and Fried Products

	Amount of lipids (%)	
Food	**Before frying**[1]	**After frying**
Chicken	3.9	9.9
Fish	1.2	13.1
Potato chips	0.1	35–40
French fries	0.1	10–15
Donuts	5.2	22
Sardines	10.0	35
Fatty acid changes in sardines fried in olive/sunflower oils (%)		
SAT	42.0	20.6/17.7
MUFA	27.3	68.1/32.1
PUFA	30.7	11.3/50.2

[1] Amount and composition of lipids in product before frying.

Adapted from Matthäus (2007) and Sanchez-Muniz et al. (1992).

MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids; SAT, saturates.

Traditionally, animal fats such as lard and tallow have been used for frying because they have excellent stability and create products with great flavor; however, they are a source of cholesterol and saturated fatty acids. When saturated fat was found to be a main dietary contributor to the higher blood cholesterol level which is linked to an increased risk for coronary heart disease, the food processing industry was urged to find alternatives. The next step in the development of frying media was a transfer to partially hydrogenated vegetable oil, pourable shortenings, mainly derived from soybean and canola. These frying media contain on average 18% and 10% of saturates and 35% and 22% of trans fatty acids, respectively.

Labelling regulations enforced the replacement of trans containing fats with available zero trans oils and in the short term tropical oils were used as an alternative. Coconut and palm kernel oils contain about 80–90% saturated fatty acid, mostly as palmitic acid which is the main culprit causing increases in blood cholesterol level. At that time, only HOLLCO, high and mid oleic sunflower oils were available, which offered expected frying stability. Modified high and mid oleic sunflower oil were marketed initially in the 1980s, but price and unsustainable market supply prohibited wide scale use in food applications.

Using conventional plant breeding, nontransgenic, non-GMO HOLLCO was developed. This oil is naturally stable without hydrogenation, is free of trans fatty acids and contains the lowest levels of saturated fatty acids. Production of HOLLCO in 2005 was 180,000 tonnes (400 million pounds) and in 2008 900,000 tonnes (2 billion pounds).

The typical fatty acid composition of HOLLCO and other oils used for frying are included in Table 8.2. Content of oleic acid is comparable to olive oil; this fatty acid does not increase blood cholesterol. The amount of saturated fatty acids in HOLLCO is about half that of olive oil. HOLLCO matches or exceeds the healthy fatty acid composition of other high oleic oils in the amount of linoleic and linolenic acids.

Available trait-modified oils were compared for frying performance with typical hydrogenated frying shortenings using the same parameters. In all tested oils and fats, French fries, chicken, and fish were fried in a rotational manner. Three food products were fried in succession forming a singular cycle; nine frying cycles were run daily. In 5 L of tested oil, 11 kg (24 lbs) of products were fried daily. The performance of oils was measured by polar components, polymer formation, anisidine value, and

Table 8.2 Fatty Acid Composition of Commodity and Trait Oils (%)

Trait description	C16:0	C18:0	C18:1	C18:2	C18:3	SAT	MUFA	PUFA
Soybean oils[1]								
Commodity	10–13	3–5	18–25	50–58	6–10	13–18	18–25	56–68
High oleic low linolenic[4]	11	4	24	57	2.5	16	24.5	59.5
Mid oleic low linolenic	10	4	53	32	1	14	53	33
High oleic	6	5	80	2	3	13	80	5
Mid oleic low saturate	3	3	75	15	2.5	6	75	18
High oleic high stearic	6	20	61	4	4	28	61	8
Canola oils[2]								
Commodity[2]	2–6	1–2	51–70	15–30	5–14	3–8	51–70	20–44
High oleic low linolenic[4]	3	2	73	13	2	7	79	15
Low linolenic[4]	4	2	62	25	3	7	64	28
Sunflower oils[3]								
Commodity	5–8	3–7	13–40	40–74	0–1	8–15	13–40	40–75
High oleic	4	4	82	9	>1	8	82	9
Mid oleic	5	4	61	27	>1	9	62	28
Other oils[2]								
Cottonseed	24	2	17	56	>1	27	18	56
Palm	44	5	40	10	>1	50	41	10
Palm olein	35	4	45	13	>1	40	46	13
Olive	12	3	70	12	>1	16	71	12

Adapted from: [1] Wilkes (2008); [2] Codex Alimentarius (2001); [3] Kleingartner and Warner (2001); [4] data from author's laboratory analysis.

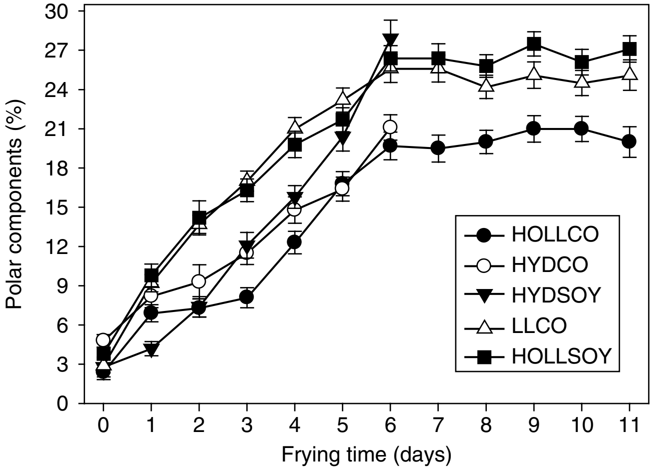

Figure 8.1 Comparison of frying performance of trait oils and hydrogenated frying shortenings as measured by the formation of polar components. HOLLCO, high oleic low linolenic canola oil; HOLLSOY, high oleic low linolenic soybean; HYDCO, pourable hydrogenated canola frying shortening; HYDSOY, pourable hydrogenated soybean frying shortening; LLCO, low linolenic canola oil. For fatty acid composition of oils see Table 8.2.

free fatty acid formation. The formation of polar components in frying oil usually best describes oxidative stability because it measures directly the products formed during oxidative degradation mainly of fatty acids. Results from this comparison verified the very good frying stability of HOLLCO, which formed the lowest amount of polar components, and its performance was better than standard hydrogenated frying fats (Figure 8.1). The main disadvantage of hydrogenated frying shortenings is their high content of trans isomers, usually at 20–35%, and also high amounts of saturated fatty acids at 10–20%. Both fatty acid groups negatively affect human blood lipids and contribute to the development of CVD (McNeill 2009; Mozaffarian et al. 2006).

The superior frying stability of HOLLCO was also confirmed during the frying of French fries, producing fries with similar sensory quality to high oleic sunflower oil (HOSO); the latter is used in Europe as a reference (Matthäus 2006). When oils used in this study were ranked for total quality and weighed combination of all tested parameters, again HOLLCO came higher than HOSO and partially hydrogenated rapeseed oil (PHRO). The authors of the study concluded that HOLLCO is a good alternative to commonly used trans containing frying fats due to production of good quality fried foods and economical benefits related to extended fry life of the oil. Furthermore, nutritional advantages included:

- low content of saturated fat
- the presence of omega 3 fatty acids; even at lowered amounts this essential fatty acid positively affects human body metabolism
- free of trans fatty acids
- high amounts of oleic acid, which is neutral to blood lipids with a tendency to increase amounts of HDL
- even with a low content of linolenic acid, the ratio of omega 6 to omega 3 is 7.5, still close to optimal (Barth 2009).

Based on these results, HOLLCO was applied to frying donuts and potato chips. For both products, quality indicators, including sensory factors, were similar to the typical hydrogenated fats used in these applications. However, storage stability of these products was slightly hampered for HOLLCO, mainly due to the higher amounts of PUFA. Nevertheless, HOLLCO can be a good alternative to hydrogenated frying fats to reduce or eliminate trans isomers from fried foods (Matthäus et al. 2009). HOLLCO is a trans free replacement for partially hydrogenated frying fats where resistance to oxidative degradation and extended shelf-life are required. Applications where it is currently used include:

- snack and grill frying
- food service frying
- pan sprays
- spray oil coatings
- bakery shortenings and margarines
- nutritional bars
- sauces and dressings
- blends with other oils in frying applications (Orthoefer 2005).

Other trait oils are available on the market but they are often in the final stages of development or available in amounts which do not provide a

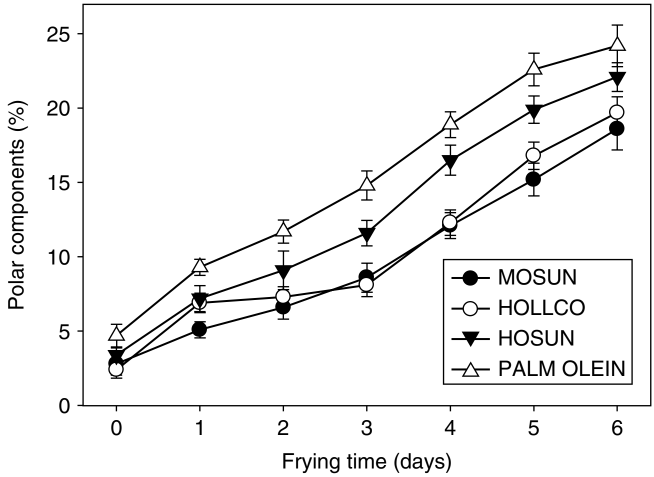

Figure 8.2 Comparison of frying performance of trait oils as measured by the formation of polar components. HOLLCO, high oleic low linolenic canola; HOSUN, high oleic sunflower; MOSUN, mid-oleic sunflower; PALM OLEIN, palm oil olein fraction. For fatty acid composition of oils see Table 8.2.

continuous supply for food processing. Two sunflower trait oils are available, namely HOSO and NuSun (mid oleic sunflower oil) containing up to 82% and 65% oleic acid respectively. However, both oils are in short supply. The latter oil showed comparable frying stability to HOLLCO, far better than high oleic sunflower (HOSUN) and palm olein (PO) (Figure 8.2) (Przybylski 2009).

Currently, soybean oil lacks traits offering frying stability comparable to the oils discussed above. low Linolenic soybean oils (LLSOY) still contain relatively high amounts of linoleic acid which make these oils less stable in frying applications, even when the linolenic acid content was reduced to a minimum (see Table 8.2, first two soybean oils). Frying performance of high oleic low linolenic soybean oil (HOLLSOY) was comparable to hydrogenated soybean shortening (HYDSOY) and low linolenic canola oil (LLCO) as measured by the formation of polar components, but it had a lower frying stability than HOLLCO and MOSUN (see Figure 8.1). In newly developed HOLLSOY oils, fatty acid composition is similar to HOLLCO, which is currently perceived as the best oil for frying applications, to eliminate trans fats (Wilkes 2008). Frying tests using a new variety of HOLLSOY established slightly better stability as HOLLCO, which is attributed to the higher content of tocopherols, which are natural antioxidants. This oil may be available on the market in the next few years (Knowlton 2009).

Alternatives to the hydrogenated commodity oils and trait oils discussed above are blends of different oils and fats to provide frying stability and good quality fried products. These blends often contain HOLLCO as a component (HOLLCO/corn oil blend), and are mainly prepared to lower cost. Blended corn oil or cottonseed oil with traditional soybean oil or canola oil can be targeted to achieve a linolenic contribution below 3%. Frying tests demonstrated that blends produced good tasting fried foods and maintained good quality oil in the fryer. Naturally stable oils are used in blending to eliminate trans fats but at the same time the amount of saturated fats is elevated in HOLLCO (see Table 8.2).

Some oils with good frying performance are by-products and their availability depends on the demand for their primary products. Corn oil depends upon the demand for starches and sweeteners; cottonseed oil on the demand for fiber; peanut oil on regulated peanut crushing; and rice bran oil on the rice processing industry extraction capacity.

8.2 SHORTENINGS AND MARGARINES

The functionality of shortenings and margarines is affected by a number of factors and is defined by the application for which the product is used. Physical properties of fats and oils are commonly associated with triacylglycerol composition and structure, crystallization, crystal type, and melting behavior. The β’ small crystal structure forms the best texture in shortenings, margarines and spreads, which facilitates integration of large volumes of liquid oil. These crystals give the product a glossy surface, a smooth luster and good spreadability. Conversely, β’-crystals have a tendency to recrystallize and grow into needle shaped agglomerates which have lower holding capacity for liquid oil and generate a grainy texture. Palmitic acid is usually the driver in formation of the β’-crystalline structure and usually stearic acid will follow. Both fatty acids encompass most of the commodity and trait oils (Neff et al. 1999).

The structure and composition of triacylglycerols are responsible for the physical property frequently described as lubricity. The latter is characterized by product pourability, homogeneity of components at specified temperature and melting in the mouth to give a pleasant effect (Bessler and Orthoefer 1983). Triacylglycerols (TG) containing different proportions of unsaturated (U) and saturated (S) fatty acids determine lubricity. TGs can be categorized into four groups according to their function and melting properties.

- Triunsaturated and diunsaturated (UUU/SUU) TGs in ratio 1:1 which melt at –13°C to 1°C. These TGs promote pourability and effortless handling at refrigeration temperatures. Nearly all commodity and trait oils are liquid at 5°C and contain 56–75% of these TGs, apart from the tropical oils.
- The second group contains mostly single saturated (SUU) TGs. They are present in most commodity and trait oils at a level of 21–37% which melt in the range 5–23°C, providing lubricity at 25°C.
- Oils used for margarine formulation consist of double saturated (SSU) triacylglycerols, melting at body temperature, 27–42°C.
- The fourth group is formed by trisaturated (SSS) TGs, melting from 56°C to 65°C.

Saturated triacylglycerols are the main components of hard basestocks used mainly in formulations of baker's and pastry shortenings and margarines. Hard basestocks are an example of extensively processed oils.

Apart from good oxidative stability, many food lipids require certain amounts of solid fats for functionality and/or textural performance. Solids define functionality in all purpose shortening, puff pastry shortening, and baking margarines. These fats are produced by blending different types of hard and semi-hard basestocks with liquid oils to provide physical properties as required for specific applications. The amount of solids in fats and oils is usually expressed as solid fat content (SFC). Typical SFC profiles of different fats are presented in Figure 8.3.

The amount of components melting at lower temperatures defines spreadability and handling at refrigeration conditions and is important in soft margarine and spreads. Harder fats, products containing more TG with higher melting points, are required for puff pastry or roll in

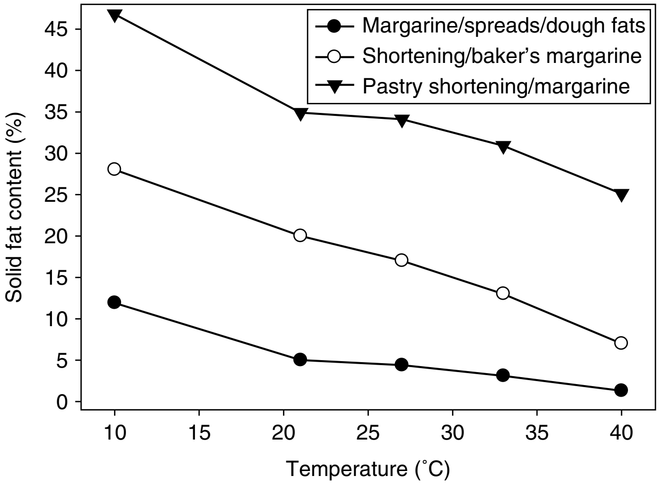

Figure 8.3 Solid fat content of standard margarine, shortening and pastry fat. Adapted from Tiffany (2008). Reproduced with permission of the author.

applications. Formulation of these fats commonly involves blending fully hydrogenated palm or cottonseed hard basestock with good oxidative stability liquid oil. A potential benefit of using fully hydrogenated fats in blends is the enhanced oxidative stability and elimination of trans fatty acids. However, on the list of ingredients, hydrogenated oils must be recorded, which may have a negative impact on consumer perception. Hydrogenation is regularly connected by consumers with the presence of trans fats.

Before labeling regulation was changed in North America, all purpose shortenings were blends of 85–90% partially hydrogenated oil with 10–15% of a fully hydrogenated cottonseed, soybean or palm oil. The hydrogenated oils contain predominantly palmitic and stearic acids, which always crystallize in β'-crystal structure. Fully hydrogenated oils form hard basestocks without trans fatty acids and are often used for formulation of bakery shortenings and margarines. All purpose bakery shortenings and margarines contain solid fats that aerate the dough during sugar and flour creaming. Aeration of the dough is crucial to the structure and texture development of the finished baked product. The shortening solids must extend their melting temperatures over a wide range to produce the desired plasticity for creaming (Orthoefer 2005).

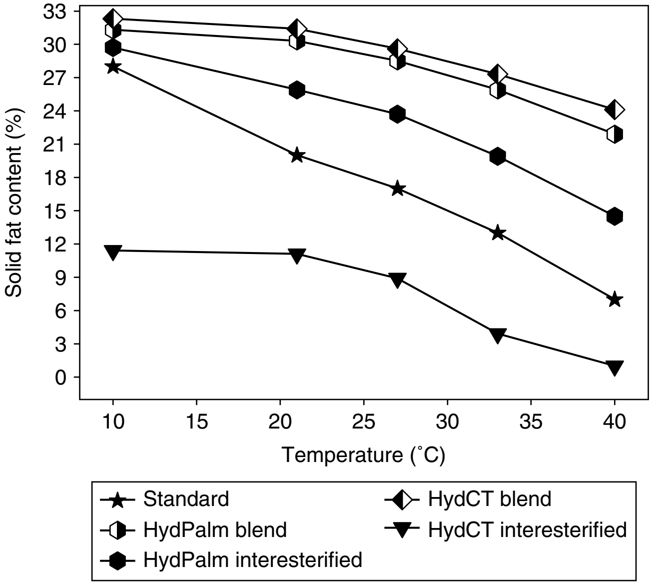

Figure 8.4 Solid fat content of standard and zero trans shortenings formulated with high oleic low linolenic canola oil. HydCT, fully hydrogenated cottonseed oil; HydPalm, fully hydrogenated palm oil. Adapted from Orthoefer (2005). Reproduced with permission of Elsevier.

The partially hydrogenated oils, the main component of shortening and baking margarines, mainly contribute to the amount of trans fatty acids. The preparation of trans free all purpose shortenings and baking margarines began by blending liquid oils with different amounts of hard fats, and blends are usually interesterified using chemical or enzymatic catalysts.

To formulate zero trans shortening, 30% of fully hydrogenated palm stearin was blended with HOLLCO, and the fat obtained after interesterification has an SFC profile similar to trans containing all purpose shortenings (Figure 8.4). However, a blend of palm hard fat and HOLLCO provided shortening with much higher amounts of solids at all temperatures and its properties were similar to pastry shortening (Orthoefer 2005). Replacing palm hardstock with fully hydrogenated cottonseed oil furnished fat with a similar SFC profile (see Figure 8.4). When the blend was interesterified, randomizing the structure and composition of TG, the SFC changed dramatically and formed fat with properties required for soft margarine formulation (bottom curve on Figure 8.4) (List et al. 1996; Orthoefer 2005).

For puff pastry or roll in applications, higher amounts of harder fats are used in formulation to obtain more solids. For this formulation, trait oils are often used, such as HOLLCO and some genetically modified soybean oils (List et al. 1996; Orthoefer 2005). Utilization of fully hydrogenated fats in blends and interesterified fats offers a double advantage: eliminating trans fat, and increasing oxidative stability of formulated fats. However, utilization of fully hydrogenated oils causes an increase in the amount of saturated fat and lowers the nutritional value of formulated fats. It is generally accepted that saturated fats negatively affect human blood lipids and increase the risk of CVD development (Mensink et al. 1992; Oomen et al. 2001).

At the outset of trans fats replacement in shortenings and baking margarines, hard palm fractions were applied together with interesterification, mainly due to the lack of other fats with similar properties. Utilization of palm olein (PO) in margarines and shortenings causes "post hardening," an increase in firmness of the finished product during storage. This phenomenon is a consequence of symmetrical TG, such as SSS and SUS, crystallization from the liquid oil used in formulation. More solid fats are formed and the physical properties are altered. Interesterification can alleviate the problem of post hardening but rearranged TGs usually change the amount of solids and alter physical properties. Thus, application of interesterification to make fat with specific properties utilizing hardstock and trait oil offers better control of physical properties, and may not only limit trans content but also control the amounts of saturated fat in the final product (Orthoefer 2005).

Elimination of trans fats started earlier in Europe than on the American continent and trans free margarines and shortenings were on the market for years. In formulations of these products, partially hydrogenated oils were replaced with liquid vegetable oils and high melting fractions were obtained frequently from palm oil, such as palm stearine. Cavillot et al. (2009) investigated properties of marketed trans free pastry and baking margarines/shortenings and found that products without partially hydrogenated fats did not have exactly the same properties as their trans containing counterparts. These authors established

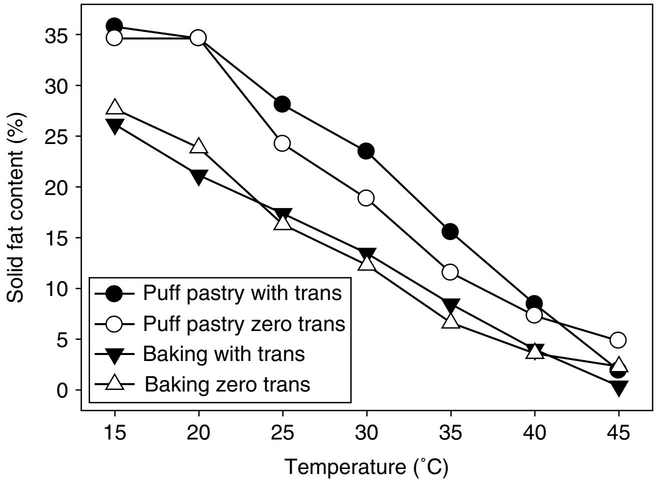

Figure 8.5 Comparison of solid fat content in European margarines and shortenings with and without trans fat. Adapted from Cavillot et al. (2009). Reproduced with permission of Elsevier.

that trans free margarines/shortenings maintained a higher level of SFC, particularly with solids having higher melting points (Figure 8.5).

These findings illustrate that for formulations more fully hydrogenated oils were used, which have different physical properties from partially hydrogenated oils. Higher dropping points and firmness of tested products further confirmed utilization of higher amounts of harder basestocks. Trans fat containing European margarines generally crystallized in the β’-form, but zero trans margarines had a tendency to crystallize mainly in β-polymorphic crystals. Both forms of crystals offer different physical properties which negatively affect the baking performance of puff pastry. These crystal structures directly influenced the texture and plasticity of these margarines and affected the quality of the final baked product.

Changes in labeling forced vegetable oil and food processors to be more creative in developing new strategies of nutritional oil utilization. This lead to the question: Do we need extensively processed oils to achieve expected properties? Before oil processing was applied for vegetable oils, usually crude pressed oils were utilized in food preparation, including baking. Currently, there is an attempt to return to “old fashion” preparations of baking using liquid oil. Olive oil has been used to replace hydrogenated baking fat in baked goods, and the cakes produced were of comparable quality (Matsakidou et al. 2010).

8.3 CONCLUSION

Dietary trans fatty acids more effectively increase levels of LDL (bad cholesterol) and decrease HDL (good cholesterol). Saturated fats are an inadequate replacement for hydrogenated oils because they increase levels of total cholesterol and triacylglycerides in the blood. The combination of blood lipids discussed above is the main factor leading to the increased risk of CVD development, the main killer in many developed countries (Mensink et al. 1992; Oomen et al. 2001). The content of trans and saturated fatty acids can be optimized through formulation and processing, where good quality trait oils have to be implemented to fulfill nutritional requirements.

Currently, not many trait oils are on the market. Probably in the near future, new trait oils will replace "bad" fats in newly formulated food products. Trait soybean oils with fatty acid composition similar to HOLLCO are being developed.

Currently high oleic low linolenic acid canola oils are produced in sufficient amounts to allow development of food formulated without trans fats. These oils contain 70% or more oleic acid, <3% linolenic acid and less than 7% saturated fatty acids. Composition of fatty acids meets dietary guidelines and they are an excellent replacement for trans containing fats used for frying, baking, and margarine applications. The vegetable oil industry and particularly food processors need to come up with creative food product formulations using available trait oils to accommodate human needs for lipids in the diet.

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9 Performance and Formulation of Trait-Modified Oils in Bakery Shortenings

Gary R. List,[1] Dilip K. Nakhasi,[2] Tom Tiffany,[3]
and Frank T. Orthoefer[4]

[1] *USDA ARS NCAUR (Retired), Peoria, IL, USA*
[2] *Bunge Oils Inc, Bradley, IL, USA*
[3] *Archer Daniels Midland, Decatur, IL, USA*
[4] *FTO Foods, Knoxville, TN, USA*

Fats and oils represent major ingredients in a vast array of bakery products, including bread, cake, cookies, crackers, cup cakes/brownies, pies, and donuts, which are a $21+ billion industry. Snack foods, many of which contain fats and oils, have sales of nearly $30 billion, with potato chips, tortilla chips, corn snacks, pretzels, and microwave popcorn accounting for over half ($15.2 billion) of snack foods sales. Traditionally both animal fats and vegetable oils have been used to formulate baking shortenings. However, over the past several decades, saturated fats from lard, tallow, and tropical oils have been implicated as risk factors in coronary heart disease. Moreover, trans fats produced by industrial hydrogenation of vegetable oils have had a marked effect on the reformulation of bakery shortenings. After the passage of the Nutrition Education Labeling Act of 1990, the final rules for labeling of both trans and saturated fats were issued in July 2003 (Anon 2003). Key provisions included that saturated and trans fats are to be included as separate lines on nutrition labels, and foods containing less than 0.5 g trans fat/serving may be declared as zero (serving size 12–14 g fats and oils); the effective date was January 1, 2006.

Trait-Modified Oils in Foods, First Edition. Edited by Frank T. Orthoefer and Gary R. List.

Many companies began to remove trans fats from food products well in advance of the 2006 mandate. Over the period 2003–2007, about 1900 foods were reformulated to meet a zero trans claim (Anon 2007). The snack food industry took the lead by replacing hydrogenated fats with liquid oils free of trans fats, including corn, cottonseed, sunflower, and canola oils. Others switched to trait-modified soybean oil (low linolenic). Other approaches to removing trans include the use of tropical oils and their fractions. This is not surprising since soybean and palm oil represent about 60% of the world's oilseed production.

The trait-modified oil industry is evolving rapidly. Having been spurred by trans fat labeling, trait-modified oils now supply about 18% of domestic fats and oils usage. At the time of writing, low linolenic, mid/high oleic soy are commercially available and low saturate high oleic soy is expected to be commercialized soon. Other commercially available trait-modified oils include low linolenic/high oleic canola and mid/high oleic sunflower.

This chapter will discuss the uses and potential applications of trait-modified oils in bakery shortenings.

9.1 BAKING OVERVIEW: FUNCTIONAL PROPERTIES OF FATS AND OILS

Fats and oils serve a number of purposes during the baking operation depending on the particular product. The classic study on the behavior of fats in baking was reported in 1944 by Carlin. Cake batters (layer/pound) appear to be suspensions of air bubbles distributed in a medium of liquid and flour. Little if any liquid appears to be emulsified in the fat phase. Soluble ingredients such as sugar and salt are dissolved in the water phase of the batter. Air spaces in cakes are invariably surrounded by fat. During baking, the fat quickly melts and releases suspended air to the flour/water medium. Gas produced by the baking powder finds its way into air spaces already existing within the batter. Microscopic examination by polarized light indicates that the cross-sections of wheat starch disappear at this stage of baking. During baking, a constant movement of air spaces follows a convection pattern until baking is almost complete. At this stage movement becomes violent and without direction. Carlin concluded that the use of monoglycerides as emulsifiers produces a finer dispersion of fat throughout the cake batter.

Thus the functional roles of cake shortening include lubricity and aeration (creaming). In the mixing stage, creaming is a function of the crystal form of the fat, emulsifier systems, and the levels of liquids and sugar that can be tolerated. Control of these factors is critical to finished cake quality whose attributes include cake volume, grain/symmetry, moistness, and storage life. Thus creaming or the ability to incorporate air into baked goods is an important factor in the selection of cake shortening. Cake batters are prepared by mixing lipids, flour, water, sugar, and possibly emulsifiers and surfactants. Creaming is dependent on the crystal habit (β') of the fat or oil, the composition of the emulsifier system, and the levels of sugar/liquids. In turn, finished cake quality as measured by volume, grain, symmetry, moistness, and storage life depends on the extent of creaming during the mixing stage.

Icing shortenings provide lubricity, structure, and aeration. Body and texture are dependent on creaming ability of the shortening. Emulsifiers/composition and sugar levels affect icing spreadability and stability. Lubricity (mouthfeel) at body temperatures is an important functional property of icings and is determined by the melting profile of the shortening and granulation of sugar. Icing shortenings are formulated with triglycerides with melting points at body temperature. Overall lubricity effects are achieved from a combination of both cake and icing (Kincs 1985).

Pie shortenings play a slightly different functional role in baking. Lubricity is dependent on the oil fraction being loosely bound in the flour and dough should not be overmixed to prevent excessive absorption which leads to tougher crusts and shrinkage. In commercial operations, mixing is conducted at colder temperatures to control absorption. Thus a pie shortening must be plastic at refrigerator temperature to ensure adequate rolling and forming. Lard has been a preferred pie shortening since flaky crusts are highly desirable. Lard has the proper composition, melting profile, and crystal habit needed for pie crusts. Unlike cake and icing shortenings where the desired β'-crystal habit is desired, lard is a β tending fat leading to flaky textures.

Fats and oils function in baking through lubricity which includes the shortening of gluten strands in flour, mouthfeel, which in turn contributes to tenderness, and richness of the baked goods. Lubricity also can be applied to the ability of the oil to form an oily film which is viscosity related and how well the fat or oil melts in the mouth. Fats melting at body temperature tend to give a pleasant cooling effect whereas those melting above body temperature yield pasty or waxy sensations (Bessler and Orthoefer 1983).

Liquid oils (unhydrogenated) are not really suitable for commercial baking unless blended with emulsifiers and/or surfactants. However, technology developed over the past 40 years has contributed to a number of liquid shortenings, many of which are used in commercial baking operations. They perform well in bread, cakes, and other dough based products. Liquid shortenings provide a trans free solution for baking and the fact that they are easily pumped, handled/stored and metered in baking operations is an additional advantage. Thus liquid shortening based on trait-modified oils and emulsifiers/surfactants should perform well in many dough based baking applications especially where shelf-life is a prime consideration. A wide range of low fat foods, including baked snack crackers, pretzels, tortillas, and pizza dough, have been successfully reformulated to zero trans with liquid oils. A recent report indicates that cereals formulated with high oleic canola oil have increased shelf-life (Lui and Issonova 2012). Soft cookies are usually formulated with solid emulsified shortenings which may be high in trans. However, trait-modified oils blended with hardstock and emulsifiers/surfactants offer a trans free solution along with needed solid fat.

Many all purpose baking shortenings can be formulated from blends of hydrogenated soybean oil, liquid (unhydrogenated) oils, and completely hydrogenated soybean or cottonseed oils (hardstocks IV<5). While highly functional, these products tend to have 20–25% trans acids and are higher in saturates as well. A report indicates that a trans free option is available through blending hardstocks with trait-modified high oleic canola oil or interesterification of the simple blends (Orthoefer 2005).

In addition, the most recent invention related to reduction of saturates utilizes cellulose fibers in conjunction with fully (less than 5 IV) or partially hydrogenated oil(s), or solid stearin fractions such as palm stearin, or other solids at room temperature, esters or partial esters such as diglycerides, monoglycerides, waxes or mixtures of these to provide a crystal matrix between liquid oils. Canola, high oleic canola, soybean, corn, or a semi-solid oil such as palm oil, or a partially hydrogenated oil with solids at room temperature allow a plastic shortening like material to be produced with reduced levels of both trans fatty acids and saturated fatty acids compared to a shortening formulated without the fibers.

The fibers aid in structuring the shortening, partly by taking some of the oil into capillaries and tying up some oil wetting the fiber surfaces and partly by physically acting to reinforce the crystal structure formed by the higher melting fractions incorporated into the blend. The sum of trans plus saturated fatty acids in an all purpose shortening formulated using partially hydrogenated oil and a heavily hydrogenated oil is about 50%, the sum of trans plus saturated fatty acids in a shortening formulated without use of hydrogenation is about 52%, and the sum of trans plus saturated fatty acids in a shortening system formed by using a novel hydrogenated basestock and a fully hydrogenated oil is about 32%. The new approach produces trans fatty acids plus saturated fat acids levels less than those mentioned above, since it allows the use of a shortening formulated to have lower solid fat content. A comparison with the shortenings mentioned above and the oil system used most frequently in this work had a saturate plus trans fatty acid content of about 18.5% (Higgins 2013).

Crisco shortening has been a household favorite for over 100 years. Since 2003, the product has been reformulated several times to be trans free. Currently Crisco contains hardstock and trait-modified sunflower oil and it is claimed to perform as well as the older formulations.

A number of baking shortenings formulated from palm oil, palm kernel, trait-modified high oleic canola, and unhydrogenated soybean oil are available commercially. Typically these products are used in industrial pie manufacture, in refrigerated and frozen dough and applications where a sharp melting point is required for mouthfeel. While low in trans acids, these products tend to be high in saturated acids. Other baking shortenings (all purpose) are available and are nonhydrogenated (zero trans) and with different degrees of firmness ranging from very soft to very firm, depending on the amount of palm/palm kernel in the formulation. Saturates range from 18% (very soft) to 50% (very firm).

Shortenings designed for puff pastry and other laminated dough can be formulated with palm oil and trait-modified soybean oils. They provide excellent flakiness, structure, and lamination as well as optimum performance on automated dough lines. Blends of trait-modified soybean and palm oils formulated with mono/diglycerides are highly suitable for breads and yeast raised dough since they provide easy dough handling and less proofing time, and less dusting flour is required.

Cake and cake mix shortenings can also be formulated from trait-modified soybean and palm oils containing an emulsifier system composed of polyglycerol monoesters, mono/diglycerides and lecithin. These shortenings produce moist cakes with improved eating qualities, structure, volume, and freeze-thaw performance. By modifying the emulsifier system to include polysorbate 60 along with mono/diglycerides, blends of trait-modified soy/palm extend the applications to cakes, icings, dough, and tortillas.

9.2 PERFORMANCE OF TRANS FREE BAKING SHORTENINGS

Protocols for the assessment of baking shortenings are given in the standard methods of the American Association of Cereal Chemists. However, they are designed to assess flour quality. The shortening is a hydrogenated vegetable oil based all purpose component.

In commercial baking of cookies, spread is a prime consideration since too much or too little spread affects packaging. The shortening must yield a uniform number of cookies (stock keeping units) per package. In addition, wicking or seepage of oil is undesirable.

A number of studies have reported on the use of liquid oils for baking bread, cakes, and sweet dough products (Hartnett and Thalheimer 1979). However, emulsifiers and surfactants are needed for optimum results. Bread baked with 3% soybean oil gave sticky dough that was difficult to handle. Incorporation of 0.5% monoglycerides/polysorbates gave improved performance equal to that of standard liquid bread shortening with respect to dough handling, grain, and softness. Similar results were obtained in cake baking tests except that 8–12%

polyglycerol monostearate (PGMS) emulsifier was required. Sweet dough made with only liquid oil handled poorly, was sticky, and had low specific volume and open irregular grain. The addition of 2% monoglycerides gave only slight improvement in dough handling but an emulsifier system of 1.5 % monoglycerides/polysorbate performed well in sweet dough.

Kamel (1992) evaluated the characteristics of bread and buns baked with liquid vegetable oils of different iodine values and compared the results to lard and palm oil. He concluded that soybean and canola oils containing emulsifiers gave baking performance equal to the solid fats with a reduction of 30% total fat. Baldwin et al. (1972) reviewed the uses of liquid oils in cakes and bread with added surfactants. These authors point out that the solid fat profiles of oil/surfactant and hydrogenated shortening are markedly different but at the temperatures (100–110°F) at which leavening power occurs, the two systems give comparable crumb softness and moisture retention.

Enzymatic interesterification of liquid oils with completely hydrogenated stearines offers a trans free solution for all purpose baking applications including sugar cookies, high ratio cakes, and pie crusts. These shortenings are available commercially. Studies comparing a hydrogenated, palm based shortening against several interesterified shortenings showed that sugar cookies had comparable stack height, but the hydrogenated shortening had the smallest spread and force to break after 3 days. Wicking or seepage of oil was comparable and the spread factor (width/height) was very similar for all shortenings tested. High ratio cakes were evaluated for texture (grain), force to break, and height and batter specific gravity. The interesterified shortenings produced cakes with finer grain than the hydrogenated shortening. Small differences were observed in batter density but the interesterified shortenings gave the best cake volume. Height, texture or peak force measurements made after 1 and 3 days showed that the interesterified shortenings were equal to the hydrogenated control, indicating equivalent cake softness. Evaluation of pie dough showed that interesterified shortenings gave the least amount of wicking and the lowest peak force required for breakage.

In summary, limited data indicate that interesterified baking shortenings perform in a wide variety of applications as well or better than the hydrogenated fats they replace.

9.3 TROUBLE SHOOTING TRANS FREE BAKING SHORTENINGS

A popular trans free option involved substitution of palm based shortenings for the hydrogenated product used previously. Thus drop in solutions did not always yield equal results. However, many of the problems were overcome with adjustments to the baking process and the storage and handling of the replacement shortenings.

Common complaints were shortenings too hard or soft, off flavors, and quality losses over time.

9.3.1 Problems

Creaming issues, off flavors, stiff dough, poor cookie texture/spread, poor icing performance/donuts.

9.3.2 Solutions

Palm oil based shortenings tend to be harder in winter and softer in summer, leading to creaming issues. They can on rare occasions develop slight off flavors in sweet rolls and pound cakes. Switching brands or adding butter flavor to the recipe may be a solution. Complaints that trans fat replacements have shorter storage life than the hydrogenated shortenings can be addressed by following the supplier's storage instructions. While hydrogenated shortenings keep for 1 year, 6–9 months have been observed for trans replacements. The purchase of smaller quantities more frequently is an option.

Some bakeries premake the dough in advance of the next day's needs, followed by resting in a cooler. As a result, the dough becomes stiff to work and roll out. Palm based all purpose baking margarines are temperature sensitive. By allowing the dough to sit at room temperature long enough to become soft enough to work, the problem can be resolved. However, dough should not be permitted to stand for more than 2 hours at ambient temperature. Sugar cookies baked with trans replacements may become too crisp but this can be resolved by adjusting baking times or temperatures. Other solutions include replacement of sugar levels with (up to 25%) liquid sweeteners. However, liquid sweeteners may increase browning, requiring control of bake time and temperatures and sweetener content. Chocolate chip cookies may spread excessively with trans replacements. Solutions include increasing baking temperature 25° higher than usual to "set" the cookies earlier in the baking cycle and then reduce baking time. Cookie spread can also be controlled by replacing some of the flour with 20% high gluten bread flour.

Trans free icing shortenings may develop off flavors and colors. Switching brands may provide a solution. Butter creams made freshly may be highly satisfactory but they may lose volume and oil off may occur. These problems can be traced to improper emulsification of the shortening. Some all purpose shortenings may not contain emulsifiers. All icing shortenings are emulsified but may not perform in the same way. Solutions include use of other brands, adding extra emulsifier (as directed by the supplier) or making smaller batches to use the same day. Icing problems include too soft or too firm. Soft icings can be refrigerated before use while stiff icings can be tempered at room temperature for up to 2 hours or by the addition of up to 5% water. The overmixing of icings may cause breakdown, Soft sandwich cookie fillings may require a longer set time before crowning.

Trans free donut frying oils may lead to greasy and bitter tasting donuts. Switching brands or the use of fresh fat at the proper temperature are possible solutions. Past wisdom suggested that donuts should be fried in shortenings with high solid contents so that when the donut cools, the solidified fat allows icing and glazes to adhere and not break or slump off. However, it is claimed that quality donuts can be fried in trait-modified canola oil and the products have excellent eating properties and icing /glaze adherence. Manufacturers have introduced frying shortenings designed specifically for donuts. They are formulated with palm oil and trait-modified oils and as such provide solids from the palm oil and increased fry life from the high oleic acid contents of the liquid component.

Several other potential applications of trait-modified oils for baking include liquid shortenings employing trait-modified oils in combination with emulsifier/surfactant systems (Doucet 1999; Skogerson and Boute 2010) or structured emulsions prepared by shearing monoglycerides, oil, and water. These products are easily made, contain low trans and saturates, and perform well in providing structure to a wide variety of baked goods, including cookies, cake, pie shells, biscuits, muffins, pizza, and frozen dough (Marangoni and Idziak 2008).

9.4 CONCLUSION

Trait-modified oils offer a zero/low trans reduced saturate solution for many baking applications. In 2008, these oils supplied about 12% of domestic edible oil consumption. Today about 18–20% of the edible oil market can be attributed to trait-modified soy, canola, and sunflower. As new oils are commercialized and supplies increase, costs will decrease. Early efforts to expand the trait-modified oil industry were hampered by the higher costs of grower premiums, identity preservation, and supply issues. Emphasis on health, nutrition, and obesity will continue to be a focal point for the food industry and the trait-modified oil industry will play a major role in addressing these issues.

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10 Trait-Modified Oils in Food Service Applications

Don Banks

Edible Oil Technology, Dallas, TX, USA

All types of oil and shortening are used in restaurants, fast food operations, hotels, institutions, and other food service operations. Frying oil accounts for the largest volume usage in food service and is the topic for this chapter.

Selecting frying oil for use in various applications can involve a variety of criteria depending on menu items, frying equipment, and other factors; however, oxidative stability is a primary consideration for all operations. Therefore, in discussing trait-modified oils (TMOs) for food service usage, the focus will be on oxidative stability and how modifications to the fatty acid composition of an oil affect its stability.

10.1 FOOD SERVICE BATCH FRYING

In food service, frying is primarily conducted using batch fryers and food is prepared throughout the day as needed to fill customer orders. Around mealtimes, fryers are used without interruption to prepare batch

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after batch, but during much of the day fryers are only used intermittently or may remain idle for extended periods.

10.2 FRYER OPERATION AND OIL QUALITY

When batch fryers are operated continuously, the evolution of steam and the addition of fresh make up oil mitigate oxidative stress on the oil. The evolution of steam helps strip out volatile oxidation products and the addition of fresh make up oil enhances overall quality as it blends with used oil. The addition of make up oil is particularly important because of its dilution effect to control free fatty acid and other quality attributes and also because it contains a full complement of natural antioxidants to further protect the oil.

10.3 FRYER OIL TURNOVER

During continuous production, make up oil equal to the total oil capacity of the fryer will usually be added within 8–12 hours. The rate of oil turnover is sufficient to maintain free fatty acid, color, smoke point, polymers and other oil quality attributes within acceptable limits. A rapid turnover rate provides support for extended oil fry life, the period of time that oil can be used for frying and continue to yield product in compliance with a company's quality standards. But with the exception of a few hours a day around meal times, food service fryers are rarely operated continuously. The rest of the time, they are either idle or operated intermittently with little if any fresh oil (i.e., make up oil) addition. The net result is that the average rate of fryer oil turnover is much slower compared to continuous frying. In food service batch frying, it can, and commonly does, take 20 hours or longer to complete one oil turnover.

Concerning the rate of oil turnover, it is important to note that when one oil turnover has been completed, that is not the same as replacing all of the oil in the fryer with fresh oil. The added make up oil blends with the oil already in the fryer, so the oil then absorbed by the product is a blend of the fresh and older fryer oil. Therefore, as frying continues, some of the fresh oil is carried out while a proportinate amount of the older oil remains in the fryer. As a result, after one turnover, half of the original oil remains in the fryer. With two turnovers, one fourth of the original oil is still in the fryer and the progression continues. Generally after three to four turnovers have been completed, essentially all of the original oil can be considered to have been replaced (Banks 2007).

As noted for continuous fryer operation, an oil turnover rate of 8–12 hours is sufficient to maintain oil quality even though some of the oil will be subjected to oxidative stress for more than 30 hours. Considering that a portion of the fryer oil will be subjected to oxidative stress for more than 60 hours when turnover rates extend to 20 hours, it becomes apparent that the frying oil will degrade over time and reach the point at which it will have to be replaced.

Slow oil turnover limits the useful fry life of oil, and slow oil turnover is very common in food service operations. As a result, frying oil usually has to be downgraded and replaced periodically. It has been conservatively estimated that half of all the frying oil used in food service frying is used to exhaustion and has to be downgraded and replaced (Hunter and Applewhite 1993).

10.4 FRYING OIL OXIDATIVE STABILITY

Oils with good oxidative stability will support longer fry life than oils with little resistance to oxidation. Historically, high stability frying fats used in food service have been produced by partial hydrogenation to make shortenings or processed in combination with winterization (or fractionation) to remove high melting components and yield liquid oils. For food service frying, liquid oils are much more convenient to use than high melting shortening with regard to fryer loading, melting, and the addition of make up oil.

10.5 TRAIT-MODIFIED OILS: OXIDATIVE STABILITY

A number of trait-modified oils are now available that have low melting points and high oxidative stability and they are well suited for food service frying. The modifications common to all of these oils have been to increase the oleic content, reduce linoleic, and especially reduce linolenic when present in the parent oil. Other factors influence oil stability including oilseed quality and oil processing (Evans 1965), the type and content of inherent antioxidants (Merrill et al. 2008; Normand et al. 2001; Warner and Fehr 2008), and triacylglycerol composition (Hoshina et al. 2004). However, the common factor for developing a TMO with a low melting point and improved resistance to oxidation is based on increasing oleic content. TMOs with increased oleic content can generally be divided into two categories, mid oleic (MO) and high oleic (HO), and herein will be used corresponding to oleic ranges of ~50–75% and ~76–85% or higher respectively. Increases in oxidative stability are not linear with respect to oleic content; rather, there is a progressive increase that can become exponential at higher values.

However, oleic content alone is not definitive for the oxidative stability of an oil. There can be major differences in stability due to differences in minor components, as will be discussed below. The differences can be notable among samples of the same type of oil with the same oleic content, and even greater variations can be seen when comparing the oxidative stability of oils with the same oleic content that are derived from different types of oilseed.

Descriptive terms such as low, medium, and high, in regard to a fatty acid component of an oil, can be helpful in providing general information about a TMO relative to the parent oil. However, the terms provide little information about the quality attributes of an oil or the uses for which it may be best suited. It is necessary to read and review product specifications, including physical, chemical, and organoleptic attributes, as a basis on which to assess oil for use in a specific application. Studying specifications is even more important for discerning differences between oils from different types of oilseed that may be referenced with names containing the same or similar descriptive terms.

10.5.1 Modification of Oleic Content

A general representation for the oxidative stability of vegetable oil versus oleic content is provided in Figure 10.1. As shown, the Oxidative Stability Index (OSI) graph is relatively flat until the oleic content exceeds 50%. Increases in stability are modest in the first part of the mid oleic range but

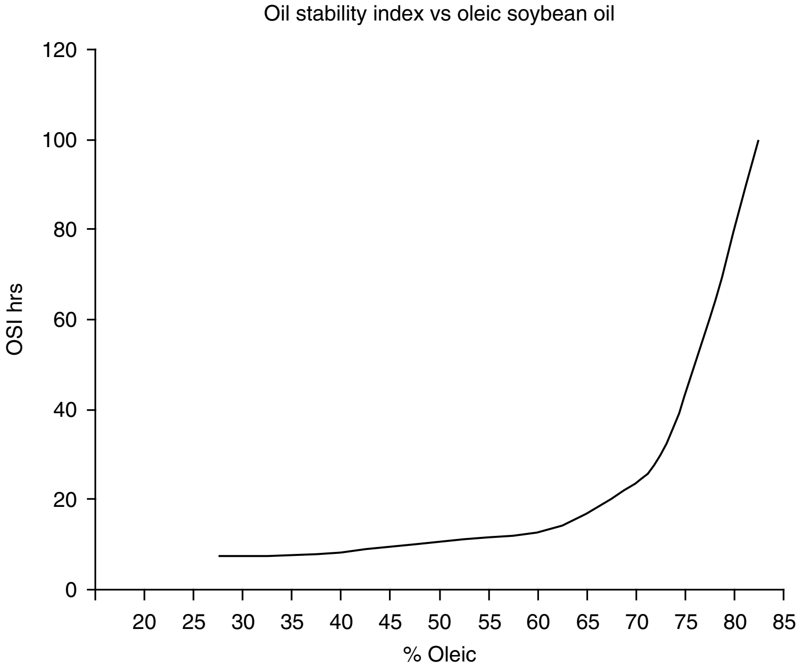

Figure 10.1 Relationship between OSI and oleic acid content.

become progressively higher toward the upper end of the range. The exponential nature of the increasing OSI values becomes apparent in the transition from the upper end of the mid oleic into the high oleic range.

Trait-modified oils with high oleic content are good candidates for food service frying. Their increased oleic content supports good oxidative stability and extended fry life; however, the oleic content per se, as noted above, is not definitive for oxidative stability. Other components, especially polyunsaturated fatty acids and natural antioxidants, are particularly important.

10.5.2 Modification of Linoleic Content

For example, Figure 10.2 shows Purdy's graph of oxidative stability (Active Oxygen Method – AOM) versus percent linoleic acid (Bartcher et al. 1968; Purdy 1985) derived from samples of regular and high oleic safflower and sunflower oils. The similarity of the graphs in Figures 10.1

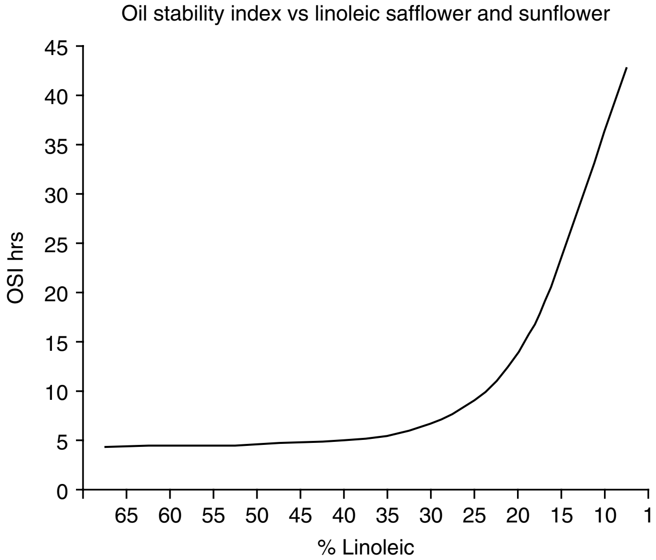

Figure 10.2 Relationship between AOM data and the fatty composition of high oleic and commodity safflower oil.

and 10.2 shows the importance of reducing linoleic in conjunction with increasing oleic to support oil stability.

Table 10.1 lists unsaturated fatty acids and OSI values for a number of samples and types of TMOs and includes principal tocopherols for several of the samples. Arguably, linolenic is a controlling factor that limits OSI stability to the area of 10 hours or less when present at a level exceeding ~4%. And when linolenic is not a factor, then the influence of linoleic on stability becomes notable. Generally, when linoleic content is present at levels of ~10% and above, the corresponding OSI value for mid oleic oils will be in the range of 15–25 hours. The influence on oil stability corresponding to variations in linoleic and linolenic content is notable in Table 10.1 and the simultaneous reduction of both fatty acids to the low single digits regularly correlates with the highest OSI values.

10.5.3 Tocopherols

Differences in the type and quantity of tocopherols are important and also have a notable impact on the oxidative stability of oils in general and the impact is even greater for the HO oils. Studies have shown

Table 10.1 Unsaturated fatty acids and OSI values for a number of samples and types of TMOs

	Fatty acids			**Tocopherols**				**OSI**
Oil	**C18:1**	**C18:2**	**C18:3**	**Total mg/100 g**	**% α**	**% γ**	**% δ**	**110°C**
HO Can[l]	84.1	3.4	4.0					24.3*
HO Can[a]	78.8	5.1	5.2	55.9	31.2	68.8	1.1	20.6
HO Can[l]	76.2	10.3	3.4					15.0*
MO Can[c]	71.3	12.3	3.9	143.8	33.3	50.8	1.2	18.5
MO Can[j]	72	18	2					17.9*
MO Can[p]	69.6	11.1	2.9	63.2	45.1	54.3	0.6	18.8
LL Can[q]	66.9	16.1	2.3	44.4	34.7	54.5		6.7
LL Can[l]	66.3	21.8	2.1					10.4
LL Can[l]	62.1	25.3	3.2					8.3
MO Corn[i]	65.1	23	0.6					14.0
HO Cotn[r]	77	4						
HO Pnut[f]	76.2	4.7						29.5*
HO Saf[n]	80.7	12.2						16.2*
HO Saf[d]	80	15						15*
MO Saf[c]	72.8	12.1	1.6	94.1	92.3	4.5	5	14.3
HO Soy[a]	85.5	1.6	2.2	160.4	5.1	71.5	23.4	80.7
HO Soy[b]	81.7	2.0	3.6	170	6.5	67.6	25.6	59
HO Soy[k]	85.1	1.3	2.0					57.5
HO Soy[o]	80.9	2.5	2.7	103	5.9	69	25	62.6
HO Soy[o]	79.2	4.2	3.2	96.6	7.0	65.1	27.8	41.6
MO Soy[o]	75	7	2.3					28
MO Soy[u]	75	15	3					18.6
MO Soy[e]	52	32.1	1.0					13.7
LL Soy[m]	25.3	58.2	1.4					8.1
LL Soy[e]	27.8	54.9	1.1					8.7
LL Soy[g]	28.6	52	2.3	71.1	8.2	70.7	19.5	6.9
HO Sun[d]	89	1.0						42.7*
HO Sun[a]	87	4.1		46.7	95.1	4.9		34.3
HO Sun[a]	82.3	9.0		50.6	93.3	6.7		20.5
HO Sun[t]	86.5	5.1						18.5
MO Sun[h]	72.4	16.8						10**
MO Sun[s]	66.9							7.0
MO Sun[s]	56.6							6.3

* Adapted from AOM data.

** Convert from Oxidative Stability Index (OSI) @ 100°C.

HO, high oleic; LL, low linolenic; MO, mid oleic.

[a]Knowlton (1997). [b]Knowlton (1999). [c]Merrill et al. (2008). [d]Purdy (1985). [e]Warner and Fehr (2008). [f]O'Keefe et al. (1993). [g]Tompkins and Perkins (2000). [h]Martin-Polvillo et al. (2004). [i]Warner and Knowlton (1997). [j]Hagen (2006). [k]Warner and Gupta (2005). [l]Kodali et al. (1999). [m]Su and White (2004). [n]Fuller et al. (1971). [o]Unpublished data. [p]Tabee et al. (2008). [q]Matthäus et al. (2009). [r]Singh and Green (2000). [s]Chang (2001) [t]Dzisiak (2006). [u]Unpublished data.

that γ- and δ-tocopherols are more effective antioxidants compared to α (Warner and Fehr 2008). For example, Table 10.1 shows samples of HO-soybean oil and HO-sunflower oil that both have oleic content exceeding 85% and the OSI of the soybean oil is 2–3 times greater than that of the sunflower oil. The difference is attributed to the fact that soy contains a higher content of total tocopherols and greater percentages of γ and δ compared to the tocopherol content of sunflower that is principally composed of α. Further, it has been shown that by adding γ- and δ-tocopherols to match the content naturally present in soybean oil, the oxidative stability of HO-sunflower oil will approach that of HO-soybean oil (Gottstein and Grosch 1990; Knowlton 1999; Warner and Fehr 2008).

Selecting frying oils for food service on the basis of oxidative stability, fry life, economics, and considerations for taste, as is commonly done for full service restaurants, hotels, institutions and similar operations, is relatively straightforward and will be addressed below. By contrast, selecting frying oils for use in national chain operations with theme menus and branded products becomes much more complex. The selection process can include requirements for taste, texture, and performance that are highly specialized and can be challenging to achieve. Some companies have spent several years conducting tests and evaluating as many as 18 varieties of oils in more than 50 blends to select just the right trans fat free oil for use in their operations (Arndt 2007; Horovitz 2006; Schmeltzer 2007). Such a selection process goes well beyond the current discussion.

10.5.4 OSI Ranges for Trait-Modified Oils

The TMOs listed in Table 10.1 include a wide range of oxidative stability that can, for discussion purposes, be divided into low, medium and high OSI ranges generally corresponding to <10 hours, 10–19 hours, and 20–30+ hours, respectively.

10.5.4.1 High stability trait-modified oils

Oils with very high OSI values ranging above 30 hours are very resistant to oxidation and are categorized as heavy duty or high performance frying oils. Historically, they have been produced by partial hydrogenation to make higher melting shortenings or further processed by winterization to make liquid or semi-solid frying oils.

With advances in seed breeding, there are now a number of TMOs that yield high performance frying oils through regular refining, bleaching, and deodorization (RBD) processing. Several oils are currently available and others are set to enter commercial production soon. These oils are not subject to rapid changes during extended usage in batch frying operations and they support the production of consistent, high quality food for extended periods. In combination with good fryer management and oil monitoring, the use of high stability oils can limit or eliminate the necessity of downgrading and replacing oil, as would be necessary when using lower stability oils. The purchase price of high stability oils can be justified based on overall economy of operation when extended fry life can be achieved.

10.5.4.2 Medium stability trait-modified oils

Frying shortenings with OSI values in the range of 10–19 hours constitute the mainstream for food service frying that has traditionally been filled by partially hydrogenated oils with melting points in the range of 88–115°F. The category now includes a wide selection of TMOs derived from essentially all types of oilseed. The numerous choices provide opportunities for selecting and using individual oils as well as for developing blends with other TMOs or regular RBD oils to achieve flavor and/or performance to meet individual needs.

The oils are liquid and free of trans fatty acid isomers. The liquid nature of these oils is especially important for safety and convenience of handling compared to shortenings. Shortenings can be difficult to cut into pieces for fryer loading and can cause problems during melting and heating for fryer startup. The TMOs with oxidative stability in the mid range are well suited for food service frying and they provide a good balance for fry life and economy of operation.

10.5.4.3 Low stability trait-modified oils

Low linolenic (LL) soybean and LL canola are lower stability TMOs with OSI values ranging around 10 hours and below. The limitation with use of the parent oils in food service batch frying is due to the characteristic painty, green, or grassy flavors/aromas that can develop during the early stages of linolenic oxidation. Reducing linolenic to below 5% supports improved flavor/aroma (Evans et al. 1965) and lowering the content below 3% essentially precludes development of the objectionable aromas.

The oxidative stability of the LL oils is moderately improved relative to the parent oils, but the major improvement is achieved by overcoming flavor issues during early oxidation. Flavor stability is the improvement that provides for usage in more applications compared to the parent oils.

As initially developed, the LL soy and canola oils were not targeted for use in batch frying, but due to two main drivers, they are now being used in a number of food service applications. The two drivers are availability and the absence of trans fatty acid isomers. As a result, food service companies have succeeded in finding ways to use the LL oils as replacements for the higher stability partially hydrogenated oils used previously.

The methodology for usage of LL oils in batch frying involves developing and implementing programs to monitor and manage both fryer operation and oil quality. However, because food service operations are highly diversified, management programs have to be tailored for each operation to be fully effective and provide support for good oil fry life.

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11 Omega 3 Oils and Blends

Ernesto M. Hernandez

Lipid Consultants, Houston, TX, USA

The increasing awareness of the health benefits of omega 3 fatty acids is reflected by the growth in consumption of omega 3 fats either as dietary supplements or in fortified foods. Physiologically, lipids play important functions in many biological processes of living organisms as a source of essential fatty acids, to facilitate absorption of fat soluble nutrients, and as an important source of energy via β-oxidation. Besides playing an important role in nutrition and biological functions, fats and oils are essential components in food processing and quality and help define the organoleptic and texture properties of most food products (Holman 1998; Kinsella 1988).

Omega 3 fatty acids, particularly the longer chain fatty acids eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), have been studied in numerous health applications. EPA is generally associated with cardiovascular protection, and has been reported to have strong antiinflammatory, antithrombotic, antiarrhythmic and antiatherogenic effects (Carlson et al. 1993; Dupont 1996; Kris-Etherton et al. 2002; Simopoulus 1997; Trautwein 2001). More recently, research into EPA has extended to study its effect on decreasing blood triglyceride levels,

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Trait-Modified Oils in Foods, First Edition. Edited by Frank T. Orthoefer and Gary R. List.

decreasing growth rate of atherosclerotic plaque, lowering blood pressure, and as a modulator of gene expression. DHA on the other hand is generally associated with cell structures, and has been found to be particularly important in neurologically related metabolism such as brain and retina development and function, and it has become an important nutrient in prenatal and postnatal nutrition for mother and child (Carlson et al. 1993; Carpentier et al. 2006; Chung 2008; Dupont 1996; Kris-Etherton et al. 2002; Simopoulus 1997; Trautwein 2001; Wang et al. 2006). EPA and DHA cannot be synthesized by the human body so they have to be derived from α-linolenic acid (ALA) through metabolic reactions or consumed directly through diet. Typical symptoms of deficiency of essential fatty acids include skin dryness, reduced growth rate, and susceptibility to infections.

11.1 PROPERTIES OF OMEGA 3 FATTY ACIDS

The main sources of omega 3 fatty acids for the general population are vegetable oils and fish. Omega 3 from vegetable sources is in the form of shorter 18 carbon chain ALA. Vegetable oils like soybean and canola and other seeds like flaxseed, walnut and chia are common sources of short chain omega 3 fatty acids. The longer chain omega 3 fatty acids, EPA and DHA, are obtained primarily from cold-water fish.

Another source of long chain omega 3, mainly in the form of DHA, is microalgae oil which is used commercially as an infant formula ingredient (Carlson et al. 1994; Jensen et al. 2000). Oil from microalgae has over 40% DHA. A relatively new source of long chain omega 3 is krill oil. Krill are shrimp-like marine invertebrates and are important organisms of the zooplankton. They are the main source of food for some large marine mammals. The main characteristic of this oil is that the EPA and DHA in it are structurally attached to phospholipid molecules. By weight, krill oil is composed of at least 30% EPA and DHA and 40% phospholipids, mostly in the form of phosphatidylcholine (Massrieh 2008).

As mentioned, oils from plants contain only the 18 carbon omega 3 polyunsaturated fatty acid or ALA. ALA is poorly converted by the human body to EPA and DHA, the actual components of many biological functions (Arterburn et al, 2006; Burdge and Wootton, 2002). However,

Table 11.1 Sources of Oils with Omega 3 Fatty Acids

Fatty acid	Menhaden %	Anchovy %	Cod liver %	Microalgae %	Flax %
Lauric (C12:0)	–	–	–	6	–
Myristic (C14:0)	7	8	4	19	
Palmitic (C16:0)	19	16	9	17	6
Palmitoleic (C16:1)	12	9	10	2	
Stearic (C18:0)	3	3	4	1	4
Oleic (C18:1)	13	9	20	9	21
Linoleic (C18:2)	2	4	1	1	16
Linolenic (C18:3)	2	1	2	4	56
Eicosapentaenoic (C20:5)	13	21	12	–	–
Docosahexaenoic (22:6)	12	10	21	46%	–

with new advances in genetic manipulation, it is now possible to engineer common omega 6 rich oilseeds such as soybean and canola to produce longer chain omega 3 fatty acids such as stearidonic acid (SDA), EPA, and DHA (Damude and Kinney 2007). Most of the studies conducted in this area are still in the lab and pilot plant phases, with the exception of SDA which is now commercially manufactured from genetically modified soybean oil (Harris et al. 2008; Ursin 2003). Table 11.1 shows common sources of long chain and short chain omega 3s.

Regarding metabolism, after absorption, omega 3 fats have several fates. They can:

- undergo β-oxidation to produce energy
- be recycled to make other fatty acids
- serve as a substrate for ketogenesis
- be stored in adipose tissue for later use by the body
- be incorporated into the phospholipids of cell membranes, where they participate in other membrane metabolic activities
- in the case of ALA, be converted into EPA, docosapentaenoic acid (DPA), and DHA.

Linoleic (LA), an omega 6, and ALA, an omega 3, cannot be synthesized endogenously and must be obtained from diet. This is the reason why they are considered essential fatty acids. LA and ALA go through a series of metabolic steps such as elongation and desaturation reactions to be converted, LA to arachidonic acid (AA) and ALA to EPA and DHA. EPA and DHA are the precursors from which many bioactive compounds are derived. The omega 3 and omega 6 metabolic pathways involve the same enzymatic reactions, thus competing for the same elongase and desaturase enzymes.

11.1.1 Omega 3 Metabolism

Metabolism of LA, 18:2n-6 (omega 6, two double bonds and 18 carbon length), begins with catalysis by the enzymes 6-desaturase, which acts on carbon 6, 5-desaturase and an elongase which continue the reaction cascade to synthesize arachidonic acid (20:4n-6, four double bonds and 20 carbon chain length). The desaturation steps in the metabolism of essential fatty acids are rate limiting and the activity rate decreases even more with age. This is the reason why in some cases it is recommended that diet be supplemented with oils rich in γ-linolenic acid for the more direct production of arachidonic acid (Carter 1988; Johnson et al. 1997). Furthermore, this competition for enzymatic activity in the omega 3 and omega 6 pathways is one of the main arguments for advocating a definition of an omega 3:omega 6 ratio and also speaks in favor of direct consumption of long chain omega 3 fatty acids such as DHA and EPA found in marine oils (Jump 2002; Wang et al. 2006).

Once the long chain omega 6 and omega 3 polyunsaturated fatty acids (PUFAs), arachidonic and eicosapentaenoic acids are present in the metabolic pathways, they become part of the synthesis cascade for the formation of eicosanoids by the action of cyclooxygenases and lipoxygenases as catalysts. This reaction cascade results in a family of oxygenated compounds with very potent bioactive properties (Dupont 1987). The relationship between essential fatty acids and eicosanoids was first reported in the mid 1960s and they were described as bioactive compounds derived originally from arachidonic acid (AA) (Van Dorp et al. 1964). The eicosanoids from omega 3 and omega 6 may act antagonistically and, as a result, an excessive and imbalanced production or deficiency can result in the onset of several pathological situations like thrombosis, arthritis inflammation or immune suppression (Jump 2002).

These eicosanoids include prostaglandins (PGs), thromboxanes (TXs), leukotrienes (LTs), lipoxins (LXs), hydroperoxyeicosatetraenoic (HPETEs), hydroxyeicosatetraenoic (HETEs), and hydroxyeicosapentaenoic acids (HEPEs). The basic mechanism of the synthesis of these eicosanoids from their precursors, either EPA or AA, involves their release from phosphatidylcholine in the cell membranes by the action of phospholipase A_2 or from membrane phosphatidylinositol-4,5-bisphosphate by the actions of phospholipase C and a diacylglycerol lipase. Then the eicosanoid synthesis begins, with the action of cyclooxygenase (COX), which yields PGs and TXs. When EPA or AA is exposed to lipoxygenases, the reactions yield HEPE, HETE, HPETE, and LTs. The more powerful series 2 PGs and series 4 LT derivatives are generated from arachidonic acid. The series 3 PGs and series 5 LT derivatives are generated from EPA. These compounds usually have a very short half-life and act in the immediate proximity of the cells where they are produced (Tapiero et al. 2002).

More specific properties of eicosanoids include modulation of renal function, mediation of allergic and inflammatory reactions, induction and inhibition of thrombotic processes and regulation of smooth muscle cell tone leading, for example, to vaso- and bronchoconstriction reactions (Sellmayer and Koletzko 1999). Eicosanoids also act as important intracellular mediators for several metabolic factions and responses. They have been identified as novel intracellular second messengers in inflammatory and mitogenic signaling (Kahn 1995). The role eicosanoids play in inflammation has been extensively researched for applications in the prevention of some diseases. Inflammation is characterized by the production of inflammatory agents such as cytokines and AA-derived eicosanoids (prostaglandins, thromboxanes, leukotrienes). Studies show that, at sufficiently high intakes, long chain omega 3 fatty acids, such as found in oily fish and fish oils, decrease the production of inflammatory eicosanoids, like cytokines and other reactive oxygen species. Long chain omega 3 PUFAs act both directly, by replacing AA as an eicosanoid substrate and inhibiting arachidonic acid metabolism, and indirectly by altering the expression of inflammatory genes through effects on transcription factor activation (Calder 2006). Increasing the (EPA + DHA)/AA ratio in membrane phospholipids has been confirmed as a form of protection in inflammatory states (Gewirtz et al. 2002).

Novel potent antiinflammatory eicosanoids and docosanoids derived from EPA and DHA, resolvins and protectins have been recently identified. They are made by the human body from EPA and DHA and produced by the COX-2 pathway, especially in the presence of aspirin. Experimental evidence indicates that resolvins reduce cellular inflammation by inhibiting the production and transportation of inflammatory cells and chemicals to the sites of inflammation. These eicosanoids have been studied in protection of the kidneys as a tool against acute renal failure (Ariel and Serhan 2007; Serhan 2005; Singer et al. 2008). This further illustrates the importance of sustaining a balance of omega 3 and omega 6 fatty acids not just because they compete for the same enzymes (desaturases and elongases), but because they can produce antagonistic types of eicosanoids.

11.2 OMEGA 3 AND NUTRITION

11.2.1 Recommended Intakes of Omega 3 Fatty Acids

The National Academies released in 2002, for the first time, the Dietary Reference Intakes Report for Energy and Macronutrients that included adequate intakes (AI) of omega 3 (as ALA) and omega 6 (as LA) (IOM IOM 2002). However, they have not issued recommendations for the longer chain omega 3, EPA, and DHA. AI is defined as a nutrient intake estimate observed in healthy individuals where sufficient scientific data are not available to suggest a recommended daily allowance (RDA). The AIs set for LA were 17 and 12 g/day for men and women aged 19–50 years, respectively. The AI for ALA was 1.6 and 1.1 g/day for men and women aged 19–70 years, respectively (IOM 2002) (see Table 11.2). Also in 1999, the National Institutes of Health (NIH) published a report from a sponsored international workshop on the essentiality and recommended dietary intakes for omega 6 and omega 3 fatty acids. This NIH working group proposed adequate intakes of 2–3% of total calories

Table 11.2 Adequate Intakes for α-Linolenic Acid

Life stage	Age	Source	Males (g/day)	Females (g/day)
Infants	0–6 months	ALA, EPA, DHA*	0.5	0.5
Infants	7–12 months	ALA, EPA, DHA	0.5	0.5
Children	1–3 years	ALA	0.7	0.7
Children	4–8 years	ALA	0.9	0.9
Children	9–13 years	ALA	1.2	1.0
Adolescents	14–18 years	ALA	1.6	1.1
Adults	19 years and older	ALA	1.6	1.1
Pregnancy	All ages	ALA	–	1.4
Breastfeeding	All ages	ALA	–	1.3

Source: IOM (2002).
ALA, α-linolenic acid; DHA, docosahexaenoic acid; EPA, eicosapentaenoic acid.
*, All omega 3 polyunsaturated fatty acids present in human milk can contribute to the adequate intake for infants.

for LA, 1% of total calories for ALA, and 0.3% of total calories for EPA and DHA. The group further recommended intakes of EPA and DHA of 650 mg/day and a minimum of 300 mg DHA/day during pregnancy and lactation. Other countries such as Canada suggest a minimum of 3% of energy from omega 6 fatty acids and 0.5% from omega 3 fatty acids or 1% for infants who do not receive a preformed source of EPA and DHA. The United Kingdom recommends intakes of 1% of energy from ALA and 0.5% from EPA and DHA combined (Gebauer et al. 2006; Kris-Etherton et al. 2002).

The World Health Organization has also issued recommendations on the basis of the ratio of omega 6 to omega 3 fatty acids of 5:1–10:1. Other countries such as Sweden recommend a ratio of 5:1, Canada recommends 4:1–10:1, and Japan recently changed its recommendation from 4:1 to 2:1. The ratio of omega 6 to omega 3 intake in the Western diet has been estimated at 20:1.

For patients with documented heart disease, the American Heart Association (AHA) recommends intake of about 1 g of EPA+DHA per day. For people who need to lower their blood triglycerides, an intake of 2–4 g of EPA+DHA per day is recommended under a physician's care. The AHA also recommends that patients without documented coronary heart disease get omega 3s through the consumption of fish (preferably fatty fish) at least twice a week and include in their diet oils rich in ALA (flaxseed, canola, and soybean oils; flaxseeds and walnuts). In England, the Scientific Advisory Committee on Nutrition (SACN) recommends intake of 450 mg of DHA+EPA per day. Europe has recently issued recommendations of 250 mg/day of EPA+DHA for adults.

Besides the type and source of omega 3 fatty acids, there have concerns regarding the risks involved in the consumption of fish versus plant origin PUFAs. Some types of fish have been reported to contain high levels of mercury, polychlorinated biphenyls (PCBs), dioxins, and other environmental contaminants (Melanson et al. 2005). Some species of fish may contain significant levels of methylmercury, considered one of the most dangerous sea food contaminants today. In general, older, larger, predatory fish and marine mammals, such as swordfish and seals, tend to contain the highest levels of these contaminants (Foran et al. 2003). PCBs and methylmercury are reported to have long half-lives in the body and can accumulate in people who consume contaminated fish on a frequent basis. In the case of PCBs, it is recommended that consumers reduce their exposure to these contaminants by removing the fat from these fish before cooking them; however, methylmercury represents a more serious problem since it is distributed throughout the skin, muscle, and organs of the fish.

The Food and Drug Administration (FDA) regulates the safety of all commercial fish, including ocean caught, farm raised, and imported fish. One example is the recommendation for pregnant women and nursing mothers to limit their consumption of sport caught fish to one 6-ounce meal per week. The Environmental Protection Agency recommends that young children consume less than 2 ounces of sport caught fish per week. The FDA also recommends that women who are pregnant or nursing and young children eliminate shark, swordfish, king mackerel in the mackerel family, and tilefish from their diets completely. Also consumption of other fish should be limited to 12 ounces per week to minimize exposure to methylmercury. The FDA has concluded that a safe level of methylmercury is less than 1 ppm in 7 ounces of fish. Sources of omega 3 grown under controlled conditons, such as vegetable oil or oil from microalgae grown in fermenters, are reported to be free of or very low in contaminants.

11.3 PROCESSING OMEGA 3 OILS

11.3.1 Refined, Bleached, Winterized, and Deodorized Fish Oil

All polyunsaturated oils such as omega 3 oils, regardless of the source, are inherently unstable and prone to oxidation. This presents problems of rapid deterioration during processing, cooking or storage and special precautions have to be taken in refining and minimizing exposure to high temperatures and air. If omega 3 oils are not properly processed and carefully handled, any residual “fishy” taste and aroma will become one of the major obstacles for acceptance of omega 3 fortified food products and nutritional supplements.

Fish oil is commonly refined using the conventional processing steps similar to vegetable oil processing, i.e., neutralization, bleaching, winterization, and deodorization (Hernandez 2013). The step of winterization is sometimes added to remove the more saturated fraction in fish oil and to enrich the polyunsaturated content of the final oil. The step of molecular distillation is practiced by some manufacturers to further purify the oil (Breivik and Thorstad 2005). First, the acidity in the oil is normally neutralized with a caustic solution in stoichiometric amounts. Removal of waste or saponified matter is then done, usually by centrifugation. Silica gels have increasingly been used in the industry to replace water washing of the oils after caustic refining.

After the neutralization step, the fish oil is bleached to remove some color, decompose peroxides, and remove contaminants. This step is particularly important for fish oils to insure the removal of harmful metals such as mercury and arsenic. The most common bleaching agent used in oil processing is acid activated clay. Activated carbon is also commonly used to help remove environmental contaminants such as PCBs and dioxins (Oterhals et al. 2007), but this method of contaminant removal is not as effective in removing polybrominated diphenyl ethers (PBDE), used as flame retardants.

Fish oils have a saturated fraction that crystallizes and forms a haze and a solid layer during storage, especially at cold temperatures. Winterization or chill fractionation is used to remove the more saturated fraction and therefore to increase the amount of omega 3 in the clear oil.

The process is carried out on the bleached oil by chilling the oil to temperatures below 5°C. The solid fraction generated can then be removed by filtration.

In order to remove the fishy odor and taste from fish oil, the last step in the process is usually deodorization. This step is done at relatively high temperatures and very high vacuums. The steam used strips off not just odors and flavors but other impurities such as free fatty acids, peroxides and contaminants such as organochlorine pesticides and polycyclic aromatic hydrocarbons.

Once the oil is deodorized, packaging is done under nitrogen to prevent oxidation. Natural and synthetic antioxidants such as tocopherols, tert-butylhydroquinone (TBHQ) and rosemary extracts are commonly used to help prevent deterioration of the oil.

The susceptibility of polyunsaturated fats to oxidization and deterioration is greatly exacerbated by the presence of metals such as copper and iron. Iron is a well known prooxidant naturally present in fish muscle and has been identified as being responsible for the generation of "fishy" notes in omega 3 oils in both short and long chain PUFAs. Fishy off flavors have been identified as volatiles comprising alkenals, alkadienals, alkatrienals, and vinyl ketones. These compounds, generally identified as fishy, metallic, and rancid off flavors, are considered one of the major deterrents for the increased consumption of fish and fish oils.

11.3.2 Molecular Distillation

Molecular or short path distillation is being more commonly utilized in fish oil processing to ensure the removal of contaminants. This step is normally conducted after bleaching and winterization (Breivik and Thorstad 2005). Molecular distillation allows for lower processing temperatures and lower residence times than conventional oil deodorization. The main reason for this is that it is conducted at very high vacuums so it is less likely that an oil prone to deterioration, such as fish oil, will be damaged during processing. This technology effectively eliminates contaminants such as PCBs, dioxins, furans, pesticides, and herbicides.

It is generally preferred that the bioactive omega 3 fatty acids in fish oil be in a concentrated form for use in supplements and pharmaceutical applications. In this case molecular distillation is used to concentrate EPA and DHA in the form of ethyl esters. Consumption of omega 3 in the form of ethyl esters is growing fast in pharmaceutical applications. A blend of ethyl esters of EPA and DHA, in concentrations as high as 80%, is the only source of omega 3 approved as a pharmaceutical for the reduction of blood triglycerides (Breivik et al. 1997).

11.4 STABILIZATION OF OMEGA 3 OILS

The properties of polyunsaturated omega 3 oils have given rise to a wide variety of new antioxidants and processes to allow for the protection of the PUFAs. The main objectives of protection of omega 3s are to prevent development of rancidity and off flavors and to preserve the bioactivity of the essential fatty acids.

Unlike the more saturated fatty acids such as omega 6 and monounsaturated fatty acids such as oleic acid, even a slight oxidation of omega 3 will produce an oil or food product with very poor organoleptic qualities. The susceptibility of polyunsaturated fats to oxidize and deteriorate is greatly exacerbated by the presence of metals such as copper and iron (Kamal-Eldin and Yanishlieva 2002). Iron has been identified as being the most responsible for the generation of "fishy" notes in omega 3 oils in both short chain PUFAs in linolenic acids (C18:3) from vegetable oils and in longer chain PUFAs from fish oils. While omega 3 oils generate fishy notes, other fatty acids such as oleic acid (18:1) have been identified with cooked beef fat flavor. Saturated and monounsaturated fatty acids have been positively correlated with pork taste. The products of oxidation of linolenic and other PUFAs have been positively identified with fishy and metallic flavors (Jeung-Horng et al. 2002). In one study, where pigs were fed a diet high in linolenic acid (18:3), the fat from the bacon was considered to have a "fishy" flavor (Romans et al. 1995). The specific compound identified as having a fishy off flavor after oxidation of fish oil was 2-trans, 4-cis, 7-cis-decatrienal (Venkateshwarlu et al. 2004).

A report on milk and mayonnaise fortified with fish oil identified over 60 different volatiles as having a strong fishy odor, including alkenals, alkadienals, alkatrienals, and vinyl ketones. The most potent odors were identified as 1-penten-3-one, (Z)-4-heptenal, 1-octen-3-one, 1,5-octadien-3-one, (E,E)-2,4-heptadienal, and (E,Z)-2,6-nonadienal, with 1-penten-3-one reported as the major contributor to the unpleasant sharp fishy off flavor in fish oil. These off flavors, generally identified as fishy, metallic, and rancid, are considered one of the major deterrents to the increased consumption of fish and fish oils (Donnelly et al. 1998; Jacobsen et al. 1999). Fish oil can also be added directly into some foods for fortification, with various degrees of success (Warnants et al. 1999).

11.4.1 Oxidation

Omega 3 oils typically oxidize by the free radical chain mechanism. This process of oxidation includes four distinct phases: initiation, propagation, chain branching, and termination. The oxidation is initiated by the abstraction of a hydrogen atom from a lipid molecule to form alkoxyl radicals. This triggers a new chain reaction where peroxyl radicals are formed. This reaction then leads to hydroperoxides (ROOH). These peroxides can themselves form several free radicals (R•, RO•, and ROO•) by branching. These reaction moieties can then trigger another chain reaction, thus propagating the oxidation reaction further. The rate of hydrogen abstraction generated in the propagation phase by RO• is in the order of 10^4–10^6 times faster than by ROO• (Frankel 1998; Kamal-Eldin and Yanishlieva 2002).

In fatty acid molecules having "methylene interrupted" double bonds, like linoleic, linolenic, arachidonic acids, EPA and DHA, only bis-allylic methylene groups are attacked. The tendency of these acids to oxidize was found to increase approximately two-fold for each bis-allylic methylene group. The relative rates of autoxidation of stearate, oleate, linoleate, and linolenate have been reported as 1, 11, 114, and 179 respectively (Donnelly et al. 1998; Frankel 1998; Frankel et al. 1996).

The autoxidation reaction of PUFAs can be prevented by two mechanisms and two types of inhibitors. The first is compounds such as aromatic phenols that can break the oxidation chain reaction. The chain reaction breaking antioxidants act by competing with the substrate for the chain carrying radical species normally present in the highest concentration. Other types of antioxidants that prevent oxidation include hydroperoxide decomposers, metal chelating agents, and singlet oxygen quenchers (Yanishlieva-Maslarova 2001).

11.4.2 Antioxidants

The main types of antioxidant used to stabilize omega 3 oils can be natural or synthetic. Common synthetic antioxidants include TBHQ, butylated hydroxy toluene (BHT), and propyl gallate. Until recently natural antioxidants had limited application in omega 3 oils. However, with the development of new extracts, the use of natural antioxidants in vegetable oils in general and omega 3 fats in particular is now more common. Extracts from herbs including rosemary and oregano have been found to be as effective as some synthetic antioxidants. Rosemary extract is particularly effective in combination with other antioxidants such as tocopherols (Xin and Shun 1996). The active compounds in rosemary extract are reported to be phenols such as carnosol, rosmanol, rosamaridiphenol and phenolic acids such as carnosic acid and rosmarinic acid. This extract has been used effectively to prevent oxidation of fish oils like sardine. Rosemary compounds also have been reported to inhibit the formation of oxidation products such as conjugated dienes and pentenal, but not propanal in fish oil emulsions (Frankel et al. 1996).

The new natural antioxidant systems seem to work more efficiently when used in combination with other antioxidants and also other chelating agents such as ascorbyl palmitate. A strong synergistic effect was reported between α-tocopherol (0.02%) and rosemary extract (0.02%) in sardine oil 9 (Wada and Fang 1992). Dry oregano, at 0.5% in mackerel oil stored at 40°C in the dark, had an antioxidant effect that was comparable to the effects of 200 ppm BHT or 0.5% dry rosemary (Tsimidou et al. 1995). When oregano was tested at 1%, the activity was comparable to 200 ppm TBHQ. A mixture of α-tocopherol and rosemary extract (0.035% + 0.035%) was useful in inhibiting fish lipid oxidation catalyzed by Fe^{2+} or hemeprotein.

Extracts of sesame seed have also been reported to be effective antioxidants. Extract from sesame seeds/cakes obtained by solvent extraction is reported to be an effective antioxidant in common vegetable oils/emulsions/lipid systems in foods, cosmetics, and pharmaceuticals (Jayalekshmy et al. 2008). The antioxidant extract/concentrate produced was a mixture of compounds including sesamol, sesamin, episesamin, sesamolin, related derivatives, tocopherols, lygophenols/ferulic acid, denatured proteins, sugars, lipids, minerals, and browning products that result from the Maillard reaction.

Extracts of marine red algae have been reported to have strong antioxidant activity when tested in linoleic acid and fish oil. This algal extract was shown to be of comparable or better efficacy than BHA and BHT when tested at 0.01%, 0.03%, and 0.05% in fish oil. Positive results have been obtained in inhibiting oxidation of linoleic acid and fish oil at 0.05%. However, this extract had a poor 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging ability. The extracts, therefore, may not be able to quench radicals from the medium, but may delay lipid peroxidation by suppressing radical initiation by metal chelation (Athukorala et al. 2003).

Green tea extracts have been reported to have both antioxidant and prooxidant activity. They were tested in seal blubber and in menhaden oils and reported to have prooxidant activity possibly due to the catalytic effect of chlorophyll. After removal of chlorophyll by a chromatographic technique, the resultant extract showed excellent antioxidant activity in both oils (Wanasundara and Shahidi 1998). It was also reported that when individual green tea catechins were separated and applied at levels of 200 ppm, this prevented the oxidation of seal blubber and menhaden oil under Schaal Oven Test conditions at 65°C for 144 hours (Ho et al. 1997).

As mentioned, antioxidants are reported to be more effective when used in combination with chelating agents such as ascorbyl palmitate, which is probably the most widely used fat soluble chelating agent. Other chelating agents such as ethylenediaminetetraacetic acid (EDTA) have also been reported to be effective when used in combination with other antioxidants (Jacobsen et al. 1999). In general, the most effective antioxidant agents involve ternary systems and include free radical scavengers, chelating compounds, and synergistic agents like phospholipids. A mixture of natural antioxidants such as tocopherols, rosemary extract, ascorbic acid, and phosphatidyl choline was reported to be an effective antioxidant system in several types of fish oils and polyunsaturated vegetable oils (Chang et al. 1991).

11.4.3 Emulsions

Emulsions with edible oils are generally manufactured as delivery systems, as an intrinsic part of particular foods or are themselves the final food product such as margarines, salad dressings, and beverages. In the case of omega 3 oils, emulsions can serve as a delivery system and also can provide protection against oxidation. An emulsion consists basically of two immiscible liquids (usually oil and water), with one being dispersed in the other in the form of small spherical droplets. The size of the dispersed droplets typically will vary between 0.1 and 100 microns (McClements and Decker 2000). Emulsions of omega 3s are usually in a system where the oil droplets are dispersed in an aqueous phase. These omega 3 emulsions with fish oil have been incorporated into different emulsified food products such as mayonnaise, yoghurt, milk, and spreads with various levels of success (Kolanowski et al. 2002; Let et al. 2004).

Oxidative stability of fish oil in emulsion has been extensively studied and a series of antioxidant systems active in both the continuous and dispersed phases have been developed. Most reports show that effectiveness of the antioxidants will depend on the partitioning of antioxidant molecules into the different emulsion phases (Coupland and McClements 1996; Frankel et al. 2002; Kolanowski et al. 2007). The principle of the antioxidant effect is that nonpolar antioxidants such as tocopherols are particularly effective in oil in water emulsion systems, and that metal chelating agents and secondary antioxidants such as EDTA and citric acid provide synergistic effects by preventing dissolved metals from triggering any further oxidation. Blending omega 3 oils with less saturated and more stable oil in the emulsion is also an effective way to protect the fish oil against oxidation. Reported results showed that addition of rapeseed oil to fish oil (1:1) prior to emulsification into milk significantly protected the emulsions against oxidative deterioration. Addition of propyl gallate and a citric acid ester to the fish oil prior to emulsification also protected the fish oil enriched milk during storage. It was suggested that the tocopherols in rapeseed oil may be the protective factor (Let et al. 2004).

11.4.4 Microencapsulation

Microencapsulation technology has been traditionally used in the food industry for flavor encapsulation where flavors are stabilized and their release controlled (Madene et al. 2006). Encapsulation is now widely used in the food and supplements industries to protect and enable the incorporation of bioactive component in fortified foods and nutritional supplements. This technology is also used to ensure that the taste, aroma, or texture of food is not adversely affected (Brazel 1999; Jónsdóttir et al. 2005; Kolanowski et al. 2007; Pszczola 1998). Also microencapsulation is used to mask off flavors contributed by certain vitamins and minerals, permit timed release of the nutrients, enhance stability at extreme storage conditions and minimize undesirable chemical interactions with other ingredients (Augustin and Sanguansri 2008).

Encapsulation has become a preferred method to protect fish oils against oxidation and it is also used as an efficient delivery system for several applications in the food and nutritional supplements industries. The most basic encapsulation consists of a dried product generated from an aqueous dispersion of an oil in water emulsion, where the water phase is removed by evaporation and the dispersed oil phase is converted into a dry powder. The water is normally removed by spraying the emulsion into a hot dry air stream, resulting in moisture evaporation. Spray drying is commonly conducted in the following stages: atomization, air contact, evaporation, and product recovery. The resulting powder then goes through a cooling phase or through other subsequent processing steps such as fluidized bed plating (Beindorff and Zuidam 2010).

Microencapsulation has been used successfully in many food and supplement applications such as cereals, nutrition bars, and beverages (Hernandez and de Jong, 2011). Milk is a particularly difficult product to fortify because of the tendency of off flavors to readily appear. This makes it necessary to protect the fish oil through microenecapsulation to prevent deterioration and shorter shelf-life (Keogh et al. 2001). In the case of fish oil, it is recommended that when encapsulating omega 3 oils relatively low spray drying temperatures be used in order to minimize lipid oxidation (Baik et al. 2004; Drusch et al. 2007). Nitrogen can be used instead of air to dry the dispersion but it increases manufacturing costs appreciably. Examples of carriers used in microencapsulated omega 3 oils include maltodextrin, glucose syrup, proteins, sugars, gums, pectin, modified cellulose (e.g., hydroxypropyl methylcellulose or methylcellulose), and/or modified starch (Drusch and Schwarz 2006; Drusch et al. 2006; Jónsdóttir et al. 2005; Kagami et al. 2003; Keogh et al. 2001; Kolanowski et al. 2004, 2006, 2007).

Silica powders and and tricalcium phosphate can be added at the end of the microencapsulation process to enhance the flowing properties of the powders (Drusch et al. 2006).

11.4.5 Nanoparticles

Emulsions are inherently unstable systems that require emulsifiers and homogenization forces to be applied to disperse an immiscible phase into another fluid. This instability is due to several factors: the fat content, the type and ratio of the emulsifier, the viscosity of the continuous phase, the volume fraction of the dispersed phase, droplet size distribution and processing temperature. Liposomes, because of their smaller particle size and other physicochemical factors, are more thermodynamically stable and are considered more stable carriers of bioactive compounds (Muller and Keck 2004).

The ability of phospholipids to form liposomes has been utilized to manufacture thermodynamically stable dispersions of omega 3 fats. These liposomes which can enclose an aqueous phase can better preserve the oxidative stability of encapsulated molecules, including several classes of lipids and fatty acid ethyl esters (Aseki et al. 2002; Imai et al. 2008).

Liposomes are essentially closed bilayer membranes in the form of vesicles or sacs containing an entrapped aqueous phase. Liposomes with a single bilayer membrane are referred to as unilamellar vesicles and lipsomes with a number of concentric lipid bilayers separated by an aqueous phase are referred to as multilamellar vesicles. A stable liposome is typically prepared by dissolving a lipophilic material in a phospholipid followed by the addition of water or an aqueous solution and mixing by an emulsification method such as sonicating to producing a liposome with the lipophilic material encapsulated in the lipid bilayer. In the case of fish oil, the resulting liposomes have been reported to provide effective antioxidant protection (Haynes et al. 1991).

Nanoemulsions made from salmon oil and marine lecithin by high pressure homogenization showed that crude salmon oil was well protected by its own natural antioxidants (tocopherols and astaxanthin). It was also reported that marine lecithin generated the most stable liposomes. The use of marine phospholipids as emulsifiers in nanoemulsion preparation notably increases the stability of salmon oil against oxidation with droplet sizes ranging between 160 and 200 nm (Belhaj et al. 2010). Nanoemulsions are also considered an efficient form of delivery of bioactive compounds in general and of omega 3 fatty acids in particular for applications in food and pharmaceutical industries.

The latest generation of lipid dispersions at nano scale levels is nanoencapsulation systems of solid lipid micro- and nanoparticles (SLN) (Cortesi 2002; Weiss et al. 2008). These systems show the advantages of liquid nanoemulsions (or microemulsions) of rapid dispersion and also of high permeability of the bioactive compounds through the walls of the digestive system, with the added benefit of stabilizing the encapsulated compound for ease of handling and delivery. Solid lipid nanoparticles consist of a core of solid lipid with the bioactives being a part of the lipid matrix (Schubert and Muller-Goymann 2005). The particle is stabilized by a surfactant layer, which may consist of a single surfactant or combination of emulsifying agents with different hydrophilic lipophilic balance (HLB) values. This allows for the manufacture of particles with distinctly different properties such as targeted applications and timed release effect. Particles from crystallized lipids instead of liquid lipids have been shown to have better release control and provide more stability of incorporated bioactives, especially in the case of omega 3s. This is explained by the fact that the mobility of bioactives can be manipulated by controlling the physical state of the lipid matrix. These properties have been used to develop new products such as drug carrier systems that can be water soluble, lipophilic, and target specific (Gupta et al. 2006; Muller and Keck 2004; Sivaramakrishnana et al. 2004).

11.5 OMEGA 3 OILS SPECIALTY BLENDS

Omega 3 oils are blended with other oils and other ingredients to increase their stability, to facilitate delivery and functionality, and to increase the nutritional value of foods and supplements. Simple blending of omega 3 oils with more stable oils has been reported to increase the overall stability of polyunsaturated fats (Sundram et al. 1999). More recently, biotechnology has had an appreciable impact on the blending and transformation of several vegetable oils and animal fats, including omega 3 oils. These new technologies have given rise to a number of new biotech based lipid products, from nontrans products to specialized delivery of bioactive lipids (Hernandez 2008; Schörken and Kempers 2009).

Immobilized lipases have now become accepted as a mainstream technology for fat modification and are widely used in commercial applications (Holm and Cowan 2008). With regard to omega 3 fats, interesterification reactions using lipases are used to chemically blend them with several types of oils and fats to improve nutritional and rheological properties of the final product (Halldorsson et al. 2004; Hernández-Martin and Otero 2008; Osorio et al. 2009; Zu-yi and Ward 1993).

11.5.1 Structured Lipids

The reaction of interesterification is basically the exchange of carbonyl groups of fatty acids within and between the triglyceride molecules. There are three reactions associated with interesterification: acidolysis, alcoholysis, and transesterification (Hernandez 2008; Huang and Akoh 1996; Willis et al. 1998). These reactions involve fatty acid exchange with other triglycerides or fatty acids or esterification of fatty acids with alcohols. In the case of omega 3, esterification with ethanol has recently found a wide application in the pharmaceutical industry. Interesterification of fatty acids can generally be conducted using either enzymes or chemical interesterification (Zu 2000).

Chemical interesterification has some advantages over enzymatic modification, including lower catalyst cost, use of existing and more available industrial procedures and equipment, and shorter reaction times (Konishi et al. 1993).

Immobilized lipases are commercially available and widely used for industrial and research applications and offer several advantages over chemical interesterification, i.e., lower processing temperatures with fewer chemicals and selectivity of the position of the esterification in the glycerol molecule. The selectivity of these reactions can be manipulated towards the production of triacylglycerols with specific fatty acid chain length or position specific in the triglyceride

(Ghazali et al. 1995). Immobilized lipases can also be manipulated for selectivity towards the ethyl esters of stearic acid, conjugated linoleic acid (CLA), and DHA. The production and yields of tailored triacylglycerols can be manipulated by changing enzyme loading, reaction times, and temperatures (Osorio et al. 2009; Torres et al. 2003).

Regarding omega 3 oils, it has been reported that the fatty acid composition of tuna oil was chemically modified to enrich omega 3 PUFAs, primarily EPA and DHA, by using sodium methoxide ($NaOCH_3$) as catalyst. The effects of reaction time and temperature, catalyst concentration, and reactants mole ratio were studied, showing an enrichment in DHA and EPA after transesterification (Klinkesorn et al. 2004).

Commercial immobilized lipase from *Thermomyces lanuginosa* (1,3 specific) was reportedly used in the transesterification of blends of palm stearin, palm kernel oil and a concentrate of triacylglycerols (TG) enriched with omega 3 PUFA. These blends were used to fortify margarines with omega 3s. Two different concentrates of TG rich in omega 3 PUFA, containing mainly EPA and DHA in different proportions, were tested (Fajardo et al. 2003).

Lipases, commercially available in an immobilized medium such as granulated silica, have been investigated in transesterification in blending of three different fats to increases the heterogeneity of the TGs and generate β' type crystals which produce a smoother, more palatable mouthfeel ideal for use also in margarines (Nascimento et al. 2004). This same technique has been used in the development of nutritionally enhanced fat products such as the synthesis of an equivalent to human milk fat by enzyme catalyzed acidolysis of tripalmitin with oleic acid and omega 3s in solvent free media at 60°C. Four immobilized enzymes were tested in the same systems: *C. parapsilosis* lipase/acyltransferase and the immobilized commercial lipases from *Rhizomucor miehei*, *Thermomyces lanuginosus* and *Candida antarctica* (Tecelão et al. 2010).

Blends of DHA and EPA along with CLA have been reported to have positive effects on alleviating or preventing obesity (Li et al. 2008). This work alludes to the balance between energy intake and expenditure and influence in body weight and/or fat deposition in animal models. These fats are also involved in the regulation of the key enzymes responsible for lipid synthesis, such as fatty acid synthase and stearoyl-CoA desaturase-1, lipid oxidation and thermogenesis as well as the incorporation of free fatty acids into adipocytes for lipogenesis.

11.5.2 Structured Phospholipids

The latest generation of specialized blends with omega 3 involves phospholipids. The major sources of phospholipids (PLs) in our diet are oilseeds and egg yolk. They are widely used in foods, pharmaceuticals, confectionery, and cosmetic products as efficient natural emulsifiers. Several nutritional applications of structured PLs have been reported (Hernandez and Quezada 2008; Hosokawa et al. 1998). Structured phospholipids can also be enzymatically manufactured by chemically combining PLs with bioactive fatty acids such as omega 3s and other fatty acids with biological functions such as CLA (Guo et al. 2005; Hossen and Hernandez 2005). It has been suggested that by replacing the existing fatty acids in an original PL molecule with bioactive one, better physiological results can be obtained from the modified PLs. Enzymatic production of both structured lipids and phospholipids is preferred to chemical methods, especially when the reaction is required to be position specific and a specific fatty acid has to be incorporated.

The modification of phosphatidylcholine (PC) was reported using phospholipase A1 to catalyze the acidolysis with the fatty acids from fish oil (Kim et al. 2007). These authors report PC as containing significant levels of EPA (C20:5), DPA (C22:5), and DHA (C22:6) acid residues. Modification of PC was accomplished in a solvent free system using phospholipase A1 from *Thermomyces lanuginosus/Fusarium oxysporum* as the biocatalyst. The effects of reaction parameters such as reaction time, enzyme loading, temperature, and vacuum on the yield of structured phospholipid with EPA and DHA were studied.

Regarding applications of structured phospholipids with omega 3 PUFAs, esterified PLs with fish were reported to have positive effects on children with impaired visual sustained attention performance. Blood lipid alterations in LC omega 3 fatty acids were correlated with these changes (Vaisman et al. 2008). DHA containing PLs has been shown to have potential medical applications such as improvement in brain function and prevention of cerebral apoplexy (Peng et al. 2002).

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12 New Users Viewpoint

Gary R. List[1] and Frank T. Orthoefer[2]

[1] *USDA ARS NCAUR (Retired), Peoria, IL, USA*
[2] *FTO Foods, Knoxville, TN, USA*

An edible fat or oil must satisfy three criteria: functionality, oxidative stability, and health/nutrition. Since no one fat or oil satisfies all the requirements, modification is needed. For many years hydrogenation has been the technology of choice because both functionality and oxidative stability are addressed. However, industrial hydrogenation produces significant levels of trans and in some cases saturated acids. Thus the focus now is on the health/nutrition requirements for fats and oils.

Over the past several decades, consumers have demanded products low in saturated and trans fats because of concerns over elevated cholesterol levels and possible links to coronary heart disease (Mensick and Katan 1990). Under the Nutrition Education Labeling Act (NELA) passed by the US Congress in 1990, trans fat labeling became law in July 2003 (Anon 2003). Key provisions are that saturated and trans fats are to be listed on nutrition labels effective January 1 2006 along with saturated fats but foods containing less than 0.5 g trans fat/serving may be declared zero. Serving size is determined by the Food and Drug Administration (FDA). The serving sizes for margarines, spreads, and shortenings are 12–14 g.

Trait-Modified Oils in Foods, First Edition. Edited by Frank T. Orthoefer and Gary R. List.

The number of foods reformulated to low/zero trans fat rose dramatically during the period 2003–2007. A recent report indicates that trans fats have been successfully removed from food groups cited to be the highest prior to labeling (Rahovsky et al. 2012). This chapter will cover approaches to reformulating foods low in saturated and trans fats from a new user point of view. Emphasis is given to deep fat frying, baking applications, and other food uses.

12.1 SOURCE FATS AND OILS

Liquid oils (unhydrogenated), including soybean, corn, cottonseed, canola, sunflower, peanut, and olive, are composed of triglycerides with double bonds in the cis configuration and are thus essentially free of trans fats. They may, however, contain small amounts (1–2%) of trans isomers that are formed during deodorization, the final step in edible oil processing. Labeling regulations cover only trans fats produced by industrial hydrogenation and are not declared on nutrition labels. In other words, trans monoenoic acids are to be declared. Palm, palm kernel, and their fractions as well as coconut oil also are essentially free of trans acids but they are high in saturated acids (50–90%). However, these oils provide needed functionality for many food applications including spreads, baking shortenings, and frying fats.

Soybean oil accounts for about 70% of edible domestic usage (nearly 17 billion pounds) and is cheap, readily available and performs well in most food products. Moreover, soybean oil is high in polyunsaturates, relatively low in saturates, and the largest commercial source of omega 3 acids. The vast majority of commercially available spreads, shortenings, and salad/cooking oils contain soybean oil in some form, either as a liquid, partially or in completely hydrogenated form. Over the past 15 years or so, a number of trait-modified soybean oils have been introduced into the marketplace, including low/ultra low linolenic, mid oleic, and high oleic oils (see Chapter 10). Soybean oils high in stearic acid are under development and should be commercialized within 3–5 years.

Cottonseed oil is an excellent source of polyunsaturates but contains high amounts of saturated fatty acids which may deter its use in some products because of nutrition labeling requirements. Nonetheless, cottonseed oil has found widespread use in fried foods and salty snacks. Partially hydrogenated cottonseed oil is found in many food products including cookies, crackers, pizza doughs, and frozen pie crusts. In 2008–2009 cottonseed oil usage amounted to about 690 million pounds.

Corn oil is considered to be naturally stable, high in polyunsaturates, low in saturates and free of linolenic acid. Over the past decade, domestic edible usage has remained fairly static at 1417–1705 million pounds. Major outlets for corn oil include frying fats, snack foods, and brand name spreads.

Sunflower oil is a very rich source of polyunsaturates (upwards of 70% linoleic acid) and an excellent choice for salad oil, margarines, and spreads as well as snack foods. However, conventional sunflower oil undergoes rapid polymerization during deep fat frying which is a distinct disadvantage because of shortened fry life. In response, the industry has commercialized mid oleic (NuSun) and high oleic sunflower oils (Gupta 1998; Miller et al. 1987). Historically, sunflower oil has commanded a higher price than other commodity oils. In 2007, when vegetable oil prices rose rapidly, sunflower oil sold for more than 90 cents per pound compared to 52–69 cents for other commodity oils.

Canola oil is distinguished from rapeseed oil (high erucic acid rapeseed – HEAR) as the latter contains significant amounts of erucic acid. Low linolenic canola (low erucic acid rapeseed – LEAR) contains about 4% linolenic acid compared to 9–10% in low erucic rapeseed. The mid-high oleic contains about 3% linolenic acid with oleic contents in the 65–75% range. Canola oil usage has increased from 1435 million pounds in 1999 to over 3000 million pounds. The major uses for canola include frying oils, spray oils and applications where improved oxidative stability and long shelf-lives are needed (see Chapter 10).

12.2 ANIMAL FATS

Butter, lard, and beef tallow represent a 2.6 billion pound market for food products in the US. Although they provide many functional advantages (sensory properties, improved structure, solid fat for baking), animal fats tend to be higher in saturated acids than vegetable oils and contain cholesterol which may impact nutrition labeling (Kincs 1985)

12.3 TROPICAL FATS

Palm, palm kernel, and their fractions as well as coconut oil represent options for food use. Although high in saturated acids (50–90%), tropical based fats are highly functional in many baking applications. For example, unfractionated palm oil serves as an all purpose shortening. Fractionated palm and palm kernel oil yields a less saturated (olein) fraction for deep fat frying and a saturate rich (stearine) fraction (Deffense 1985) that can be used as a structuring fat for shortening and spreads (Ullanoormadam 2004). Palm oil usage in the US has increased over the past 5 years because of trans fat labeling. Palm oil usage topped 2700 million pounds in 2012 compared to about 650 million pounds a decade ago. For further information on the food uses for palm oil, the reader is directed to a number of recent reviews (Basiron 2005; Berger 2007, 2010; Berger and Idris 2005).

12.4 TRANS FATS

The chemistry, occurrence, and functional properties of *trans* fats have been reviewed by Kodali (2005), Floter and Van Duijn (2006), and List and King (2006). Loh (2006) discussed the reformulation of foods to meet nutrition labeling requirements. The trans and saturated acid content of foods prior to the 2006 deadline for nutrition labeling has been reported by Satchithanandam et al. (2004) and commercial innovations for providing trans free fats have been reported by Tarrago-Trani et al. (2006). Kodali (2005) and List and Pelloso (2007) have reviewed trans fat alternatives and trans fats in foods and should be consulted for further information. Of particular interest to reformulation of foods, the former reference contains a detailed description of commercial solutions for trans fat replacements. At least seven US companies offer trans free fats for a wide variety of applications including salad/frying oils, margarines/spreads, and baking shortenings, all of which are soybean, canola, cottonseed, corn or palm oil based.

12.4.1 Trans Fats as Functional Components in Food Systems

Hydrogenation of an edible oil serves to increase oxidative stability and raise the melting point. Under typical selective commercial conditions (high temperatures, low pressures, low agitation, and light catalyst loadings), reduction of polyunsaturated acids is favored along with the formation of trans isomers. Under selective conditions about 0.73% trans is formed per unit drop in iodine value (List and King 2006). Some examples using soybean oil will illustrate how the industry formulates salad/cooking oils, margarine/spreads, and baking shortenings.

Liquid salad cooking oils are prepared by reducing the iodine value from about 130 to 115 and fractionating the oil to remove high melting components so the oil will remain clear at refrigerator temperatures. Typically these products contain 9–10% trans acids. Margarine/spread bases involve reduction of the iodine value from 130 to 65 with a trans acid content of about 40%. However, after blending with liquid unhydrogenated oil, trans acids are reduced. A 75/25 blend of liquid oil and base oils yields a soft margarine oil with about 10% trans and a 50/50 blend yields stick margarine oil with about 20% trans acids. Preparation of shortening base involves reducing the iodine value from 130 to about 80 and will contain about 32% trans acids. Formulation of baking shortenings is accomplished by adding completely hydrogenated soybean or cottonseed flakes and liquid oil to achieve the desired product with regard to solid fat and melting point. Commercial baking shortenings contain 12–25% trans acids.

These examples show why hydrogenation has been so popular as a food formulation tool. With just four oils (IV 65, IV 80, IV less than 1, and liquid oil) any fat or oil can be be prepared for use in a wide variety of food applications. Trans fats are extremely functional. A soft margarine/spread must be spreadable at refrigerator temperatures, hold together at room temperatures and melt readily at body temperature. Stick products require more solid fat because they are often stored at ambient temperatures. Thus, sharply melting trans acids are ideal for furnishing these requirements. In bakery systems, fats serve to tenderize, lubricate and provide aeration to initiate cell structure. In addition, they define the structure of the product through separation of protein films.

Fats also provide softness to products required for long shelf-life as well as emulsifying and holding water. Baking margarines also may contribute flavors to baked goods since some are processed to taste like butter. Many flavors are fat soluble and, as such. fats can serve as a carrier in the desired application (Strouts 2006).

12.4.2 Processing to Reduce Trans Fats in Food

A review of processing technologies for trans reduction is beyond the scope of this chapter. The reader is referred to a number of reviews.

- Interesterification – random/directed/chemical: Screenivasan (1978), Going (1967), Rousseau and Marangoni (2002), Rozendaal and McRae (1997).
- Interesterification – enzymatic: Xu et al. (2006), Binder et al. (2006), Anon (2004), Lee (2008).
- Fractionation – palm, palm kernel oils: Timms (1997), Gibon (2006). Krishnamurthy and Kellens (1996), De Greyt and Dijkstra (2009).
- Modified hydrogenation: Van Toor et al. (2009, 2010), Higgens (2010), Beers et al. (2009).
- Blending: Berger (2010), Berger and Idris (2005), Orthoefer (2005), Sundrum et al. (1998).
- Combinations – fractionation, interesterification, hydrogenation, blending: Mat Sahri and Idris (2010), Graffelman (1967), Rajah (1994).
- Oleogels/emulsifiers: Marangoni and Idziak (2008), Doucet (1999), Skogerson and Boute (2010).

12.5 DEEP FAT FRYING

For extensive information on the chemistry, nutrition, and applications of deep fat frying, the reader is referred to a number of textbooks covering all aspects of the technology (Dellaporta 2008; Erickson 2007; Gupta et al. 2004). The latter reference provides much practical information on oil selection, purchasing of oil supplies, handling and storage, and cleaning of equipment. Friedman (2006) discussed quality parameters for many of the common frying oils with regard to cost, foaming, polymerization, and free fatty acid formation as well as comparing both the positive and negative factors for each oil. Refined, bleached, and deodorized (RBD) soybean oil, while suitable for home and light frying, is not stable enough for heavy duty frying because of the 7–8% linolenic acid in the fatty acid composition. In addition, the oil tends to polymerize and foam under extended use in heavy duty frying. However, RBD soy is cheap and readily available. Ordinary LEAR has a similar fatty acid composition, i.e., 9–10% linolenic acid. It should be pointed out that the newer trait-modified canola oils have a reduced linolenic acid content (3%) and increased oleic acid which are desirable in a frying fat. The partially hydrogenated soybean oils, both solid and clear, containing 20–40% trans fat are more expensive than commodity oil but cheaper than trait-modified oils and more resistant to polymerization and foaming. The trait-modified (low linolenic/high mid oleic soybean, high oleic canola, high/mid oleic sunflower) oils, while more expensive than commodity or hydrogenated, show good resistance to foaming and polymerization. The partially hydrogenated frying shortenings have long fry life but are high in trans acids. Edible tallow (beef) is low in trans, contains cholesterol, and is highly saturated. However, foods fried in animal based shortening have a distinctly pleasant taste.

12.5.1 Assessment of Frying Oil Quality

Assessment of the initial quality of frying oils has been reviewed by Orthoefer and List (2007). Methods to determine the extent of oil deterioration and the chemistry of used frying fats have received much attention from researchers and the reader is directed to a number of reviews (Crosby 2008; Dobarganes and Marquez-Ruiz 2007; Erickson 2007; Orthoefer and List 2007; Perkins and Erickson 1996; Sebedio and Juaneda 2007).

The safety, nutritional and regulatory issues surrounding used frying fats have been reviewed by Artz et al. (2007), Firestone (2007), Wainwright et al. (2007), and Stier (2004). Design of laboratory frying studies has been reviewed by Banks (2007) and protocols for the sensory evaluation of deep fat fried foods have been outlined by Melton (1996), White (1995), Warner et al. (1997), and Gupta (2008).

12.5.2 Laboratory Frying Studies Using Trait-Modified Oils

Numerous frying studies have been made in the laboratory. Space does not permit a detailed discussion but in general, trait-modified oils performed well in the evaluations. The reader is referred to the following studies (Kiatsrichart et al. 2003; Matthäus et al. 2009; Normand et al. 2006; Soheli et al. 2002; Warner and Fehr 2008; Warner and Gupta 2003; Warner and Knowlton 1997; Warner and Mounts 1993; Warner et al. 1997).

12.5.3 Case Studies of Frying Oils (Fast Food Chains)

The food service industry uses about 5 billion pounds of fats and oils for deep fat frying, pan frying, griddle frying, and as spray oils. Historically, these products (mainly soybean based) have evolved from heavily hydrogenated solid shortenings (40% trans) to pourable fluid shortenings made from a less hydrogenated component and hardstocks held as suspensions (20% trans). Such products have a long fry life and are relatively cheap. Although the food service industry and restaurants are exempt from federal trans fat labeling regulations, many local and state governments have enacted or proposed legislation to ban trans fats. Consequently, many companies began the task of replacing high trans oils with trans free alternatives well before the January 2006 deadline.

Many factors influence the choice of frying oils including cost, availability, fry life, and consumer acceptance (Tiffany 2007). In addition, little or no flavor is added to the food (chicken, fish, and fried potatoes), the oil should resist polymerization and not form films or sticky residues in equipment. From a health/nutrition standpoint, the oil should be low in trans and saturated acids. Frying oils tend to increase in color after extended use and ideal frying oil should remain clear for the entire fry life. Frying oils also tend to foam after extended use. Thus an oil that resists foaming is highly desirable.

A major national chain (using 160 million pounds/year) began the task of replacing a hydrogenated fluid shortening with a trans free alternative by testing 26 different oils and blends for fry life and consumer acceptance and, by 2004, had narrowed the search to two oils. The next phase consisted of in-house testing of the two oils for fry life and product quality and taste. One of the oils was test marketed in several stores because it was available in jugs but was considered unsuccessful because of lower purchases of key products. Although the two final options performed equally well in testing, it was decided that a trait-modified soybean oil should be test marketed in eight resturants in New York City, Chicago, and Louisville. Consumers were asked for their reaction to foods cooked in a zero trans oil. The results were overwhelmingly positive and the company decided to move forward with a plan to supply some 5500 restaurants with the new oil. A major concern was the stability of the new oil. The company uses an active filtration system that polishes the oil with magnesol which not only extends fry life but retains seasonings added to the food. The company concluded that fry life and performance were equal to the shortening it replaced. In October 2006 the company announced that by April 2007 all stores would be serving zero trans foods (Miller 2007).

A regional chain having 1800 employees and operating 40 restaurants who pride themselves on offering nutritional, great tasting food made with fresh local ingredients sought to find a trans free frying/cooking oil. They cited the decision as the right thing to do for their customers. They began by surveying and gathering information on what was available in the marketplace. Their supplier furnished a soybean oil trans free product packaged in 35 pound jugs. Testing began by educating employees about trans fatty acids and the new oil was tested in one of the restaurants by comparing French fries fried in the new oil with those fried in the existing shortening. After testing, which showed satisfactory performance, a decision was made to switch despite increased costs (2 dollars/35 lbs) and a decrease in fry life from 16 days to 14 days and several fry lives ranging from 7–12 days. It is interesting to note that this chain left some products (fries, cookies, shortcakes) on their menu containing trans fats (Nagy-Nero 2006).

The results of these case studies indicate that trait-modified oils perform well in food service applications for restaurant use and offer a trans free option. Increased costs, supply, and availability can be major issues but as the trait-modified oil (soybean, canola, sunflower) industry grows and expands, costs will decrease. In 2008, trait-modified oils supplied about 12% of domestic consumption. Today, this figure has increased to about 20%. However, it was estimated that 870 million pounds of trans and saturated have been taken out of the diet through usage of trait-modified oils (Heinzt 2009). Today these figures are even higher.

12.6 TRAIT-MODIFIED OILS IN BAKING APPLICATIONS

Fats (triglycerides) perform a number of functions in baking: aeration/creaming or the incorporation of air into batters, structure, eating properties, tenderness, richness, carriers of flavors and surface active additives (emulsifiers, surfactants), lubricity. They also permit the shortening of gluten strands in flour such that doughs may be worked into the desired shapes. In addition, fats allow water to be dispersed in batters and doughs so that during baking, steam is released, giving volume to the finished product. Fats and oils contain a variety of triglycerides melting over a wide range and it is convenient to group them as such (Bessler and Orthoefer 1983).

Group 1 are highly unsaturated and common to liquid oils. Examples are trilinolein and oleodilinolein. Typically group 1 triglycerides melt at very low temperatures, ensuring that oils are liquid at temperatures of 10°C or 50°F. Group 2 triglycerides melt at about 6–25°C and will remain liquid only if stored at ambient temperatures. They consist mainly of monounsaturated triglycerides, i.e., SOL, OOP, SOO where S = stearic, P = palmitic, L = linoleic, O = oleic. Group 3 triglycerides consist of mainly disaturated acids and melt at near body temperature and serve to provide a cooling effect in the mouth. Examples are PPL, SPL, SSL, PPO, SPO, and SSO (melting points 27–40°C). In addition, group 3 triglycerides act as a moisture barrier and incorporate air (aeration) into batters.

Group 4 triglycerides melt at high temperatures (56–65°C) and are not found in vegetable oils except in trace amounts and are formed from the complete hydrogenation of soybean, cottonseed, and palm oil (PPP, SPP, SSP, SSS). They provide structure to margarine/spreads and baking shortenings as well as lubricity at cooking temperatures. Group 4 triglycerides provide plasticity to dough based baked goods. In spreads, they provide resistance to “oil off “or exudation of oil from the emulsion.

The structure/functional relationships of triglycerides are useful in formulating food fats according to solid fat requirements that are often different depending on the end use. As an example, blending a large amount of group 1 and small amounts of group 4 yields a baking fat with plasticity over the temperature range required for dough based foods. Similarly, spreads can be formulated from liquid oils high in groups 1, 2, 3 and fractionated palm oil containing high amounts of primarily groups 3 and 4 triglycerides.

Many baking recipes call for vegetable oil. Although commodity oils serve well (with the exception of those calling for olive oil), trait-modified oils should serve equally as well in baking as they do in frying. Since they are liquid over a wide temperature range, they are easily pumped and handled and are often packaged in 35 lb plastic jugs, a distinct advantage in food service operations. Solid shortenings are packaged in plastic liners and cardboard boxes which make disposal more difficult.

The fact that trait-modified oils have increased oxidative stability makes them ideal candidates for baked goods where extended shelf-life is needed. The use of liquid oils in baking has been accelerated with the introduction of improved emulsifier systems and a liquid oil with added emulsifiers and surfactants has proven to be an excellent liquid shortening system for bread, cakes, buns, and muffins.

Baked snack crackers need to have a fairly long shelf-life. Although commodity soybean oil (unhydrogenated) is commonly used in their manufacture, trait-modified oils should extend the shelf-life of these and similar products. A recent report confirms that the shelf-life of cereals can be extended significantly by incorporation of high oleic canola oil into the products (Lui and Issonova 2012).

Many baking shortenings are formulated with solid fat needed for functionality. Orthoefer (2005) reported that zero trans baking shortenings can be formulated by blending high oleic canola oil with fully hydrogenated soybean oil. Crisco shortening has been a popular household item for over 100 years and has been reformulated several times over the past 10 years to be trans free. Currently Crisco is formulated from trait-modified sunflower oil and fully hydrogenated hardstock and is claimed to perform as well as the older products.

Crackers are commonly sprayed with oil to serve a moisture barrier. Traditionally, high stability oils made by hydrogenation and fractionation or coconut oils have been the industry standard. However, high trans and saturate contents of these spray oils have stimulated interest in trait-modified oils because they are zero trans/low saturate options. Erickson and Frey reported in 1994 that trait-modified soy and sunflower oils performed very well in cracker spraying applications.

Although not amenable to commercial pie production, trait-modified oils can be used at home. Numerous recipes calling for vegetable oils in pie crusts can be found on the internet.

In summary, trait-modified oil can be used in many applications where a trans free product is desired or when extended shelf-life is a consideration. Trait-modified oils will find extensive use in the food service sector for deep fat frying, pan/griddle use, as a spray oil and many baking applications where solid fat is not a major criterion. Although more expensive than commodity oils, trait-modified oils will continue to furnish a significant amount of domestic oil needs. In 2011, trait-modified oils supplied about 18% compared to 12% in 2008.

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13 Modified Composition Oils for Food and Nonfood Applications

Monoj K. Gupta

MG Edible Oil Consulting, Richardson, TX, USA

The term “modified composition oil” implies that these oils have fatty acid compositions that are distinctly different from their corresponding garden varieties. Many of these oils are higher in oleic acid with or without reduced saturated fat contents. These are commonly known in the industry as high oleic (HO) oils. Some of these oilseeds containing modified composition oils are derived through the transgenic method while the others are obtained via mutagenic as well as the conventional crossbreeding process. Regardless of the method by which these oilseeds are derived, these HO oils have higher oxidative stability (due to the higher oleic acid contents), making them highly suitable for frying and baking processes as well as formulation of packaged products that require a longer shelf-life for storage and distribution needs.

Typically, oils that are stable under the frying condition are very stable in all other food applications. This is because the oil in the other food applications is not subjected to the same harsh conditions as in frying. Therefore, the HO oils can be used in all food applications with success.

Trait-Modified Oils in Foods, First Edition. Edited by Frank T. Orthoefer and Gary R. List.

Modified composition oils with high stability are also highly suitable for nonfood applications, such as biodiesel, lubricants, as transformer oils, in cosmetics, printing inks, and many other products.

13.1 BASIS FOR OIL SELECTION FOR FRYING AND BAKING

Traditionally, the food industry selected oils for frying, baking, and other applications using the following criteria (Gupta 2006).

1. Product flavor
2. Product texture
3. Product structure in baked products
4. Product appearance
5. Product taste
6. Oil stability in process as well as in the packaged product
7. Product shelf-life
8. Meets nutritional requirements
9. Cost
10. Availability

The finished product must have good flavor and texture. It must be appealing from the standpoint of color. The product must have good initial taste as well as good aftertaste with no lingering unpleasant aftertaste. In the process of frying or baking, the oil is subjected to very high temperatures in the presence of air, causing oxidation of the oil. Oxidized oil develops unpleasant flavors in the product. Sometimes the product may have acceptable flavor while fresh but develops a rancid flavor soon after it is stored due to the formation of oxidized polymers (Frankel 1985). Therefore, it is very important that the oil must be able to withstand the high temperature condition during frying and baking and subsequently maintain good flavor while the packaged product is stored. The oil must meet the current trend in nutritional guidelines recommended by food nutritionists and governmental guidelines, where applicable. The price of the oil cannot be outrageously high because the food processors have to make a certain amount of profit on their processed food products in order to sustain their business. Finally, the oil, however good it is, must be available in sufficient quantities to the food processors.

In modern times, item #8 above has become one of the top priority criteria for oil selection. This means the oil must have low saturated fatty acids (SFA), high monounsaturated fatty acids (MUFA) and low polyunsaturated fatty acids (PUFA). This trend has been developing in the food industry for over 20 years and has led to the vast amount of research work done by the seed companies, universities, private organizations, the United States Department of Agriculture (USDA), Canola Council (Canada), National Sunflower Association (NSA-USA), as well as the palm oil industry in Malaysia, Indonesia, Colombia, Costa Rica and Australia.

13.2 BACKGROUND

Garden variety soybean, canola, and sunflower oil exhibit low oxidative stability (see OSI in Table 13.2). The high concentration of PUFAs (linoleic and linolenic) makes these oils less stable under elevated temperatures and exposure to oxygen from the atmosphere. The three common unsaturated fatty acids in these oils and their relative propensities for oxidation are listed below (Bokish 1993):

• oleic acid	1
• linoleic acid	120
• linolenic acid	260.

Thus, oils rich in polyunsaturated fatty acids tend to be oxidized fast and form oil breakdown compounds that impart unpleasant odor and flavor to the oil used in the product formulation and processing.

Scientists developed the process of hydrogenation where the double bonds in the unsaturated fatty acids in the oil were broken and two hydrogen atoms were inserted into the oil molecule, making it less prone to oxidation. Hydrogenation provided the means to improve the following attributes of the oil:

- oxidative stability
- increased melt point

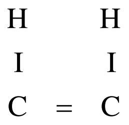
- improved functionality in baking applications
- desired melting characteristics in margarines.

Unfortunately, the hydrogenation process (partial hydrogenation) produces trans isomers of the unsaturated fatty acids. Europe started to impose regulations on trans fat levels in food products in the 1990s and USA and Canada followed suit. Trans fatty acids (TFA) have enjoyed the Generally Recognized as Safe (GRAS) designation in the USA but the Food and Drug Administration (FDA) is seriously questioning the validity of this GRAS status and the US food industry is being challenged by the FDA.

Hydrogenation of vegetable oil was introduced in 1903 to increase the shelf-life of the fat system (Normann 1903). In 1910 the first hydrogenated fat was converted to the shortening form, known for over a century to the world as Crisco, all purpose shortening.

In the 1930s soybean oil containing 7–8% linolenic acid started to become more available. High linolenic acid and linoleic acid content of the garden variety soybean oil was reduced to low levels through the hydrogenation process.

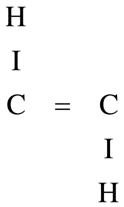
Hydrogenation of the oil converts the linolenic acid to less unsaturated fatty acids like linoleic and oleic acids and also into saturated fatty acid, known as stearic acid. This provides more oxidative stability to the oil. The sequence of conversion of the unsaturated fatty acids to less unsaturated ones in the hydrogenation process can occur under the reaction condition called perfect selective hydrogenation. In reality, perfect selective hydrogenation does not occur in most cases of hydrogenation. Trans fatty acids are unsaturated fatty acids where one of the hydrogen atoms around the double bond shifts to the opposite side of the double bond. This occurs predominantly during the hydrogenation process. Unsaturated fatty acids have double bonds between the carbon atoms at certain positions in the fatty acid molecule. Hydrogen atoms, at the double bonds, are present in the following configuration, known as the cis form, in nonhydrogenated vegetable oils.



$$\begin{array}{ccc} \mathrm{H} & & \mathrm{H} \\ \mathrm{I} & & \mathrm{I} \\ \mathrm{C} & = & \mathrm{C} \end{array}$$

Cis isomer

During hydrogenation, some of the unsaturated fatty acids, which are in their natural cis form, are converted to the trans forms by changing the position of the hydrogen atoms around the double bonds.



$$\overset{\displaystyle H}{\overset{|}{C}} = \underset{\displaystyle H}{\underset{|}{C}}$$

Trans isomer

Linolenic acid (with three double bonds) is converted to linoleic acid which can be converted to oleic acid and finally to stearic acid. However, this mode of conversion can occur only when hydrogenation is carried out in a highly selective fashion. Most hydrogenation operations are less selective. Therefore, the linoleic acid or oleic acid can be hydrogenated before the linolenic acid is completely depleted.

Formation of high trans fat in the oil allowed the oil processor to make products like margarine, imitation cocoa butter, coating fats, etc. Hydrogenation processes for low and high trans fat products were developed. Special catalysts were introduced to produce high trans fats.

In the 1960s, nutritionists indicated that PUFAs lowered cholesterol in human blood. This was the beginning of our understanding of fat composition and its influence on human blood chemistry. The recommendation was made that in the fat system the polyunsaturated/saturated fatty acid ratio (P/S ratio) should be 1 or higher to minimize atherosclerosis (internal communication, Procter & Gamble).

In the mid-1980s the food industry learned that saturated fatty acids (as found in tallow and other animal fats) have harmful effects on human health. The nutritionists concluded that high consumption of saturated fat would lead to higher cholesterol in human blood serum and atherosclerosis. Further studies with refined analytical techniques allowed the scientists to understand the effects of different types of fatty acids, their positional isomers in the triglyceride molecules of the fat, total fat intake and the overall diet that influences the lipid profile in the human blood (Mensink and Katan 1990).

The unfortunate fall out of these findings was that palm oil, palm kernel oil, and coconut oil were categorized as being the same type of fat as tallow and lard. In the USA, the three vegetable oils, palm, palm kernel and coconut oil, were called "tropical oils" and the food industry began to stop using these oils in practically all food products.

Use of tallow and lard was also stopped (or reduced). Tallow in the fast food industry was replaced with highly hydrogenated soybean oil because without the use of palm oil, the fat system needed solids that could only be generated in the garden variety seed oils through heavy hydrogenation. In several cases, a highly selective hydrogenation process was used to obtain the required functionality and melting characteristics in the shortening for various food products. Unfortunately, this process produced high levels of trans fatty acids in the fats, although that was not of any concern in the USA. Use of hydrogenated vegetable oil skyrocketed in the US and so did the consumption of trans fats. Food scientists and nutritionists in the US did not fully agree with their European counterparts on the negative impact of trans fatty acids on human health.

Food scientists used the process of hydrogenation to provide both oxidative stability and functional properties to shortening and margarine products for nearly a century until European scientists found that trans fatty acid increased low density lipoprotein (LDL), reduced high density lipoprotein (HDL), and increased triglycerides in human blood serum. Confirmatory reports began to be published in the 1980s and 1990s.

In the early 1990s, European scientists uncovered the impact of trans fat and found that it was equally harmful as saturated fat and in some instances worse. Therefore, seed researchers in North America started to focus on oilseeds containing low linolenic acid so the oil could be used without any hydrogenation for frying and baking where the oil is subjected to high temperatures in the presence of air.

High oleic sunflower oil was developed in Ukraine before 1980. In the early 1980s, Frito Lay in the USA developed a high oleic sunflower variety that had excellent oxidative and flavor stability. Frito Lay sold the patent rights on the high oleic sunflower seed to Lubrisol. Lubrisol wanted to market the oil as a specialty oil at a substantial premium. Lubrisol's marketing model did not allow this oil to be widely used by food processors.

The garden variety canola oil contained lower saturated fatty acids than all other oils. Therefore it was perceived by the consumers as healthy and its application in the food industry grew rapidly. However, its high linolenic acid content made it less stable to oxidation. In that respect, this oil (like the garden variety soybean oil) could not be used for heavy duty industrial frying or baking without hydrogenation to reduce the linolenic acid content to <2%.

Low linolenic acid canola oil was made commercially available in the USA in the early 1990s by Cargill. The oil produced good product flavor and stability but was more costly to the food processors.

It was around the same period that low linolenic soybean (LL soy) oil was made available to the market by Pioneer Hi-Bred (currently DuPont-Pioneer). Owing to the low linolenic acid content (<3%), the LL soy oil exhibited promise in industrial frying, margarine, and baking applications. Despite its good performance, production of the oil did not reach the expected potential. The primary reason was that the oil contained high total saturated fat (15%, the same as in the commodity soybean oil). This gave canola oil the edge because it contained only 7% saturated fat. LL soy oil, like the commodity soybean oil, contained high levels of PUFAs (linoleic acid) that caused rapid polymerization of the oil on the conveyors, fryers, baking ovens, and other parts in the plant where the oil was subjected to high temperatures.

Mid oleic sunflower (NuSun) oil was developed in the USA and the first commercial quantity of this oil was made available to food processors in 1998 but it faced extremely stiff competition from soybean and other cash crops in the north western USA and Canada for securing growing acreage.

Modified composition oils were being used in the USA by a few food processors but the great majority of the snack food companies maintained a “wait and see” position until the FDA made trans labeling of food products mandatory in 2006. One could justify the position of the snack food companies because:

- modified composition oils were available in very limited quantities
- the cost of the oil was very high

- the IP (Identity Preserved) process for the modified composition oilseeds made the oil very costly because of the lack of large-scale demand from food processors
- there were no open discussions on the regulatory mandates to reduce or declare trans fat on the product labels until 2002
- declaration of mandatory trans fat labeling by the FDA in 2006 changed the game plan for the entire food industry in the USA and oilseed research and thrust for the production of modified composition oils significantly increased.

Active research work went on to optimize the composition and yield of high oleic soybean and high oleic canola oilseeds. Research on high oleic palm oil made progress in South America. This oil has also produced promising results in all applications, including industrial frying.

It would be appropriate to mention that development of any new variety of oilseed is not only expensive but also time consuming. Without going into detail, suffice it to state that it would take:

- a decade or two to develop the seed variety, test for performance, and grow commercial quantities to produce oil from the seeds
- hundreds of millions of dollars of investment to develop and commercialize a new variety of oilseed
- willingness on the part of food processors to test the oil in commercial products to confirm the fact that it delivers the desired performance in finished products
- a strong consumer preference for more nutritious oil in prepared foods
- finally, a mandate from the regulatory agency such as the FDA to provide the impetus to the industry for the acceptance and development of modified composition oils.

13.3 TYPES OF MODIFIED COMPOSITION OILS

A number of modified composition oils have been made available to food processors for evaluation. Some are available in large quantities while some are still in the IP production stage and some are under study by industrial food processors.

The primary thrust in developing modified composition oils has been in the areas of increased oleic acid and reduced levels of polyunsaturated and saturated fatty acids. This provides the following desirable attributes to the oils:

- increased oxidative stability
- improved nutritional value
- elimination of hydrogenation in heavy duty industrial frying applications.

High oleic sunflower was commercially available to the market in the 1980s, sold as "specialty" oil. There are a few other modified composition oils that were introduced to the market in the 1990s. These are listed in Table 13.1. These include the low linolenic acid canola and soy varieties and mid oleic sunflower (NuSun) oil.

13.3.1 High Oleic Oils

These oils have 50% or higher oleic acid content that gives the oils higher oxidative stability as measured by the Oxidative Stability Index (OSI) or Active Oxygen Method (AOM). The stark comparisons between some of the modified composition oils and their garden variety counterparts are listed in Table 13.2.

All HO oils have significantly higher oxidative stability compared to the corresponding garden variety. These oils are also very low in linolenic acid, which makes them suitable for high temperature food applications without hydrogenation, such as heavy duty industrial frying and baking.

All garden variety seed oils listed in Table 13.2 require hydrogenation in order to reduce the linolenic acid content to <2% for industrial frying applications. Palm oil and palmolein are exceptions because of their low linolenic acid and very low linolenic acid content and high oxidative stability, which allows these oils to be used without hydrogenation for industrial frying and baking.

Other oilseeds containing oil such as high stearic acid, high lauric acid, and oil containing omega 3 fatty acid have also been developed for specific applications. Production of these varieties of oilseeds is

Table 13.1 Comparative Composition Data on Modified Composition Oils in the Market (Before HO Oils)

			Polyunsaturated		
Oil type	**Total saturated**	**Monounsaturated**	**Linoleic acid**	**Linolenic acid**	**OSI, hours @110°C**
Low lin canola (Clear Valley)	7	65	24	4	8–9
Mid oleic sun	9	56	33	<1	7–8
Low lin soy	15	25	56	3	6–8

OSI, Oxidative Stability Index.

Table 13.2 Comparative Composition Data on Garden Variety Versus HO Variety Oils

			Polyunsaturated		
Oil type	**Total saturated**	**Monounsaturated**	**Linoleic acid**	**Linolenic acid**	**OSI, hours @110°C**
Garden variety oils					
Reg. soybean	15	23	54	8	5–6
Reg. canola	7	60	20	10	6–7
Reg. sunflower	10	20	65	<1	7
Palm oil	48	40	11	1	25
High oleic variety oils					
HO soy	10	>75	3	3	>20
Vistive Gold[++]	6	68–75	15	<3	23
Plenish**	12	>80	3	<3	>25
HO canola (Clear Valley 75*)	7	75	14	3	18
HO canola (Natreon)[+]	7	72	18	2	21
Highest oleic canola (Clear Valley 80*)	7	80	9	3	26
HO sun	8	82	10	<1	18
HO sun (Natreon)[+]	8	87	4	–	26
HO palm	30	55	15	<1	30

* Cargill; [+] Dow AgroScience; [++] Monsanto; ** DuPont/Pioneer.

expanding as industries are showing interest in these oils for very specific product applications.

13.4 APPLICATION OF VEGETABLE OILS

13.4.1 Food Applications

Vegetable oil is used for numerous food and nonfood applications.

- Cooking
  - Home cooking
  - Cooking at restaurants and food services
- Frying
  - At home
  - At restaurants and food services
  - Industrial frying
  - Par fried products – packaged and distributed for homes, restaurants, and food services
  - Shelf stable salty snacks
  - Freshly fried donuts
- Salad dressing
  - At home
  - Manufactured and packaged for distribution
- Baking
  - Bread
  - Cookies and crackers (dough and spray)
  - Fresh at local bakeries
  - Manufactured and packaged for distribution
  - Pastries: fresh in local bakeries and shelf stable baked goods (packaged)
- Donuts (fried and baked)
  - Fresh
  - Shelf stable packaged
- Releasing agents
  - Pan grease in the bakery
  - Release agent in the candy and chocolate industry
- Table margarines and spreads

13.4.1.1 Cooking

Both home cooked products and foods cooked at restaurants or other food services require good tasting oil that will not impart any unpleasant flavor to the cooked food. The food is consumed within minutes or hours after it is prepared. There is no need for a long shelf-life. Therefore, all garden variety oils are suitable for these applications.

13.4.1.2 Frying

Fried foods at home, in restaurants and food services do not require a long shelf-life. The food is consumed shortly after it is fried although some restaurants or food services may hold French fries, chicken or other fried foods under an infrared lamp or in hot boxes for short periods. Sometimes, the food stored in this fashion can develop an off flavor when garden variety oil is used for frying.

The oil in the restaurant or food service fryer remains at high temperature for 16–18 hours per day. Such prolonged exposure to high temperatures oxidizes and polymerizes the oil in the fryer. Since the trans fat labeling mandate of 2006, most restaurants have switched to trans free nonhydrogenated oil (mostly refined, bleached, and deodorized [RBD] garden variety soybean oil). This oil degrades fast and the restaurants discard the fryer load of oil every 3–5 days. Very few restaurants are using high oleic sunflower or safflower oil that lasts longer but is more expensive.

High oleic oils exhibit significantly higher oxidative stability than the gardenvariety soybean oil (see Table 13.2). Figure 13.1 shows the Peroxide Value (PV) of Plenish® HO soy oil and the garden variety oil stored at 63°C. Plenish had a PV of 10 after 12 days while the garden variety soybean had a PV of 140.

Figure 13.2 shows the data from DuPont, where the Plenish lasted nearly three times as long in frying French fries in a restaurant fryer when compared against lightly hydrogenated garden variety soybean oil. The endpoint for the fry time was decided when the polar material content of the oil reached 25%. The partially hydrogenated soybean oil reached the 25% polar mark after 4.5 days while the HO soy (Plenish) reached the same upper limit of polar compounds at 12 days.

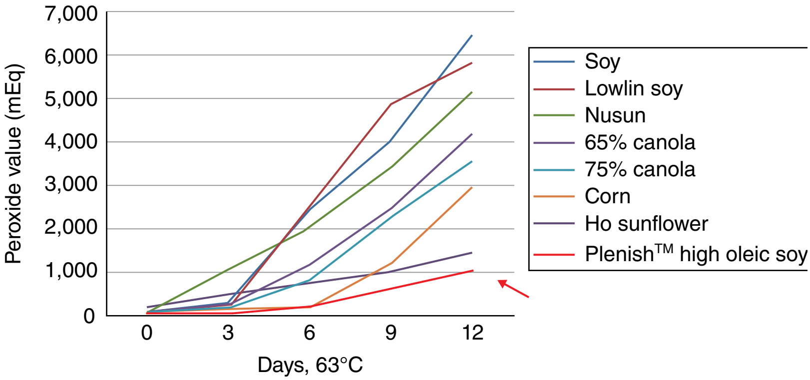


Figure 13.1 Higher oxidative stability (PV) of HO soy (Plenish, DuPont).

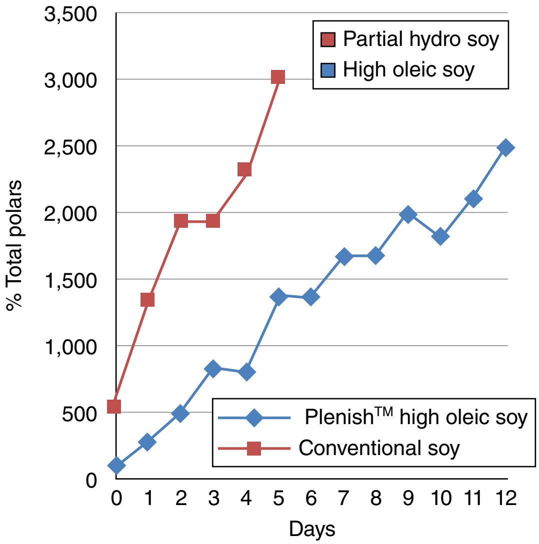


Figure 13.2 Fry life improvement with HO soy (Plenish, DuPont).

Besides longer oxidative stability, these oils also maintain better flavor in the fried foods. Sensory test results showed that the flavor of French fries fried in Plenish was preferred over those fried in lightly hydrogenated garden variety soybean oil. Figure 13.3 shows the comparison of the two products after 10 days of frying. The product fried in Plenish had significantly better texture, flavor, and overall acceptability than that fried in partially hydrogenated soybean oil.

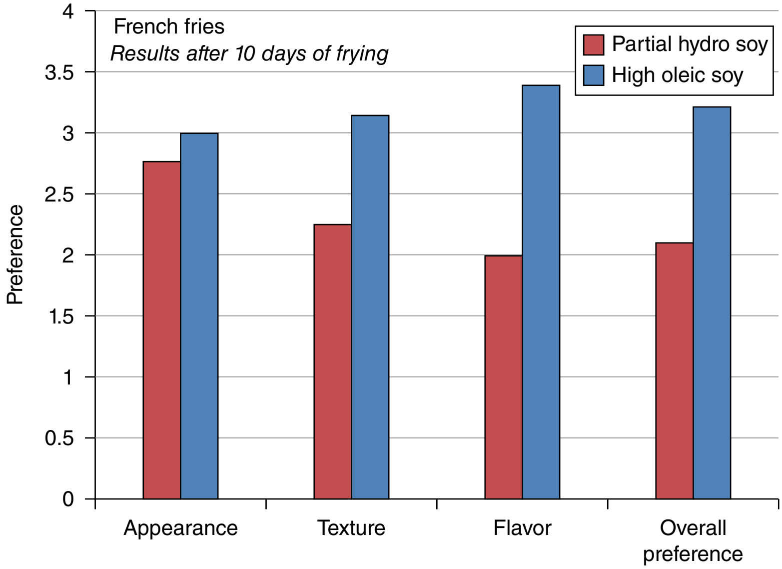


Figure 13.3 Improved attributes of French fries fried in HO soy (Plenish, DuPont).

Frying is a process where the food is either partially or fully dehydrated (<2% moisture) using the thermal energy from the oil. The oil undergoes numerous reactions concurrently during frying.

- *Hydrolysis*, where the fatty acids from the triglyceride molecule react with a molecule of water. A molecule of fatty acid is formed as a result of the reaction along with the creation of a molecule of diglyceride. Sometimes, two fatty acid moieties of a triglyceride molecule can react with two molecules of water, forming two molecules of fatty acids and a molecule of monoglyceride. The fatty acids formed in this manner are called free fatty acids.
- *Oxidation* (*autoxidation*) of the fatty acids on the triglyceride molecules as well as the free fatty acids, forming a series of compounds that can impart unpleasant odor and flavor to the product. Sometimes, the unpleasant flavor can be detected in the fresh product. Other times the unpleasant flavor is not detectable in the fresh product but the flavor can turn bad (highly oxidized or even rancid) within a few days.

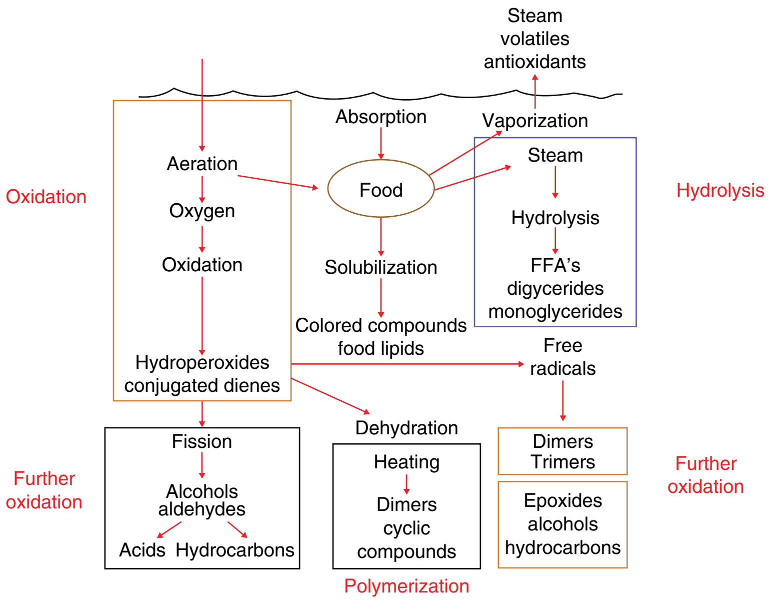


Figure 13.4 Multiple reactions occurring in frying. Source: Fritsch (1981). Reproduced with permission of JAOCS.

- *Thermal degradation* of the oil also occurs during frying and its degree can vary with the type of oil and also the frying conditions as well as how the frying process is managed.

Figure 13.4 depicts the various reactions in the frying process. Here we can truly appreciate the complexity of reactions in the oil in frying. We can see that polymers are formed in the oil during frying via two different pathways:

- through the free radical or oxidative pathway
- through the heat or thermal pathway.

The polymers formed in the thermal pathway can impart a bitter taste to the freshly fried product, whereas those from the oxidative pathway may not do so. However, if the oil contains high amounts of the oxidative polymers, the product develops an off flavor in a few days, leading to rapid development of product rancidity.

Oxidative polymers are highly reactive free radicals and they decompose readily even under nitrogen protection and vacuum. They also contain oxygen atoms in the molecule and sometimes as much as nine times what is contained in a triglyceride molecule. Therefore, these molecules can dissociate and continue the autoxidation reaction, consuming the oxygen that is already associated with the molecule. This can deteriorate the product flavor rapidly even when it is under nitrogen flush or frozen or stored in the dark.

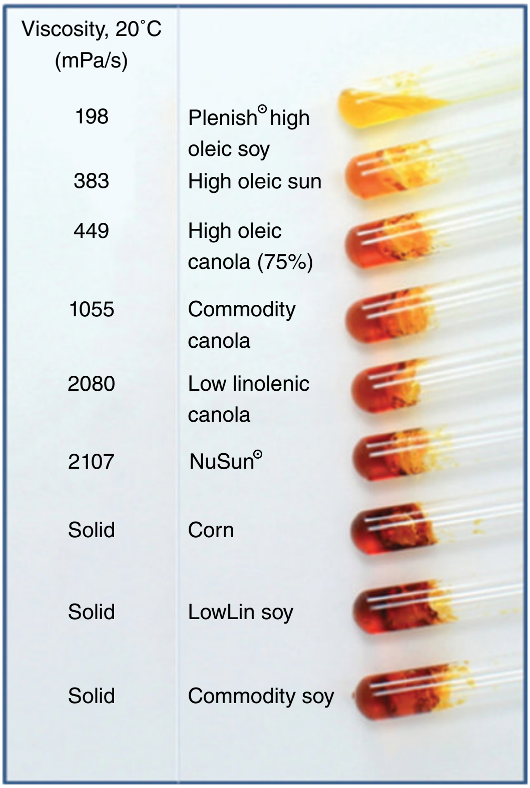
High oleic oils are more resistant to oxidation and the author believes that the better flavor of the product is due to the low levels of oxidative polymers formed in HO oils under normal frying condition. However, under abusive conditions, product flavor may deteriorate faster but the product fried in the HO oil would retain better flavor than the product fried in the garden variety oil under the same conditions.

DuPont's study shows a dramatic difference between various oils when they were allowed to polymerize at 150°C for 284 hours. Figure 13.5 shows picures of polymerized oils in test tubes. Plenish HO soy, HO sunflower, olive and HO canola showed very low formation of polymers under the test condition. The oil was still somewhat fluid. Mid oleic canola and commodity canola were very viscous. NuSun, LL soy, commodity soy, and corn oil were extremely viscous (almost solid).

In frying operations, LL soy, cottonseed, commodity soy, and corn oil produce high amounts of polymers. It is believed that high linoleic acid (>50%) in these oils is responsible for high polymer formation. HO soy and other HO oils exhibit significantly reduced amounts of polymer formation. Figure 13.6 shows two fryer pots side by side. Commodity soybean oil was used for frying on the left while Plenish was used in the fryer on the right. The fryer on the left was heavily coated with polymers while the one on the right was clean at the end of frying operations.

Based on the above discussions on frying, it is clear that high oleic oil is desirable because it provides the following benefits.

- Longer fry life for the oil
- Improved product flavor
- Longer product shelf-life
- Less cleaning of the equipment
- Zero trans in the oil and product
- Reduced overall cost



Viscosity, 20°C (mPa/s)	
198	Plenish® high oleic soy
383	High oleic sun
449	High oleic canola (75%)
1055	Commodity canola
2080	Low linolenic canola
2107	NuSun®
Solid	Corn
Solid	LowLin soy
Solid	Commodity soy

Oils were heated at 150°C. Viscosity measurements were made after 10 days; tubes had been heated for 17 days before being photographed.

Figure 13.5 Viscosity of various oils heated at 150°C.

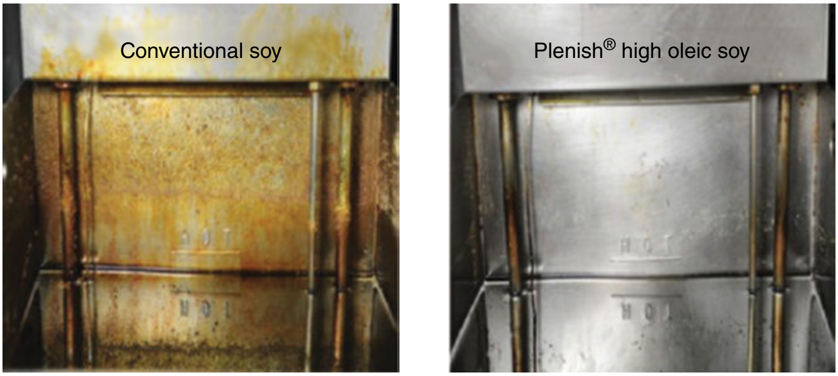


Figure 13.6 Comparison of polymer formation in commodity soy versus HO soy (Plenish, DuPont).

13.4.1.3 Salad dressing

Salad is made at home using salad oil, seasoning and sometimes plain or balsamic vinegar. The salad dressing thus prepared is consumed immediately. Any amount leftover is generally stored in the refrigerator and used within a day or so. This does not involve any shelf-life requirement for the product.

Salad dressing made in a manufacturing plant is packaged in bottles, metallized pouches, and institutional containers for distribution. The products generally carry a code date of 12 months. That means the consumer must find the product flavor acceptable when it is used before the code date is expired. It is primarily the stability of the oil in salad dressing that dictates the shelf-life of the product. The seasoning in the salad dressing can, to some extent, mask any off oil flavor but the rancid oil flavor can even override the flavor of the seasoning. Thus, with a highly stable oil like HO soy, HO canola, HO sunflower or HO safflower, one can expect better storage stability of the finished salad dressing. It must be mentioned that stale or rancid seasoning in the salad dressing can also degrade the product flavor by oxidizing the oil.

13.4.1.4 Baking

In the baking process, the dough requires a certain amount of fat crystals for functionality. The fat crystals provide the necessary consistency to the dough at various stages of the process. It provides viscosity and desired density to cake batter. Seed oils, even the HO oils, do not contain enough saturated triglycerides to fulfill the need for fat crystals.

Oil companies in the USA attempted to make shortening for baking using mixtures of commodity soybean oil, fully hydrogenated seed oils, and a cocktail of antioxidants. These shortenings provided the required product functionality but could not provide the required shelf-life for all products because of the presence of the commodity soybean oil.

Traditional shortening used in baking contains a liquid fraction, which is generally lightly hydrogenated commodity soybean oil, an intermediate melting fraction which is usually partially hydrogenated commodity soybean oil or a mixture of cottonseed and commodity soybean oil and, finally, a high melting fraction which is composed of fully hydrogenated cottonseed or palm oil. The light fraction, made from commodity soybean oil, was typically hydrogenated to an iodine value of 103–110. This improved oxidative stability of the oil. The intermediate melting fraction was also partially hydrogenated to meet the required specifications on solids contents at various temperatures. The high melting fraction, which is fully hydrogenated oil, provided the crystal properties for the shortening, high temperature stability and the desired batter consistency in the baking process.

High oleic oils have been found to be excellent replacements for the lightly hydrogenated commodity soybean oil. The HO oil not only provided the required functionality, it also provided better shelf-life for the finished product.

High oleic or other more stable oil that did not require hydrogenation was interesterified with fully hydrogenated cottonseed or palm oil. This provided the desired functionality in the intermediate melting fraction for the shortening with zero trans. In some cases, interesterification was carried out with only two components of oil. One component was HO or other oil with high stability and the other was fully hydrogenated cottonseed or palm oil. The last option produced trans free shortening but it contained higher levels of saturated fat than the conventional high trans shortening.

Thus, a shortening made from HO or other stable oil, an interesterified intermediate fraction as described above and some fully hydrogenated oil can lower the overall saturated fat content of the trans free shortening.

Some bread manufacturers prefer pourable shortening. Trans free pourable shortening can be made from HO or other stable oil and fully hydrogenated soybean oil or canola oil.

High oleic soy and other HO oils have been tested successfully by various food product manufacturers in making cookies and crackers.

13.4.1.5 Spray oil on crackers

Crackers, apart for few exceptions like saltine crackers, are sprayed with oil. The amount of oil varies depending on the type of cracker. Traditional spray oil for crackers has been partially hydrogenated soybean or cottonseed oil. The oil is sprayed on the crackers while they travel on stainless steel perforated belts or chain conveyors. The excess oil drips through the openings on the conveyor belt while the oil on the crackers soaks in and crystallizes. By the time the crackers reach the packing machine, there should be no free oil on the product.

Switching to nonhydrogenated stable oil as a spray oil is an option and the author tested LL soy oil as spray oil. Initially it appeared to be successful but soon the plant experienced the following nightmare.

- Oil was polymerizing around the oil spray applicator.
- Oil polymers were hanging like strings and icicles from practically every conveyor that conveyed the crackers after the oil spray was applied.
- The packing machine had to be shut down every 2 days for cleaning.

It was quite clear that while LL soy worked well on certain types of crackers for short pilot plant operation, long plant production revealed the fact that the oil did not have any saturated triglycerides to make it crystallize. When HO soy was used as a replacement for LL soy, polymerization was stopped but there was oil coating on the conveyors because the oil did not crystallize. One can argue that the spray oil for crackers needs a small amount of saturated triglyceride to prevent oil dripping via rapid crystallization.

13.4.1.6 Pan grease

In the baking process, a small amount of grease is applied to the baking pans for easy removal of the baked product. Traditionally, the baking industry has used liquid oil to make pan grease. The pan grease was found to cause rancidity of the packaged baked product if it contained commodity oil, such as soybean, canola or sunflower oil. Use of HO oil eliminated the product rancidity issue.

Similar improvement can be obtained by using HO oil as a release agent in candy and chocolate making processes.

13.4.1.7 *Table margarines and spreads*

There are two basic types of margarine used for domestic consumption.

1. Stick margarine
    - Soft stick
    - Hard stick
2. Margarine spread (also called tub margarine)
    - Regular spread
    - Soft spread

Stick margarine typically contains 80% oil and the regular spread contains 60% oil, while the soft spread contains up to 40% oil or less. Part of the oil can be liquid, while the other part needs to provide the crystal to form the margarine matrix, whether stick or spread. As an alternative to partially hydrogenated oil, which introduces trans fat, one can use fractionated palm oil or interesterified stocks, using liquid oil and fully hydrogenated oil as the starting feed for the interesterified product.

In essence, there is a great opportunity for HO soy oil to be used in margarine formulation when it is available in sufficient quantities.

Currently, the liquid oil comes primarily from three major modified composition oilseeds.

- Soybean
- Canola
- Sunflower

Besides seed oils, palm oil fractions of various iodine values, solid contents, and melt points are also used in many countries outside the USA. Modified composition palm oil with lower saturated and higher monounsaturated fatty acids is under study.

Margarines and spreads are stored under refrigeration. Therefore, use of nonhydrogenated soybean and canola oils has been quite common in these products. However, both of these oils have been known to develop some off flavor during storage, even under refrigeration. Use of HO oil will improve the flavor stability of these products.

When HO soy oil is fully commercialized, it will become the oil of choice for stability as well as cost. This is because soybean is grown over more acreage worldwide. HO canola oil will be the next contender. HO sunflower oil will remain more costly compared to HO soybean and HO canola oil because of its smaller acreage of cultivation.

13.4.2 Nonfood Applications

The nonfood applications for vegetable oil are numerous. The following list outlines some of the nonfood products that are being made or researched at present.

- Cosmetics
- Lubricants for machine parts
- Engine oil
- Cutting oil
- Biodiesel
- Biofuel for heating
- Transformer fluid
- Printing ink
- Industrial chemicals
- Vegetable oil based polyols
- Ingredients for surfactants

Nonfood use of vegetable oil is quite extensive. Besides the physical consistencies of cosmetics, it is essential that the products retain their aromas until they are used. The HO oils offer higher oxidative stability to all products that are currently using the commodity oils or some of their derivatives.

13.5 AVAILABILITY OF HO OILS

This is a proprietary area. Therefore, it is difficult to get a full picture of the current production volumes of the HO oils and figures for their projected production in the next 5–10 years. The only figures available

Table 13.3 Potential Availability of HO Soybean and HO Canola Oils

Year	HO canola oil	HO soybean oil
2016	5 billion	1 billion pounds
2020	>6 billion	4 billion pounds

are those obtained through personal communications with the seed companies, which are listed in Table 13.3.

13.6 CONCLUSION

Modified composition oils will improve nutritional factors and product shelf-life in all food applications. These oils will be especially desirable in difficult applications such as frying and baking. Cosmetics manufacturers found these oils to be superior in terms of their product shelf-life. Industrial applications are also made easy because of the long stability of these oils.

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