

VEGETABLE OILS IN FOOD TECHNOLOGY: Composition, Properties and Uses

*FRANK D. GUNSTONE,
Editor*

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VEGETABLE OILS IN FOOD TECHNOLOGY

Composition, Properties and Uses

Edited by

FRANK D. GUNSTONE
Professor Emeritus
University of St Andrews and
Honorary Research Professor
Scottish Crop Research Institute
Dundee



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Editorial Offices:

Osney Mead, Oxford OX2 0EL, UK

Tel: +44 (0)1865 206206

108 Cowley Road, Oxford OX4 1JF, UK

Tel: +44 (0)1865 791100

Blackwell Munksgaard, Nørre Søgade 35,

PO Box 2148, Copenhagen, DK-1016,
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Tel: +45 77 33 33 33

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Tel: +61 (0)3 9347 0300

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Preface

Our dietary intake comprises three macronutrients (protein, carbohydrate and lipid) and a large but unknown number of micronutrients (vitamins, minerals, antioxidants, etc.). Good health rests, in part, on an adequate and balanced supply of these components. This book is concerned with the major sources of lipids and the micronutrients that they contain.

Supplies and consumption of oils and fats are generally described in terms of seventeen commodity oils, four of which are of animal origin and the remainder of which are derived from plants. This selection of oils does not include cocoa butter with an annual production of around 1.7 million tonnes, which is used almost entirely for the purpose of making chocolate. Nor does it include oils consumed in the form of nuts. The production and trade data that are available and are detailed in the first chapter relate to crops either grown and harvested for the oils that they contain (e.g. rape and sunflower oils) or crops that contain oils as significant byproducts (e.g. cottonseed and corn oils).

Annual production and consumption of oils and fats is about 119 million tonnes and rising steadily at a rate of 2–6 million tonnes per year. This is required to meet the demand, which also grows at around this rate, partly as a consequence of increasing population but more because of increasing income, especially in developing countries. Around 14% of current oil and fat production is used as starting material for the oleochemical industry and around 6% is used as animal feed (and indirectly therefore as human food). The remaining 80% is used for human food—as spreads, frying oil, salad oils, cooking fat, etc. These facts provide the framework for this book.

After the first chapter on production and trade, there follow ten chapters covering thirteen oils. The four dominant oils are discussed first: soybean, palm, rape/canola, and sunflower. These chapters are followed by chapters on the two lauric oils (coconut and palmkernel), cottonseed oil, groundnut (peanut) oil, olive oil, corn oil and three minor but interesting oils (sesame, rice bran, and flaxseed). The authors—from Europe, Asia, and North America—were invited to cover the following topics: the native oils in their original form and in modified forms resulting from partial hydrogenation, fractionation or interesterification, and related oils produced by conventional seed breeding and/or genetic modification. For each of these, information is provided on component triacylglycerols, fatty acids, minor components (phospholipids, sterols, tocopherols, carotenoids, etc.) and their major food uses.

The book will serve as a rich source of data on these oils and the important minor components that they contain. It should therefore be of special value to food producers requiring up-to-date information on their raw materials, which will probably already have been processed, at least in part.

The editor thanks the authors for their efforts to convert his concept into a reality and for their patience and willing cooperation, and he acknowledges the generous help and advice that he has received from the publisher, Dr Graeme MacKintosh, and his colleagues.

Frank Gunstone

Contributors

Dr Yusof Basiron	Malaysian Palm Oil Board, Bandar Baru Bangi, Selangor, Malaysia
Dr Dimitrios Boskou	Laboratory of Food Chemistry and Technology, School of Chemistry, Aristotle University of Thessaloniki, University Campus, Thessaloniki, 54006, Hellas, Greece
Professor Frank D. Gunstone	Scottish Crop Research Institute, Invergowrie, Dundee DD2 5DA, Scotland, UK
Dr Monoj K. Gupta	MG Edible Oil Consulting International, 9 Lundy's Lane, Richardson, TX 75080, USA
Dr S. Parkash Kochhar	SPK Consultancy Services, 48 Chiltern Crescent, Earley, Reading RG6 1AN, UK
Dr Siew Wai Lin	Malaysian Palm Oil Board, P.O. Box 10620, 50720 Kuala Lumpur, Malaysia
Mr Theodor Mag	T. Mag Consulting Inc., 35 Old Church Road, King City, ON L7B-1K4, Canada
Dr Robert A. Moreau	Crop Conversion Science and Engineering Research Unit, Eastern Regional Research Center, United States Department of Agriculture, Agricultural Research Service, 600 East Mermaid Lane, Wyndmoor, Pennsylvania, USA
Mr Richard O'Brien	4305 Barnsley Drive, Plano, TX 75093, USA
Mr T.P. Pantzaris	Malaysian Palm Oil Board Europe, Brickendonbury, Hertford, Hertfordshire SG13 8NL, UK

Mr Roman Przybylski

Department of Human Nutritional Sciences,
University of Manitoba, Winnipeg, MB
R3T2N2, Canada

Dr Timothy H. Sanders

United States Department of Agriculture,
Agricultural Research Service, Market
Quality and Handling Research Unit, Box
7624, North Carolina State University,
Raleigh, NC 27695-7624, USA

Professor Tong Wang

Department of Food Science and Human
Nutrition, 2312 Food Sciences Building,
Iowa State University, Ames, IA 50011,
USA

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2 Soybean oil

Tong Wang

2.1 Introduction

Soybean is the dominant oilseed produced in the world, due to its favorable agronomic characteristics, its high-quality protein, and its valuable edible oil. It contributes over a half of all oilseeds produced worldwide (Figure 2.1). The US ranks first in soybean production (8.24 million tonnes), followed by Brazil, Argentina, China and EU-15 (4.28, 3.28, 3.26 and 2.87 million tonnes, respectively, see Chapter 1). The production of soybeans and soybean oil is driven by the need for soy protein meal, which is used extensively in commercial feeds for poultry, swine and cattle. Soybean oil accounted for 80–90% of total edible oil consumption in the US (USDA–NASS) in 1998 because of its

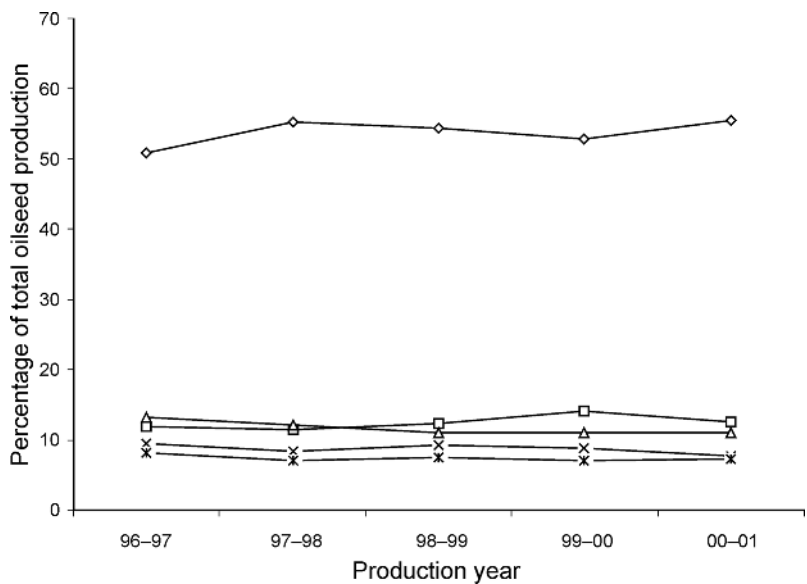


Figure 2.1 Five major oilseeds as a percentage of total worldwide oilseed production for the period 1996/97 to 2000/01 (Gunstone 2001), based on ten major oilseeds. Key: —◇—, Soybean; —□—, Rapeseed/Canola; —△—, Cottonseed; —×—, Sunflower; —✱—, Peanut.

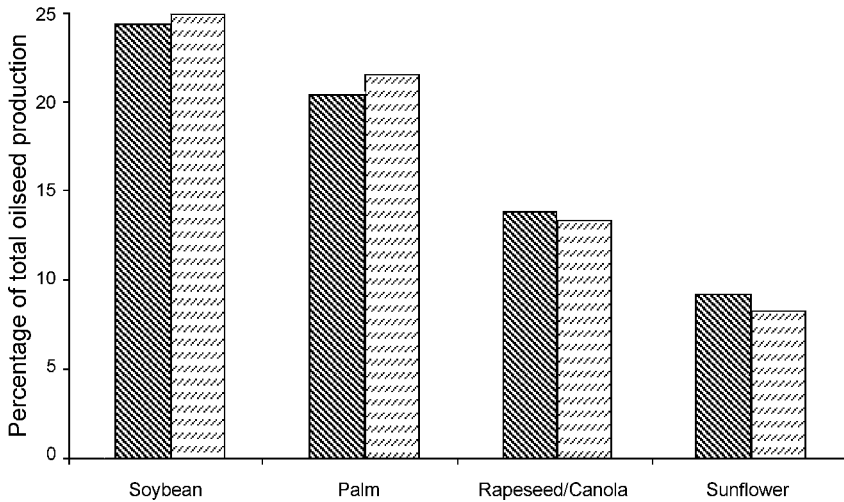


Figure 2.2 Four major oils as a percentage of total worldwide oil production for the period 1999/2000 to 2000/01 (Gunstone 2001), based on 17 commodity oils and fats. Key: , 99–00; , 00–01.

availability and its many desirable characteristics, including compositional and functional properties. Soybean oil is the predominant vegetable oil produced in the world, with palm oil being the second (Figure 2.2).

2.2 Composition

2.2.1 Seed composition

Mature soybeans are oval shaped and their sizes are variety-dependent. The seed consists of three major parts: seed coat or hull, cotyledon, and germ or hypocotyls. These structural components have the approximate composition shown in Table 2.1.

Table 2.1 Chemical composition (wt%) of soybean and its components (dry weight basis)

Components	Yield	Protein	Oil	Ash	Carbohydrate
Whole seed	100.0	40.3	21.0	4.9	33.9
Cotyledon	90.3	42.8	22.8	5.0	29.4
Hull	7.3	8.8	1.0	4.3	85.9
Hypocotyl	2.4	40.8	11.4	4.4	43.4

Perkins 1995a.

Table 2.2 Average compositions for crude and refined soybean oil

Components	Crude oil	Refined oil
Triacylglycerols (%)	95–97	>99
Phospholipids (%)	1.5–2.5	0.003–0.045
Unsaponifiable matter (%)	1.6	0.3
Phytosterols	0.33	0.13
Tocopherols	0.15–0.21	0.11–0.18
Hydrocarbons	0.014	0.01
Free fatty acids (%)	0.3–0.7	<0.05
Trace metals		
Iron (ppm)	1–3	0.1–0.3
Copper (ppm)	0.03–0.05	0.02–0.06

Pryde 1980a.

2.2.2 Oil composition

Oil recovered by solvent extraction or mechanical pressing is termed crude soybean oil and contains various classes of lipids. It consists primarily of neutral lipids, which include tri-, di- and monoacylglycerols, free fatty acids, and polar lipids such as phospholipids. It also contains a minor amount of unsaponifiable matter that includes phytosterols, tocopherols, and hydrocarbons such as squalene. Trace metals are found in soybean oil in ppm concentration. When the oil is refined, concentrations of all minor constituents are reduced. The typical composition of crude and refined soybean oil is shown in Table 2.2.

2.2.3 Fatty acid composition

Typical fatty acid composition of commodity soybean oil, in comparison with the other major vegetable oils, is shown in Table 2.3. Soybean oil has a high content of linoleic acid, and a lower level of linolenic acid. These are both essential fatty acids for humans and therefore of dietary importance, but they are also the cause of oxidative instability of this oil. Processing techniques, such as hydrogenation and lipid modification through traditional plant breeding or genetic transformation, have been used to modify the fatty acid composition to improve its oxidative or functional properties.

Triacylglycerols (TAG) are the primary neutral lipids in soybean oil. Due to the high concentration of unsaturated fatty acid in soybean oil, nearly all the TAG molecules contain at least two unsaturated fatty acids, and di- and trisaturates are essentially absent (List *et al.* 1977). In natural oils and fats, the fatty acids are not usually randomly distributed among the three hydroxyl groups of glycerol but are associated in particular patterns. Several theories of regiospecific distribution exist (Litchfield 1972), but the 1,3-random, 2-random theory is most widely accepted. The stereospecific distribution of fatty acyl groups in soybean oils

Table 2.3 Average fatty acid composition (wt %) of oils from soybean and other oilseeds

Fatty acid		Soybean	Canola	Cottonseed	Sunflower	Peanut
Lauric	12:0	—	—	—	0.5	—
Myristic	14:0	0.1	—	0.9	0.2	0.1
Palmitic	16:0	11.0	3.9	24.7	6.8	11.6
Palmitoleic	16:1	0.1	0.2	0.7	0.1	0.2
Stearic	18:0	4.0	1.9	2.3	4.7	3.1
Oleic	18:1	23.4	64.1	17.6	18.6	46.5
Linoleic	18:2	53.2	18.7	53.3	68.2	31.4
Linolenic	18:3	7.8	9.2	0.3	0.5	—
Arachidic	20:0	0.3	0.6	0.1	0.4	1.5
Gadoleic	20:1	—	1.0	—	—	1.4
Eicosadienoic	20:2	—	—	—	—	0.1
Behenic	22:0	0.1	0.2	—	—	3.0
Lignoceric	24:0	—	0.2	—	—	1.0

Orthoefer 1996.

Table 2.4 Fatty acid composition (mole %) and stereospecific distribution of neutral and polar lipids of a commodity soybean

		16:0	18:0	18:1	18:2	18:3
TAG		11.5	4.3	25.4	52.0	6.9
	<i>sn</i> -1	19.5	7.6	22.0	43.1	7.9
	<i>sn</i> -2	2.8	1.1	22.7	66.3	7.1
	<i>sn</i> -3	13.0	5.1	31.7	44.8	5.4
PC		15.1	4.5	11.5	61.3	7.6
	<i>sn</i> -1	29.6	7.5	10.0	46.6	6.4
	<i>sn</i> -2	2.4	0.7	12.5	75.4	9.1
PE		22.1	3.4	9.4	56.8	8.6
	<i>sn</i> -1	44.2	5.5	6.9	38.1	5.4
	<i>sn</i> -2	3.1	1.0	11.1	76.6	8.4
PI		33.0	9.1	7.7	43.2	7.0
	<i>sn</i> -1	66.3	14.6	6.4	11.2	1.6
	<i>sn</i> -2	9.1	2.8	7.5	70.4	10.2

Abbreviation: TAG: triacylglycerols; PC: phosphatidylcholines; PE: phosphatidylethanolamines; and PI: phosphatidylinositols.

with a wide range of composition was studied by Harp and Hammond (1998), and some deviation from the previously established distribution model was found. In soybeans with typical fatty acid composition, palmitic and stearic acids were associated more with the *sn*-1 position than with the *sn*-3 position, as shown in Table 2.4. When, however, the percentage of saturated acids increased, their accumulation at the *sn*-3 position was greater than at the *sn*-1 position. Linoleic acid showed a strong preference for the *sn*-2 position, but oleic acid was distributed relatively equally among the three positions. Linolenic acid had

greater enrichment at the *sn*-2 followed by *sn*-1 and *sn*-3 positions. To calculate the percentage of a particular molecular species present (e.g. ABC) in the oil, the equation

$$\% \text{ ABC} = (\% \text{ A at } sn-1) \times (\% \text{ B at } sn-2) \times (\% \text{ C at } sn-3) \times (10^{-4})$$

can be used (Litchfield 1972).

The stereospecific distribution of the fatty acyl groups has a significant influence on the oxidative stability of the soybean oil. It was suggested that concentration of unsaturated fatty acid at the *sn*-2 position stabilizes the oil against oxidation (Raghuveer and Hammond 1967; Lau *et al.* 1982). It was believed that TAG structure affected stability by altering the accessibility of substrate to free radical attack. Konishi and co-workers (1995) also observed that normal soybean oil randomly interesterified with stearate was far less stable than when stearate was placed selectively on the *sn*-1 and *sn*-3 positions. However, Neff and List (1999) found that randomization of soybean oil TAG improved the oxidative stability compared to the natural soybean oil. The relationship between TAG structure and its oxidative stability and how the regiospecific distribution affects the initiation, propagation and termination of the lipid autoxidation needs to be better understood.

2.2.4 Minor components

2.2.4.1 Phospholipids (PLs)

PLs are the major polar lipids in crude soybean oil. They are the primary component of cell membranes and play important roles in cell biological functions. The three major classes of PLs in soybeans are phosphatidylcholines (PC), phosphatidylethanolamines (PE) and phosphatidylinositols (PI), present in the relative proportions of 55.3, 26.3 and 18.4%, respectively (Wang *et al.* 1997). Wang and co-workers (1997) and Wang and Hammond (1999) studied class composition, stereospecific distribution, and molecular species composition of PLs in normal soybeans and in beans with genetically modified fatty acid composition. It was shown (Table 2.4) that PI had higher palmitate and stearate percentages than did PC and PE, that PC had the lowest palmitate percentage, and that PE had the lowest stearate percentage. Stereospecific analysis indicated that saturated fatty acids were concentrated at the *sn*-1 position, and the unsaturated fatty acids preferred the *sn*-2 position of the PL molecules.

2.2.4.2 Sphingolipids

Sphingolipids are ubiquitous constituents of the cell membrane and are highly bioactive. The hydrolyzed products of sphingolipids are used by cells to regulate growth, differentiation and apoptosis. There is evidence that sphingolipids inhibit colon carcinogenesis in experimental animals at a human diet-equivalent

concentration. They may reduce colon cancer risk in humans (Vesper *et al.* 1999) and inhibit skin cancer development (Merrill and Schmelz 2001). Soybeans are a relatively rich source of sphingolipids (Vesper *et al.* 1999) and ceramides and cerebrosides are the primary sphingolipid classes (Ohnishi and Fujino 1982). Little is known about how sphingolipid content varies with soybean variety and processing.

2.2.4.3 Unsaponifiable matter

The unsaponifiable matter (1.6%) in soybean oil includes several compounds, such as phytosterols (0.33%) and tocopherols (0.15–0.21%), which have important commercial value (Sipos and Szuhaj 1996a). Phytosterols, fatty acid esters of phytosterols, and sterol glycosides are present in very low concentrations in soybean oil and are further reduced during refining. The composition of phytosterols in crude and refined soybean oils is shown in Table 2.5, along with the composition of some modified oils. Soybean-germ oil, recovered from hypocotyl-enriched raw material, is a rich source of phytosterols (Ozawa *et al.* 2001) containing four times as much as does soybean oil. It may be an effective cholesterol-lowering functional oil (Sato *et al.* 2001).

Tocopherols are minor components of most vegetable oils and are natural antioxidants with various degrees of effectiveness. There are at least four types tocopherols in soybean oil. The γ -tocopherol is the major tocopherol present in soybean oil with the δ , α , and β compounds present in decreasing quantities (Table 2.6).

Table 2.5 Sterol content (mg/100 g) of soybean oils

Reference source and sterol	Crude	Refined
Weihrauch and Gardner (1978)		
Sterol		
β -Sitosterol	183	123
Campesterol	68	47
Stigmasterol	64	47
Δ^5 -Avenasterol	5	1
Δ^7 -Stigmasterol	5	1
Δ^7 -Avenasterol	2	<0.5
Total	327	221
Vlahakis and Hazebroek (2000)		
β -Sitosterol	125–236	
Campesterol	62–131	
Stigmasterol	47–77	
Total	235–405	

Table 2.6 Tocopherol content of crude soybean and wheat germ oils

	Mechanically pressed soybean oil	Solvent extracted soybean oil	Solvent extracted wheat germ oil
Total tocopherol (ppm)	1257	1370	2682
α-Tocopherol (%)	9.3	10.5	67.8
β-Tocopherol (%)	1.2	1.2	32.2
γ-Tocopherol (%)	62.8	63.5	–
δ-Tocopherol (%)	26.7	25.0	–

2.3 Extraction and refining of soybean oil

2.3.1 Oil extraction

The two common processes for soybean oil extraction are solvent extraction and mechanical pressing but in the US less than 1% of the soybeans is processed by mechanical means. Solvent extraction with hexane is the standard practice in today’s modern processing facilities, and its use has been reviewed by Woerfel (1995). There are three major steps in solvent extraction: seed preparation, oil extraction, and desolventizing of the oil and meal. Conventional seed preparation includes drying, cleaning, cracking, optional dehulling or decortication, conditioning, and flaking of the seeds. The option of expanding after flaking is used to improve oil extraction, percolation, and solvent drainage, and is accompanied by a doubling of the throughput. In another variation in seed preparation (hot dehulling), hulls are removed from the split seeds by alternate slow and rapid heating before cracking and flaking. Hot dehulling is more energy efficient than conventional dehulling. The Alcon process (Penk 1986) is a flake-heating treatment aimed to improve the degumming efficiency of the crude oil. A very low level of phospholipid in degummed oil can be achieved and therefore the oil can be physically refined. However in the US the majority of soybean oil is chemically refined.

Solvent (hexane) extraction of soybeans is a diffusion process achieved by immersing solid in solvent or by percolating solvent through a bed of solids. Rotary (deep-bed), horizontal belt, and continuous loop extractors are used for soybeans (Woerfel 1995). Solvent is recovered from the mixture of solvent and extracted oil (miscella) by double-effect evaporator and steam stripping and from flake by a desolventizer–toaster, and is recycled.

Solvent extraction in vegetable oil production has been recognized by the US Environmental Protection Agency (EPA) as a major hazardous air pollutant and ‘National Emission Standards for Hazardous Air Pollutants’ (NESHAP) for oil extraction were established (Federal Register 2001). In the 1970s, US extraction plants had typically 1 gallon solvent loss/ton of soybean seed (2.8 kg hexane/tonne) as standard. The new regulation is 0.2 gallon/ton (0.56 kg hexane/

tonne). The design and operation of extractor, evaporator, and desolventizer-toaster thus become very important.

The two major mechanical processes for soybeans are continuous screw pressing with extensive heating and extrusion-expelling (Nelson *et al.* 1987). Extrusion-expelling technology is used increasingly for processing identity-preserved seeds for niche market soybean oil and protein products (Wang and Johnson 2001a). The advantages of small tonnage requirement (easy switch-over for various types of seeds, no flammable solvent used, low initial capital investment, and unique products) have made this processing technology very appealing for many soybean growers and processors. Quality comparisons of crude oils and meals obtained by solvent and mechanical extraction is presented in Table 2.7.

Although mechanical pressing of soybeans accounts for a only very small percentage of soybean processing, it is used by many farm cooperatives or family-owned on-farm operations in the US, primarily to produce protein meals for use as animal feed.

Table 2.7 Quality comparison of oils and meals obtained by solvent extracted, extruded-expelled and screw pressed soybeans^a

	Solvent extraction		Extrusion-expelling		Screw pressing	
Oil						
PV (meq/kg)	0.96	y	1.73	x	1.76	x
FFA (%)	0.31	xy	0.21	y	0.33	x
Phosphorus (ppm)	277	y	75	z	463	x
AOM stability (h)	39.8	x	23.9	y	36.2	x
Tocopherols (ppm)	1365	x	1257	y	1217	y
Color (red)	11.1	y	10.2	y	17.5	x
Meal						
Oil ^b (%)	1.2	y	7.2	x	6.3	x
Protein ^b (%)	48.8	x	42.5	y	43.2	y
Fiber ^b (%)	3.7	y	5.4	x	5.9	x
Urease (ΔpH)	0.04	x	0.07	x	0.03	x
KOH solubility (%)	89.1	x	88.1	x	61.6	y
PDI	44.5	x	18.1	y	10.6	z
Rumen bypass (%)	36.0	y	37.6	y	48.1	x
Hunter color ‘L’	69.1	x	65.8	x	51.5	y
Hunter color ‘a’	2.0	y	0.4	z	4.8	x
Trypsin inhibitor activity						
(mg/g)	5.46		5.52		0.30	
(TIU/g)	5275		12254		2000	

^aThe values of each row with different letters are significantly different at 5%.

^bPercentages are based on 12% moisture content.

Wang and Johnson 2001a.

2.3.2 Oil refining

The non-TAG portion of soybean oils includes phospholipids, free fatty acid, chlorophyll pigment, oxidation products, and other unsaponifiable components such as tocopherols, sterols and hydrocarbons. Some of these minor components negatively affect oil quality, while some may play a positive role in nutrition and function. The goal of refining is therefore to remove the undesirable components and, at the same time, to maximize retention of the beneficial components.

2.3.2.1 Degumming

Degumming is a process for removing phospholipids (gums) from crude soybean oil, to improve its physical stability and to facilitate further refining. The water degumming procedure is simple, but its efficacy is influenced by the quality of crude oil. Phospholipids can exist in hydratable form that can be readily removed after addition of water, or in non-hydratable form that cannot be removed by this procedure. The non-hydratable phospholipids (NHP) are probably calcium and magnesium salts of phosphatidic acids, resulting from enzymatic hydrolysis of the phospholipids. This degradation results from seed damage during storage and handling or from improper seed preparation. List and co-workers (1992) showed that four interrelated factors promote NHP formation: (i) moisture content of beans or flakes; (ii) phospholipase D activity; (iii) heat applied to beans or flakes prior to and during extraction; and (iv) disruption of the cellular structure by cracking and/or flaking. These results suggest that NHP formation can be minimized by control of the moisture of beans and/or flakes entering the extraction process, by inactivation of phospholipase D enzyme, and by optimizing temperature during the conditioning of cracked beans or flakes. Normal quality soybean oil from conventional solvent extraction has about 90% hydratable PLs and 10% NHP. Phosphoric acid or citric acid can be used as an aid for more complete removal of NHP, but their presence in the gum will reduce its quality due to darkening. Total phospholipid in crude soybean oils ranges from 1.1–3.2%. The quantity of phospholipids in the crude oil depends on the extraction method, particularly seed preparation before solvent extraction. Use of an expander or Alcon process will increase total phospholipid content in the crude oil and increase the proportion of phosphatidylcholine in the gum (Kock 1983).

Degumming can be achieved in batch or continuous fashion. In batch degumming, soft water at the same percentage as total phospholipids is added to heated (70°C) oil and mixed thoroughly for 30–60 min, followed by settling or centrifuging. In continuous water degumming, heated oil is mixed with water by an in-line proportioning and mixing system and the mixture is held in a retention vessel for 15–30 min before centrifugation. A well-degummed soybean should contain less than 50 ppm of phosphorus, well below the 200 ppm level specified in the National Oilseed Processors Association (NOPA 1993) trading

rules for crude degummed soybean oil. A commonly used calculation to convert phosphorus concentration to that of phospholipids is to apply a multiplication factor of 30. Degumming, prior to physical refining of soybean oil, requires a more complete removal of the phospholipids to prevent darkening during fatty acid distillation, and several modified degumming methods have been described (Seger and van de Sande 1990; Dijkstra 1992).

Recently, polymeric ultrafiltration membranes have been used for degumming crude soybean oil. Pagliero and co-workers (2001) showed that membranes were suitable for removing phospholipids from the miscella of crude oil and hexane. When surfactant-aided membrane degumming was applied to crude soybean oil, the degummed oil contained 20–58 ppm of phosphorus (Subramanian *et al.* 1999). Supercritical CO₂ extraction (List *et al.* 1993) and ultrasonic degumming (Moulton and Mounts 1990) were also successfully used to reduce the gum content of soybean oil.

2.3.2.2 *Neutralization*

Neutralization is also described as deacidification or caustic refining. It is achieved by treating the soybean oil with aqueous alkaline solution (generally sodium hydroxide) to neutralize the free fatty acid (FFA) in a batch or continuous system. The soap formed in the reaction also adsorbs natural pigments, unhydrated gum and mucilaginous substances contained in the oil. Settling or centrifugation is used to remove the soap. More details on soybean oil neutralization are discussed by Erickson (1995a) (see also Section 2.3.3). Soybean oil can also be neutralized by methanol extraction of the free fatty acid from crude oil. The extractant is separated into fatty acid and solvent by a membrane filter (Raman *et al.* 1996).

2.3.2.3 *Bleaching*

Bleaching is a process designed not only to remove the pigment (chlorophyll) but, more importantly, to break down peroxides (primary oxidation products) into lower molecular weight carbonyl compounds that can be subsequently removed by deodorization. In soybean oil refining color reduction occurs at each step of degumming, neutralization, bleaching, hydrogenation and deodorization. Nevertheless, the most significant reduction of chlorophyll, which is involved in photosensitized oxidation of soybean oil, is in the bleaching step. Acid-activated bleaching clay is most effective in adsorbing chlorophyll and decomposing peroxides. Low levels of phosphorus (5–10 ppm P) and soap (10–30 ppm) in the neutralized oil are required to maximize the bleaching effect. The desired bleaching end point is zero peroxide so the amount of bleaching earth should be adjusted to the quality of oil to be bleached. Earth dosage ranges from 0.3–0.6% for typical soybean oil. Successful bleaching can be achieved by atmospheric batch bleaching, vacuum batch bleaching, or continuous vacuum bleaching at

temperatures between 100 and 120°C for 20–30 min. More details of soybean oil bleaching are described by Erickson (1995b).

2.3.2.4 Deodorization

Deodorization, usually the last step in oil refining, is a steam-stripping process in which good-quality steam (1–3% of oil), generated from de-aerated and properly treated feed water, is injected into soybean oil under high temperature (252–266°C) and high vacuum (< 6 mm Hg). Under these conditions peroxides are decomposed and the FFA and odorous compounds are vaporised. Heat bleaching is achieved by holding the oil for 15–60 min at high temperature to ensure considerable decomposition of carotenoid pigments. During the deodorization process many desirable reactions are taking place, but there are also some undesirable reactions such as lipid hydrolysis, polymerization and isomerization. Therefore, the deodorization temperature must be carefully controlled to achieve optimum quality finished soybean oil. Kemeny and co-workers (2001) studied the kinetics of the formation of *trans* linoleic acid and *trans* linolenic acid in vegetable oils during deodorization at temperatures of 204–230°C for 2–86 h. Applying the established model, the *trans* fatty acid level of refined oils can be predicted for given deodorization conditions. The conditions to meet increasingly strict consumer demands concerning the *trans* isomer content can be calculated and the deodorizer design can be characterized by deviation from the theoretical level of *trans* fatty acid in the deodorized oil.

There are three types of deodorization operations. The batch process is the least common, due to its low efficiency and inconsistent product quality. Semi-continuous and continuous deodorizers have improved processing efficiency. There are several configurations of the continuous deodorizer, including single-shell cylindrical vessel type, vertically stacked tray type, and the thin-film packed column type. This last provides excellent fatty acid stripping with minimum use of steam, but it achieves neither desired heat bleaching nor effective deodorization due to the relatively short retention time. A retention vessel has to be used after the column distillation (De Greyt and Kellens 2000).

Changes in oil quality during refining of soybean oil (Jung *et al.* 1989) are shown in Table 2.8. A study of oxidative stability of soybean oil at different stages of refining indicated that crude oil was the most stable and highly purified oil the least stable (Kwon *et al.* 1984). Ferrari *et al.* (1996) and Ramamurthi and co-workers (1998) studied changes in composition of minor components during refining with the results shown in Table 2.9.

2.3.3 Modified non-alkaline refining

Alternative techniques of vegetable oil refining have been developed. Simple refining methods were explored to process extruded-expelled (E-E) soybean oils with various fatty acid compositions (Wang and Johnson 2001b, 2001c). E-E

Table 2.8 Effect of processing steps on quality of soybean oil

	Phosphorus (ppm)	Iron (ppm)	Free fatty acid (%)	Peroxide value (meq/kg)	Tocopherol (ppm)
Crude	510	2.9	0.30	2.4	1670
Degummed	120	0.8	not available	10.5	1579
Refined	5	0.6	0.23	8.8	1546
Bleached	1	0.3	0.08	16.5	1467
Deodorized	1	0.3	0.00	0.0	1138

Jung *et al.* 1989.

Table 2.9 Effect of processing on content of tocopherols, sterols, and squalene in soybean oil

Processing step	Tocopherols		Sterols		Squalene	
	ppm	% Loss	ppm	% Loss	ppm	% Loss
Crude	1132	—	3870	—	143	—
Degummed	1116	1.4	3730	3.6	142	0.7
Neutralized	997	11.9	3010	22.2	140	2.1
Bleached	863	23.8	3050	21.2	137	4.2
Deodorized	726	35.9	2620	32.3	89	37.8

Ramamurthi *et al.* 1998.

oils can be easily water-degummed to low phosphorus levels. Free fatty acids were reduced to 0.04% by adsorption with Magnesol, a commercial magnesium silicate product. This material also adsorbed primary and secondary oil oxidation products. A final mild steam deodorization produced good-quality soybean oil. This adsorption refining procedure is much milder than conventional refining as indicated by low formation of primary and secondary lipid oxidation products and reduced loss of tocopherol (Figure 2.3). Sodium silicate was also used as a mild neutralizing agent to refine specialty oils (Hernandez 2001). Its agglomerating property allowed the removal of the soap by filtration, and its low alkalinity minimized saponification of neutral oil and loss of minor nutrients.

2.3.4 Co-products from oil refining

2.3.4.1 Lecithin

Soybean is the predominant source of lecithin for pharmaceutical and food purposes because of its availability and outstanding functionality. The composition of crude soy lecithin is shown in Table 2.10. It contains a large amount of neutral oil, and crude lecithin is usually deoiled to improve its functionality. This separation is based on the solubility difference of neutral and polar lipids in acetone. Phospholipids are precipitated from solution and separated.

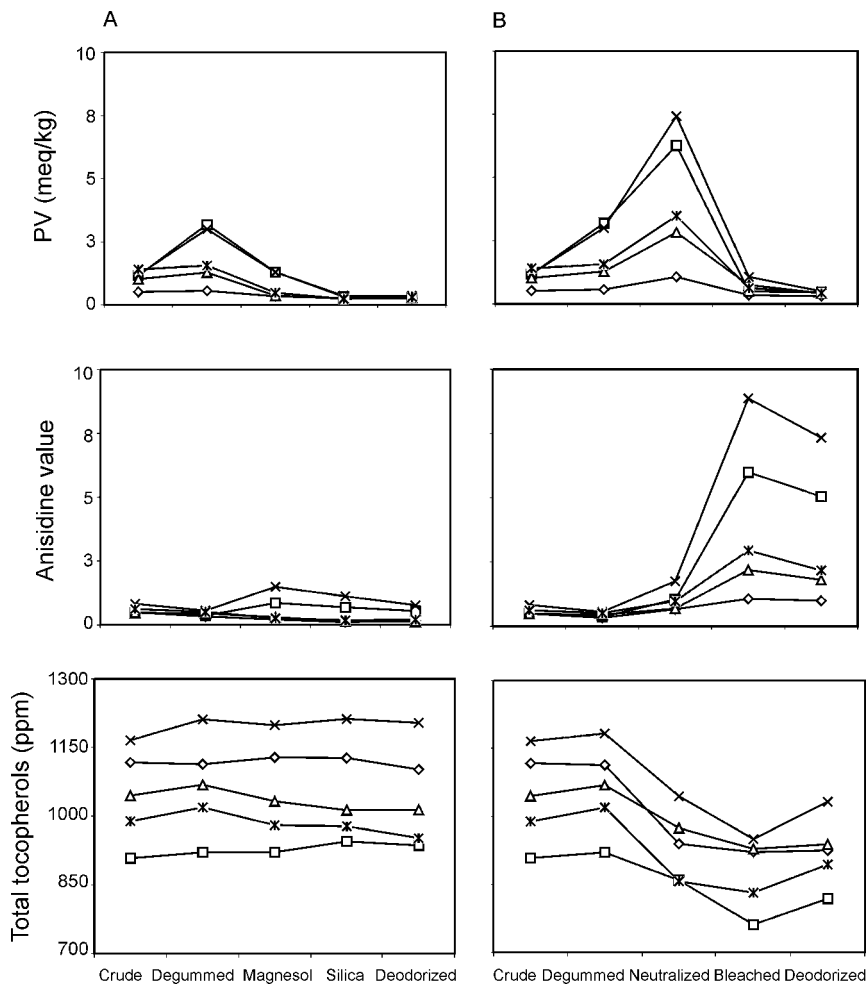


Figure 2.3 Oxidation and tocopherol retention during modified (A) and conventional (B) refining of various types of soybean oils. Key: $\diamond$, high-oleic acid soybean oil (HO); $\square$, low-linolenic acid soybean oil (LLL); $\triangle$, lipoxigenase-free soybean oil (LOX); $\times$, low-saturated fatty acid soybean oil (LS); $\bullet$, commodity soybean oil (CS). *Source:* Wang and Johnson 2001b.

Alcohol fractionation of deoiled lecithin provides alcohol-soluble and alcohol-insoluble fractions enriched with PC and PI respectively. The PC-enriched fraction is an excellent oil-in-water emulsifier. The PI-enriched fraction is a good water-in-oil emulsifier often used in the chocolate industry to increase the viscosity of the mass, therefore reducing the need for cocoa butter. The typical composition of these lecithin products is shown in Table 2.11.

Table 2.10 Composition of commercial soy lecithin and egg lecithin

Compounds	Soy lecithin (wt %)	Egg lecithin (wt %)
Phosphatidylcholine	10–15	65–70
Phosphatidylethanolamine	9–12	9–13
Phosphatidylinositol	8–10	–
Phosphatidylserine	1–2	–
Phosphatidic acid	2–3	–
Lysophosphatidylcholine	1–2	2–4
Lysophosphatidylethanolamine	1–2	2–4
Phytoglycolipids	4–7	–
Phytosterines	0.5–2.0	–
Other phosphorus-containing lipids	5–8	–
Sphingomyelin	–	2–3
Carbohydrate	2–3	–
Free fatty acids	max 1	max 1
Mono-, diacylglycerols	max 1	trace
Water	max 1.5	max 1.5
Triacylglycerols	35–40	10–15

Wendel 1995.

Table 2.11 Typical composition (%) of commercially refined lecithin products

	Lecithin oil-free	Lecithin alcohol-soluble	Lecithin alcohol-insoluble
Phosphatidylcholine	29	60	4
Phosphatidylethanolamine	29	30	29
Phosphatidylinositol and glycolipid	32	2	55
Neutral oil	3	4	4
Others	7	4	8
Emulsion type favored	w/o or o/w	o/w	w/o

Brekke 1980a.

Supercritical CO₂ extraction has been used to extract PC from deoiled soybean lecithin selectively (Teberikler *et al.* 2001). The effects of temperature, pressure and amount of ethanol on PC extraction were examined and optimum conditions described to yield a high-purity product. Soybean lecithins can be chemically altered to modify their emulsifying properties and to improve their dispersibility in aqueous systems. Phospholipids may be hydrolyzed by acid base or enzyme (phospholipase A) to achieve better hydrophilic and emulsification properties. Hydroxylation of lecithin improves its oil-in-water emulsification property and water dispersibility. Acetylation (of PE) creates improved fluid, emulsification, and water dispersion (List 1989).

Lecithin recovered from solvent extracted and mechanically pressed soybean oils has different phospholipid class composition (Wu and Wang 2001).

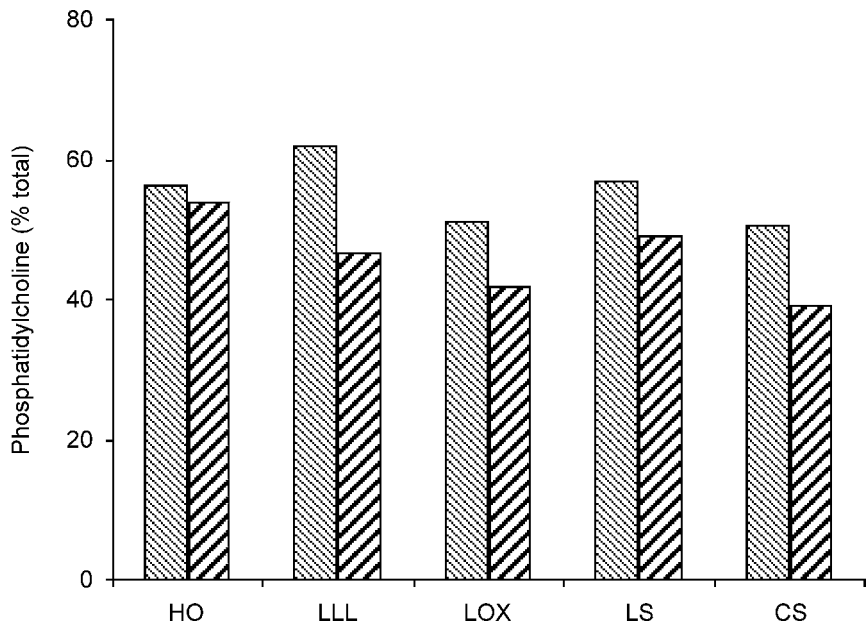


Figure 2.4 Phosphatidylcholine content of lecithin recovered from extruded-expelled (E-E) and solvent extracted (S-E) soybean oils. Abbreviations: HO, high-oleic acid soybean oil; LLL, low-linolenic acid soybean oil; LOX, lipoxygenase-free soybean oil; LS, low-saturated fatty acid soybean oil; and CS, commodity soybean oil. Key: ▨, E-E; ▩, S-E.

The percentage of PC was considerably higher in lecithin recovered from extruded-expelled oil than from solvent extracted oil, as shown in Figure 2.4.

The utilization of soybean lecithins is reviewed by Schneider (1986). Table 2.12 summarizes the most common applications in the food, feed, cosmetic, and pharmaceutical industries. The food industry relies on lecithin in bakery, beverage, and confectionery product development because of its functionalities.

2.3.4.2 *Deodorizer distillate*

Soybean deodorizer distillate (SBDD) is the material collected from the steam distillation of soybean oil. It is a mixture of free fatty acids (particularly during physical refining), tocopherols, phytosterols and their esters, hydrocarbons, and secondary lipid oxidation products. The quality and composition of SBDD depends on feedstock oil composition and on processing conditions. Tocopherols and sterols are valuable components that can be further separated from the distillate and used in the nutrition-supplement and pharmaceutical industries (Pickard *et al.* 1996). Table 2.13 shows the composition of deodorizer distillates

Table 2.12 Uses and functions of soybean lecithins

Product	Function
Food	
Instant food	Wetting and dispersing agent; emulsifier
Baked goods	Modification of baking properties; emulsifier; antioxidant
Chocolate	Viscosity reduction; antioxidant
Margarine	Emulsifier; antispattering agent; antioxidant
Dietetics	Nutritional supplement
Feedstuffs and technical	
Calf milk replacer	Wetting and dispersing agent; emulsifier
Insecticides	Emulsifier; dispersing agent; active substance
Paints	Dispersing agent; stabilizer
Magnetic tapes	Dispersing agent; emulsifier
Leather	Softening agent; oil penetrant
Textile	Softening; lubricant
Cosmetics	
Hair care	Foam stabilizer; emollient
Skin care	Emulsifier; emollient, refatting, wetting agent
Pharmaceuticals	
Parental nutrition	Emulsifier
Suppositories	Softening agent; carrier
Creams, lotions	Emulsifier; penetration improver

Schneider 1986.

Table 2.13 Composition (wt %) of deodorizer distillate from various oils

%	Soybean	Sunflower	Cotton	Rapeseed
Unsaponifiable	33.0	39.0	42.0	35.0
Total tocopherol	11.1	9.3	11.4	8.2
α -Tocopherol	0.9	5.7	6.3	1.4
Total sterol	18.0	18.0	20.0	14.8
Stigmasterol	4.4	2.9	0.3	1.8

Winters 1990.

from soybean oil and other vegetable oils. Soybean tocopherols are the major source of natural fat-soluble antioxidants and vitamin E. The human body has a strong preference for the natural D- α -tocopherol. Synthetic vitamin E is less active because it is a mixture of eight different stereoisomers (Clark and Frandsen 1998). Phytosterols are used as raw materials for over 75% of the world's steroid production. The more recent application of phytosterol and phytostanol and their fatty acid esters in margarine and table spreads is related to the cholesterol-lowering effect of these compounds (Law 2000; Normen *et al.* 2000). Hollingsworth (2001) and Hicks and Moreau (2001) have reviewed the recent development of functional foods containing phytosterols.

Preparation of high-purity tocopherols and phytosterols involves a series of physical and chemical processing steps, such as molecular distillation, adduct

formation, liquid–liquid extraction, supercritical fluid extraction, saponification and chromatography (Ramamurthi *et al.* 1998). Extraction of tocopherols from soybean oil deodorizer distillate by urea inclusion and saponification resulted in high recovery of tocopherols (Wu *et al.* 2001). To improve the separation of sterols and tocopherols, Shimada and co-workers (2000) used a lipase to esterify sterols with FFA. The sterol esters and tocopherols are then better separated from one another by molecular distillation. Chang and co-workers (2000) used supercritical fluid CO₂ extraction to recover tocopherols and sterols from soybean oil deodorizer distillate. An isolation process for sterols and tocopherols from soybean deodorizer distillate is reported in a patent (Sumner *et al.* 1995). Treatment of the distillate with methanol converts fatty acid esters into fatty acid methyl esters that can then be removed by a stripping operation. Separation of sterols and tocopherols was subsequently carried out by molecular distillation.

2.3.4.3 Soap-stock

Soap is recovered after alkaline neutralization of the crude or degummed soybean oil. The neutralisate consists of water, free fatty acids, neutral oil, phospholipids, unsaponifiable matter, proteins and mucilaginous substances. Its composition depends on seed quality and oil extraction and refining conditions and efficiencies. Soap-stock is the lowest-priced by-product from oil processing and is generated at a rate of about 6% of the volume of crude oil refined (Golbitz 2000) amounting to as much as 1.8 billion pounds (0.9 million tonnes) in the US annually. The majority of the soap or the acidulated soap is used as feed. Soybean oil can also be refined using caustic potash (KOH) and acidulated with sulfuric acid, followed by neutralization with ammonia rather than NaOH. In this way the potassium and ammonium salts in the wastes produced can be used as fertilizer (Daniels 1989). Soybean oil methyl esters can also be produced from soap-stock for biodiesel application (Stern *et al.* 1986; Basu and Norris 1996; Haas and Scott 1996; Haas *et al.* 2000; Wang *et al.* submitted).

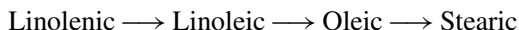
2.4 Oil composition modification by processing and biotechnology

To extend its food applications, soybean oil is often modified by chemical or genetic manipulation. The primary objective of these changes is to improve its physical, chemical, and functional properties.

2.4.1 Hydrogenation

The high degree of unsaturation, particularly the significant level of linolenic acid, of soybean oil limits its food application due to its low oxidative stability. Partial hydrogenation is used to increase the melting temperature and, at the same time, to improve the oxidative stability of soybean oil.

When oil is treated with hydrogen gas in the presence of a catalyst (nickel) under appropriate agitation and temperature conditions, it becomes a semi-solid or plastic fat, suitable for many food applications. Selectivity is the term used to describe the relative reaction rates of the fatty acids from the more unsaturated to the more saturated forms. A perfect selectivity provides sequential elimination of unsaturated acids as follows:



Generally, selectivity increases with increases in temperature and in catalyst concentration and with decreases in hydrogen pressure and in agitation rate (Erickson and Erickson 1995). The effect of pressure on hydrogenation selectivity of soybean oil was reported by List and co-workers (2000) who showed that the linoleate-containing triacylglycerols were reduced at a much faster rate than the linolenate-containing triacylglycerols under their experimental conditions. Pressure had a significant effect on the course of hydrogenation. At higher pressures (500 psi), the reaction is truly nonselective, whereas at 50 psi, the reaction becomes selective. More comprehensive reviews on reaction and formulation can be found in Erickson and Erickson (1995), Hastert (1996) and Kellens (2000). During hydrogenation various side-reactions occur, some of which have a strong impact on the physical and nutritional properties of the products. Double bond isomerization and *trans* fatty acid formation are the most important side-reactions. The *trans* double bond is a thermodynamically more stable configuration than its *cis* counterpart, and it is produced in significant quantity during partial hydrogenation. The *trans* fatty acids have a much higher melting point than their *cis* isomers, therefore fat products with considerable *trans* fatty acids will have elevated melting points, which is desirable in shortening and margarine applications. However, the recently established link between *trans* fat consumption and ill health has prompted research to minimize this double bond isomerization.

2.4.2 *Interesterification*

Interesterification is a term used to describe reactions in which fatty acid esters react with free fatty acids (acidolysis), alcohols (alcoholysis), or with other fatty acid esters (transesterification). In food application, interesterification often refers to the reaction between different oils or fats with their fatty acyl groups rearranging among the molecules.

Interesterification is conveniently achieved by an alkali methoxide-catalyzed reaction at mild temperatures (20–100°C). Microbial lipases are also widely used as biocatalysts in enzymatic interesterification. In contrast to the chemical process, the enzymatic process can be more selective if an enzyme with positional specificity is used, and it is usually much slower and more sensitive to the reaction conditions. New developments in lipase-catalyzed interesterification

have resulted in industrial applications of this process (Hoy and Xu 2001). The reaction can be performed in batch form with the enzyme immobilized, or in continuous form where the enzyme is immobilized in the packed-bed. Nevertheless, the high cost of the enzyme and process equipment restricts its wide adoption, and it may be economically feasible only with very high-value applications. Most interesterification reactions are still effected with a chemical catalyst.

One modification of typical interesterification is directed interesterification in which the reaction is conducted at a relatively low temperature. Under these conditions the more saturated TAG molecules crystallize and equilibrium is continuously re-established in the liquid phase. A product with desired functional properties can be obtained by selection of appropriate reaction conditions. Randomization is a special form of interesterification in which acyl groups of a single oil or fat rearrange, resulting in a change from the natural distribution ultimately to a completely random pattern. Chemical and physical properties change as a consequence of this acyl group redistribution. For example, the oxidative stability of soybean and corn oils decreased three to four times by randomization (Fatemi and Hammond 1980; Lau *et al.* 1982) and the crystallization behavior of natural lard changed from the β to β' form (Lutton *et al.* 1962).

2.4.3 Crystallization and fractionation

Fractionation or winterization is a process in which the more saturated molecular species in the oil are solidified during low temperature treatment and subsequently removed; cold storage stability is thereby increased. When partially hydrogenated soybean oil is fractionated, the more saturated molecular species are removed to produce a clear oil that meets the requirements of a salad oil and a high-stability liquid oil.

Recent reports linking consumption of *trans* fatty acids to the risk of coronary heart disease have generated much interest in producing margarines and shortenings that do not contain *trans* fatty acids. To achieve this, liquid oil and completely hydrogenated hard stock is interesterified to give a product with proper plastic property. These products need to have a proper solid fat content (SFC) or solid fat index (SFI) profile to maintain good integrity or firmness at room temperature, to resist temperature cycling (ie frequent changes of temperature from ambient to refrigeration), and to melt completely at body temperature.

Various methods of laboratory scale, pilot plant processing, and batch reaction were described by Erickson (1995c). List and co-workers (1977) pioneered the development a zero *trans* margarine by interesterifying 80% RBD soybean oil with 20% RBD and fully hydrogenated soybean oil. The resulting product has comparable SFI to the conventional products. In a more recent study,

Table 2.14 Example of a combined hydrogenation, interesterification and fractionation to produce low-*trans* fat from soybean oil

	Iodine Value	M.P. (°C)	SFC (% at °C)			
			10	20	30	40
Soybean oil (SBO) feedstock	134	-7	0	-	-	-
Fully hydrogenated SBO (FHSBO)	1	71	95	94	94	93
Blending of SBO and FHSBO (60:40)	81	63	44	42	39	35
Random interesterification of SBO and FHSBO (60:40)	81	53	38	33	20	11
Fractionation of the interesterified oil						
Soft fraction	91	24	25	1	0	0
Hard fraction	63	58	60	58	45	32

Kellens 2000.

margarines were prepared from interesterified soybean oil–soybean trisaturation blends (80:20) and compared with a product made from hydrogenated soybean oil (List *et al.* 1995). Penetration, yield values and water/oil-off data (the tendency of a margarine emulsion to break down physically) were determined. These products tended to crystallize slowly after passing through a rotator and this resulted in a product somewhat harder than desirable. However, addition of 20% soybean oil to the interesterified oil yielded a softer product. Table 2.14 presents a typical example of the combined use of hydrogenation, interesterification, and fractionation to produce low *trans* fats with physical properties comparable to partially hydrogenated soybean oil with a high *trans* content.

Soybean oils with elevated levels of saturated fatty acids (by genetic modifications) can be randomized to produce margarines with desirable physical properties. Kok and co-workers (1999) interesterified a soybean oil containing 23.3% palmitic acid and 20.0% stearic acid to produce a *trans*-free margarine. The interesterified oil had a slip melting point of 34.5°C (compared with 9.5°C in the non-interesterified oil), and increased melting and crystallization temperatures were found using differential scanning calorimetry. A 50:50 blend of interesterified oil and regular soybean oil was used to make margarine. Compared with commercial soft-tub margarine, the maximal peak force on the texture analyzer of this blended margarine was about 2.3 times greater, the hardness about 2.6 times greater, and adhesiveness about 1.5 times greater. There were small but statistically significant differences ($\alpha = 0.05$) in the sensory properties of 'spreadability', graininess and waxiness between the commercial and blended margarines at 4.5°C. These very small differences suggest a potential use for the modified high-stearic soybean oil in margarine products.

A similar study of zero-*trans* margarine from soybean oils with modified fatty acid composition was conducted by List and co-workers (2001). A soft margarine was prepared from interesterified soybean oil with elevated stearic

acid content (16–21%). The product had penetrations of 75–92 mm, indicating a harder product than that obtained with hydrogenated soybean oil. The margarines showed spreadability values of > 6 compared with 3–5 found for commercial samples. Mouth-melt data and oil-off test indicated that the interesterified products was comparable to commercial products. Other vegetable oils, such as palm and cottonseed oils, or fully hydrogenated hardstocks can be blended with genetically modified soybean oils to improve their plastic range (List *et al.* 1996).

2.4.4 Traditional plant breeding and genetic modification

Conventional or traditional breeding of soybean includes selective breeding by crossing among the selected populations and mutagenesis through chemicals or irradiation. Genetic modification implies transfer of a gene from one species to another (transgenic). The drivers for these seed modification are nutrition, functionality and agronomics (Gunstone and Pollard 2001). Soybean oil composition is modified to increase its oxidative stability (low 18:3, high 18:1), to modify its physical properties (high saturates), and to improve its nutritional properties (low saturates and high 18:3). In addition to change in oil composition, soybean is also modified to improve its agronomic performance, in areas such as disease resistance, herbicide resistance and yield. Herbicide-resistant Roundup soybeans account for over 60% of soybean production in the US and they are planted in significant quantity in South America, especially in Argentina.

Modified soybean oils have been developed and some have been commercialized. They include: low saturated fatty acids, high-palmitic acid, high-stearic acid, high-palmitic and stearic acids, low-linolenic acid, and high-oleic (Table 2.15). The high-oleic oil (> 80%) has low linolenic acid content (2%) and lower total saturated content (9%). According to Wolf and Knowlton (1999), this type of oil has significantly improved oxidative stability. A mid-oleic acid oil (55%) was developed at North Carolina State University (Wilson 1999). This oil has an optimum composition and is predicted to be the soybean variety of the future. It will have improved shelf life and flavor quality when used as salad oil. It can also replace the hydrogenated oils in light-duty frying applications. It is anticipated that a frying fat with zero-*trans* fatty acid and low saturated acid will gain wide acceptance.

Oils from soybeans developed to contain changed levels of palmitic and linolenic acid were evaluated for oxidative stability (Shen *et al.* 1997). Raising palmitic and/or reducing linolenic acids increased the oxidative stability of soybean oils. Oxidative stability and high temperature stability of oils with altered fatty acid compositions have been examined. Generally oils with higher saturated fatty acid content or lower polyunsaturated fatty acid content showed higher oxidative stability (Miller and White 1988; White and Miller 1988; Liu and White 1992a, b).

Table 2.15 Soybeans with modified fatty acid composition

Type	Composition (%)					Reference
	16:0	18:0	18:1	18:2	18:3	
Commodity	11	4	23	54	8	
Low saturates	3	1	31	57	9	Liu 1999
	4	3	28	61	3	Reske <i>et al.</i> 1997
High-palmitic	25	4	16	44	10	Neff and List 1999
	23	5	21	47	4	Shen <i>et al.</i> 1997
High-stearic	9	26	18	39	8	Neff and List 1999
	11	21	63	1	3	Knowlton <i>et al.</i> 1999
High-palmitic and stearic	24	19	9	38	10	Neff and List 1999
	22	18	9	41	10	Wilson 1999
Low-linolenic	10	5	41	41	2	Fehr <i>et al.</i> 1992
	15	6	32	45	2	Fehr <i>et al.</i> 1992
High-oleic	6	3	86	2	2	Liu 1999
	9	3	79	3	6	Wilson 1999

Soybean oils with elevated saturated fatty acids may not need hydrogenation, thus reducing processing costs, and they may be used to make the zero-*trans* margarine and shortenings discussed earlier. Liu (1999) presented more information on soybean oil modification and discussed hurdles in commercialization of these new oil products.

Minor components in the oil are altered along with fatty acid modification. Changes in total tocopherols and their composition in soybean have been reported (Wang and Johnson 2001b, Dolde *et al.* 1999, Almonor *et al.* 1998). According to Abidi and co-workers (1999), genetic modification resulted in changed total tocopherols and showed greater variation in the concentration of α - and γ -tocopherols than δ -tocopherol. Phytosterol composition was also markedly affected by genetic modification. Brassicasterol, campesterol, and β -sitosterol levels were consistently lowered in one genotype and increased brassicasterol content was observed in another variety (Abidi *et al.* 1999). The study of genetic modification of fatty acid on content and composition of minor bioactive components of oil showed that soybeans with elevated palmitic and stearic acids had lower tocopherol content and β -sitosterol varied greatly with fatty acid modification (Mounts *et al.* 1996). The effect of plant growth temperature and fatty acid composition on tocopherols and phytosterols suggested that linolenic acid and total tocopherol have a positive correlation (Dolde *et al.* 1999), and that total phytosterol increases with elevation in temperature and tocopherols (Vlahakis and Hazebroek 2000). A multivariate study of the correlation between tocopherol content and fatty acid composition in vegetable oil showed positive correlation between polyunsaturated fatty acid and tocopherols (Kamal-Eldin and Andersson 1997). The composition of tocopherols has been modified by over

expressing the methyl transferase gene to change the tocopherol composition in *Arabidopsis thaliana* (Shintani and DellaPenna 1998).

Phospholipid fatty acid composition, altered at the same time as oil modification in soybeans, may have a significant consequence on seed viability and seedling growth. Wang and co-workers (1997) examined the fatty acid composition and stereospecific distribution of fatty acyl groups of three individual phospholipid classes (PC, PE and PI) in 25 genetically modified soybeans, and found that PL fatty acid composition changed with changing fatty acids, particularly for palmitic, stearic and linolenic acids. Thermal transitions of the neutral and polar lipids of soybeans with elevated saturated fatty acids were also investigated by Wang and co-workers (2001), who established that the melting temperature of both classes of lipid was increased. Occasional poor germination and field performance of these seeds may be attributed to the modification in their PL composition and consequent changes in the physical properties of their membranes.

2.5 Physical properties of soybean oil

2.5.1 Polymorphism

Oils and fats go through a series of increasingly organized crystal phases upon cooling. This multiple form of crystallization (polymorphism) is an important characteristic of fats and oils because it greatly influences the textural and functional properties of fats and fat-based products.

The three commonly observed fat crystal forms are the α , β' , and β forms. The β' form, with small and needle-like crystals which form smooth and fine-grained structures, is the most desired form in shortening and margarine applications. Oil composition plays an important role in crystal formation. Unmodified soybean oil has a tendency to form β -crystals but the hydrogenated soybean oil can be crystallized in the β' -form. Controlled crystallization (under defined conditions of temperature, time and mixing) and tempering is used to manipulate or stabilize the crystal forms to achieve products with the desired functional properties.

2.5.2 Density

Most information concerning the physical properties of soybean and other vegetable oils comes from early work, but there have been recent developments in establishing mathematical models to predict changes in physical properties with fatty acid composition and temperature.

For vegetable oils, it has been shown that density decreases linearly with increase in temperature (Formo 1979).

$$\rho = b + mT$$

where ρ is the density, T is the temperature, and b and m are constants. These constants are different for different oils. A widely used method for density prediction of vegetable oils was developed by Lund and discussed by Halvorsen and co-workers (1993). The Lund relationship is:

$$sg (15^{\circ}\text{C}) = 0.8475 + 0.00030 \text{ SV} + 0.00014 \text{ IV}$$

where sg is the specific gravity of vegetable oil at 15°C , SV is the saponification value, and IV is the iodine value of the oil. This equation can be used for a wide variety of oils. For further details, readers are recommended to examine the paper by Halvorsen and co-workers (1993). A generalized method of density estimation, which was developed by Rodenbush and co-workers (1999), was also extended to predict oil viscosity, thereby relating these two key physical properties.

2.5.3 Viscosity

The effect of temperature on viscosity of various vegetable oils and fatty acids was investigated by Nouredini and co-workers (1992). The relationship was expressed as

$$\ln \mu = A + B/(T + C)$$

in which μ is viscosity in centipoises, A , B and C are constants and T is temperature in Kelvin. For each oil and fatty acid, there is a set of constants that can be used to predict how temperature affects viscosity of individual oils. Viscosity of fatty systems was also predicted by Rabelo and co-workers (2000), using the same temperature–viscosity relationship. The set of A , B and C values for each fatty compound class was then correlated with the number of carbon atoms and double bonds, and rather complicated relationships were established.

Wang and Briggs (in press) studied viscosity of soybean oils with modified fatty acid composition. The viscosity was expressed as

$$\mu = Ae^{(Ea/RT)}$$

in which R is the universal gas constant, T is temperature in Kelvin, and Ea is energy of activation. The concept of effective carbon number was used to describe acyl chain length and degree of unsaturation, and was correlated with viscosity and Ea . Linear relationships were established indicating that the more

the saturation or the longer the fatty acyl chains, the more viscous the oil and the faster the viscosity changes with temperature. Geller and Goodrum (2000) reported that viscosity of pure and saturated TAGs of 6:0 to 18:0 correlated with the carbon number in a second order polynomial fashion.

2.5.4 Refractive index

The refractive index (RI) is a parameter that relates to molecular weight, fatty acid chain length, degree of unsaturation, and degree of conjugation. A mathematical relationship between refractive index and iodine value (IV) has been described by Perkins (1995b) as

$$n_D^{25} = 1.45765 + 0.0001164 \text{ IV}$$

The reverse relationship can be used to calculate the iodine value of crude soybean oil when the RI is known. RI was shown to increase by 0.000385 for each degree rise of temperature.

2.5.5 Specific heat

Specific heat (C_p , in J/g K) of vegetable oil is influenced by temperature (Formo 1979) as described in the following equation:

$$C_p = 1.9330 + 0.0026 T$$

Liquid specific heat capacity for fatty acids, triacylglycerols, and vegetable oils was estimated based on their fatty acid composition (Morad *et al.* 2000). A Rowlinson–Bondi equation was used to estimate specific heat (C_p) for pure fatty acid. The liquid specific heat capacities of oils were estimated by using mixture properties corresponding to the fatty acid composition and a correction factor, which accounts for the TAG form. The Rowlinson–Bondi equation used is as follows:

$$(C_p - C_p^0)/R = 1.45 + 0.45(1 - T_r)^{-1} \\ + 0.25\omega[17.11 + 25.2(1 - T_r)^{1/3}T_r^{-1} + 1.742(1 - T_r)^{-1}]$$

where C_p is the liquid specific heat capacity, C_p^0 is the ideal gas specific heat capacity, R is the universal gas constant, T_r is the reduced temperature, and ω is the acentric factor. C_p^0 is calculated using the method of Rihani and Doraiswamy (1965):

$$C_p^0 = \Sigma a + T \Sigma b + T^2 \Sigma c + T^3 \Sigma d$$

The constants a , b , c and d for various chemical groups were used to calculate the ideal gas capacity for pure fatty acids. The reduced temperature is calculated

as $T_r = T/T_c$ (critical temperature). For a vegetable oil with x_i being the molar fraction of a fatty acid that has $C_{p_i}^0$,

$$C_p^0(\text{mix}) = \sum x_i C_{p_i}^0$$

A factor was used to correct the difference between calculated and experimental values as derived from Morad's study. For $MW > 850$, as in our sample,

$$\text{Correction factor (F)} = -0.2836 - 0.0005(MW - 850)$$

$$C_p(\text{estimated for oil}) = C_p(\text{calculated for mixed fatty acid}) + F$$

The accuracy of Morad's estimation method was determined to be $\pm 5\%$. This model was used by Wang and Briggs (in press) to estimate C_p of soybean oils with modified fatty acid composition at various temperatures. All oils had the same slope of 0.0024, but the constant ranged from 1.7992 to 1.8583, compared with a slope of 0.0026 and a constant of 1.9330 from Formo's equation.

2.5.6 Melting point

The melting points (m.p.) of TAGs are related to the fatty acids present. For fatty acids, melting point depends on chain length and the number and position of double bonds. It increases with increasing chain length and decreases with increasing *cis* unsaturation. The *trans* form has a significantly higher melting point than its *cis* isomer. Polymorphism is an important factor affecting melting point. The melting points of fatty acids and their triacylglycerols of soybean oil and partially hydrogenated soybean oil are presented in Table 2.16.

2.5.7 Heat of combustion

A general equation linking the heat of combustion of vegetable oils to IV and SV (i.e. average fatty acid composition) has been developed by Bertram (Perkins 1995b)

$$-\Delta H_c(\text{cal/g}) = 11,380 - \text{IV} - 9.158(\text{SV})$$

Therefore, the higher the degree of saturation and the longer the fatty acyl groups, the higher the energy content of the oil.

2.5.8 Smoke, flash and fire points

These parameters are related to the free fatty acid content of oils because fatty acids have higher vapor pressure than the triacylglycerols. Smoke point is the temperature at which smoke is first seen. Flash point is the temperature at which the volatiles are produced in amounts that ignite but do not support a flame. Fire point is the temperature at which the volatiles are produced in a quantity that

Table 2.16 Melting point of fatty acids and triacylglycerols of soybean oil and its partially hydrogenated product

Fatty acid		Triacylglycerol		
		Composition*	Melting point (°C)	
Name	Melting point (°C)		β Form	β' Form
Palmitic	62.9	PPP	65.5	56.0
Stearic	69.6	SSS	73.0	65.0
		SPP	62.5	59.5
		PSP	68.0	65.0
		SPS	68.0	64.0
Oleic	16.3	OOO	5.5	−12.0
		POP	35.2	30.4
		SOS	41.6	37.6
		POO	19.0	−
		SOO	23.5	−
Elaidic	43.7	EEE	42.0	37.0
Linoleic	−6.5	LLL	−13.1	−
Linolenic	−12.8	LnLnLn	−24.2	−

Sipos and Szuhaj 1996.
*These symbols represent the acyl groups of the TAG molecule: P= palmitic, S= stearic, O= oleic, L= linoleic, Ln= linolenic, E= elaidic acid.

will support a flame. These temperatures are lower for oils with a higher free fatty acid content or with short chain free fatty acids.

2.5.9 Solubility

Soybean oil is miscible with many non-polar organic solvents. The solubility characteristics of vegetable oils in various solvents can be estimated from their dielectric constants or solubility parameters (Sipos and Szuhaj 1996a). Anhydrous or aqueous ethanol is not a good solvent for soybean oil at ambient temperature. Solubility increases with temperature until the critical solution temperature is reached, at which point the oil and ethanol become miscible. The solubility of oxygen in soybean oil contributes to the oxidative stability of the oil. It varies from 1.3 to 3.2 ml/100 ml in refined and crude oils. The solubility of water in soybean oil is about 0.071% at −1°C and 0.141% at 32°C (Perkins 1995b).

2.5.10 Plasticity and ‘spreadability’

The most important functionality of a solidified oil and fat is its plasticity, consistency or ‘spreadability’. A shortening or margarine product may appear to be in a homogeneous solid state, but it consists of discrete solid (crystal

Table 2.17 Representative values for selected physical properties of soybean oil

Property	Value
Specific gravity (25°C)	0.9175 ^a
Refractive index, n_D^{25}	1.4728 ^b
Specific refraction, r_D^{20}	0.3054
Viscosity (centipoises at 25°C)	50.09 ^a
Solidification point (°C)	−10 to −16
Specific heat (cal/g at 19.7°C)	0.458
Heat of combustion (cal/g)	9478 ^c
Smoke point (°C)	234
Flash point (°C)	328
Fire point (°C)	363

^aIV = 132.6, ^bIV = 130.2, ^cIV = 131.6.
Pryde 1980b.

particles) dispersed in a liquid (oil) phase. The essential conditions for plasticity are proper proportions of solid and liquid phase, and the solid particles have to be very fine so the mass is held together by internal cohesive forces. SFI and SFC measurements may be used to describe plasticity and ‘spreadability’.

2.5.11 Electrical resistivity

Certain industrial applications of soybean oil, such as printing ink, require high electrical resistivity to maintain the sharpness of the image. There is limited information on electrical properties of oil, and most deal with its dielectric properties. Resistivity is the resistance to current passing through the material and factors such as temperature, applied voltage and charging time will affect the value. Polar minor components including FFA, PLs, monoacylglycerol, tocopherols, phytosterols, β -carotene, peroxides and water all decrease the resistivity of purified soybean oils (Tekin and Hammond 1998) and of soybean oil methyl esters (Tekin and Hammond 2000). Selected physical properties of soybean oil are summarized in Table 2.17.

2.6 Oxidative quality of soybean oil

Soybean oil is a polyunsaturated or linoleic type of oil that is highly susceptible to lipid oxidation. The rate of lipid oxidation depends primarily on the fatty acid composition and only secondarily on the stereospecific distribution of the fatty acyl groups, as described earlier. The mechanism of lipid oxidation and lipid hydroperoxide breakdown has been discussed thoroughly by Frankel (1998).

Oxidative instability limits the use of soybean oil in certain applications, but hydrogenation and other means of composition modification have made soybean oils the most widely used of all vegetable oils. The following analytical methods are frequently used to quantify oxidation of soybean oil.

2.6.1 *Sensory evaluation*

Sensory evaluation provides information most closely associated with the quality of food lipids. Flavor or odor defects may be detected by panelists before they are recognised by chemical or instrumental methods. For example, the 'fishy' and 'grassy' taste produced in linolenic acid-containing oils such as soybean oil occurs at very low levels of oxidation only detected by sensory analyses. The limitations of this method are poor reproducibility and high cost of panelists and the necessary facilities. The recommended approach is to use more reproducible chemical or instrumental methods to complement or support the sensory analyses (Frankel 1998).

2.6.2 *Peroxide value*

Peroxide value (PV) is the most commonly used measurement of lipid oxidation. The standard iodometric method requires a relatively large sample (5 g) when the lipid is only slightly oxidized. The ferric thiocyanate method, based on the oxidation of ferrous to ferric ion, involves colorimetric measurement of ferric thiocyanate. This method is more sensitive than the iodometric method and requires a relatively small sample (0.1 g). The PV is a useful measure for samples with low levels of oxidation and when the hydroperoxides are not decomposed. During prolonged oxidation, a maximum PV is reached and the value then begins to decrease due to peroxide degradation. This maximum value occurs early for soybean and rapeseed oil, due to the more rapid decomposition of the hydroperoxides of the polyunsaturated fatty acids.

2.6.3 *Carbonyl compounds*

Carbonyl compounds in oxidized lipids are the secondary oxidation products resulting from the decomposition of the hydroperoxides. They can be quantified by the reaction with 2,4-dinitrophenylhydrazine and the resulting colored hydrazones are measured spectrophotometrically at 430–460 nm. The carbonyl value is directly related to sensory evaluation, because many of the carbonyl molecules are those responsible for off-flavor in oxidized oil. The anisidine value is a measure of carbonyl compounds that have medium molecular weight and are less volatile (Frankel 1998). It can be used to discover something about the prior oxidation or processing history of an oil.

2.6.4 *Conjugated diene*

Conjugated diene hydroperoxides produced from polyunsaturated lipids can be determined quantitatively by their strong absorption at 234 nm. This sensitive method can only apply to undegraded hydroperoxides.

2.6.5 *TBA test*

The thiobarbituric acid (TBA) value test is a popular way of measuring rancidity in certain foods and oxidation products in biological systems. It is based on the formation of a colored complex between two molecules of TBA and one molecule of malonaldehyde resulting from thermal decomposition of polyunsaturated peroxides. This reaction is not specific due to the presence of many TBA-reactive substances (TBARS), such as browning reaction products, protein and sugar decomposition products, amino acids, nucleic acids and nitrite.

2.6.6 *GC method*

Gas chromatographic (GC) methods have been used for determining volatile oxidation products. Static headspace, dynamic headspace or direct injection methods are the three commonly used approaches. These methods were compared in an analysis of volatile compounds in an oxidized soybean oil. It was found that each method produced significantly different GC profiles (Frankel 1985). The dynamic headspace and direct injection methods gave similar results, but the static headspace is more sensitive to low molecular weight compounds. Lee and co-workers (1995) developed a dynamic headspace procedure for isolating and analyzing the volatiles from oxidized soybean oil, and equations were derived from theoretical considerations that allowed the actual concentration of each flavor component to be calculated.

2.6.7 *Oxidative stability*

The oxidative stability of lipids has been evaluated by a variety of methods under a wide range of conditions. Temperature is the most important factor to consider in oxidative stability determination, because the rate of oxidation is exponentially related to temperature increase. Therefore the shelf life of a lipid decreases logarithmically with increasing temperature. The mechanisms of oxidation and peroxide decomposition are different at different temperatures. Therefore to predict oxidative stability of food lipids realistically the test conditions should be as close as possible to those under which the lipid is stored. Storage at ambient conditions or at elevated temperatures and measurement of weight gain, flavor analysis, peroxide value, conjugated diene or carbonyl compounds are commonly used. The active oxygen method (AOM) and the

automated Rancimat or OSI (oxidative stability index) methods use high temperatures (about 100°C), and were criticized as being unreliable because the mechanism of oxidation changes at this elevated temperature (Frankel 1998). The usefulness of OSI as an accelerated test was studied by correlating OSI with sensory evaluation (Coppin and Pike 2001). Good correlation was obtained, and OSI appeared to be an acceptable accelerated method for measuring the oxidative stability of light-exposed soybean oil that varied in metal catalyst content.

2.7 Nutritional properties of soybean oil

Soybean oil is the dominant edible oil in the US. In 1998 about 51% of the soybean oil was used in a partially hydrogenated form (USDA–NASS 2000) and this contributes a significant portion of the daily *trans* fatty acids intake in the US. The health effect of *trans* fatty acid in partially hydrogenated soybean oil has been a concern for many years. The physical property of the *trans* fatty acids (i.e. straighter hydrocarbon chain and higher melting point compared with the *cis* counterparts) contribute to their biological effect. The bio-absorption of *trans* and *cis* fatty acids was similar (Emken 1984) but *trans* isomers are metabolized differently from the *cis* isomers, in that they are more rapidly bio-oxidized (Emken *et al.* 1989). Study of the cholesterol-raising effect of *trans* fatty acids showed that they raised total cholesterol and LDL-cholesterol and lowered HDL-cholesterol compared with the *cis* isomers (Judd *et al.* 1994).

Commodity soybean oil is composed of 61% polyunsaturated fatty acids, 25% monounsaturated fatty acid and 15% saturated fatty acids. The essential fatty acids linoleic (18:2, *n*-6) and α -linolenic (18:3, *n*-3) acids account for 89 and 11% of the total essential fatty acids from this source. The *n*-6 acid content in soybean oil is slightly lower than that in corn and sunflower oils, but it is more than double that in canola oil. Soybean and canola are the only two common plant oils that have a considerable amount of the *n*-3 linolenic acid.

The physiological effects of vegetable oil are based on their fatty acid composition. Current US dietary guidelines recommend that diets contain less than 30% calories from fat, of which less than 10% is from saturated fat, 10–15% from monounsaturated acid, and 10% from polyunsaturated acids. The primary concerns with fatty acid consumption relate to two chronic diseases—coronary heart disease (CHD) and cancer. Research has shown that high levels of dietary saturated fatty acids are related to increased CHD and that dietary modification can lower plasma cholesterol. Consequent changes in cholesterol level can be predicted by the following relationship (Hegsted *et al.* 1993).

$$\Delta \text{ cholesterol} = 2.10(\Delta \text{ saturates}) - 1.16(\Delta \text{ polyunsaturates}) \\ + 0.06(\Delta \text{ dietary cholesterol})$$

The amount of total fat consumed, rather than the specific type of fat, has been positively associated with cancer risk (Dupont *et al.* 1990). However, animal studies suggested that linoleic acid promotes carcinogenesis under special circumstances (Sundram *et al.* 1989; Dupont *et al.* 1990), and that linolenic acid has a potential anticarcinogenic effect (Fritsche and Johnson 1988). Involvement of linolenic acid in carcinogenesis has not been found in humans. The amount of fat and its unsaturation significantly influence normal immune response and expression of inflammatory diseases (Connor 2000).

2.8 Food uses of soybean oil

According to Agricultural Statistics 2000 (USDA–NASS 2000), margarine, shortening and salad/cooking oils accounted for 12, 31 and 41% of total domestic consumption of oils and fats in the US in 1998. Soybean oil was used to produce 95% of the total margarine and 83% of the total shortening. Based on 1998/1999 soybean utilization in the US (Golbitz 2000), 95% of the total soybean oil produced was used in food applications. Among the food uses, 13, 38 and 48% of the soybean oil was used in margarine, shortening, and cooking oil, respectively.

2.8.1 Cooking and salad oils

Oil can be used for cooking either in its natural state or after processing, depending on custom and nutritional beliefs. In most parts of the world, cooking oil is processed or refined to a bland taste. In addition to its common household uses, the use of cooking oil in deep fat frying is very important. Salad oil is a refined or sometimes fractionated liquid vegetable oil remaining liquid at 4.4 °C. An important distinction between salad and cooking oils is the difference in their oxidative and thermal stability (Krishnamurthy and Witte 1996). Cooking oil is more stable than salad oil at higher temperatures such as deep fat frying. Fully refined soybean oil can be directly used as salad oil, whereas other oils, such as sunflower and corn, have to be dewaxed before they can meet the criteria of a salad oil. Because soybean oil contains a relatively high amount of the polyunsaturated and unstable linolenic acid, it is usually partially hydrogenated to produce salad or cooking oils. However, soybean oil is also used without hydrogenation in the preparation of salad dressings. Synthetic antioxidants, such as butylated hydroxyanisole (BHA), butylated hydroxy toluene (BHT), propyl gallate (PG), ascorbyl palmitate, and tertiary-butyl hydroquinone (TBHQ), have been used in cooking oils. Natural antioxidants derived from sage, rosemary and green tea are increasingly used meet to the consumer's preference of natural food ingredients (Chen *et al.* 1992).

New nutrition-oriented salad and cooking oils are being developed. LoSatSoy is a low-saturated acid oil developed at Iowa State University and marketed

commercially as a salad and cooking oil. It has half of the saturated fatty acid compared with commercial soybean oil; therefore, it is believed to have nutritional benefit. Low-linolenic acid soybean oil has improved oxidative stability in salad and cooking oil applications.

A unique vegetable oil, diacylglycerol (DAG) oil, developed and successfully marketed in Japan by Kao Corp, is being produced from soybean oil by an Archer Daniels Midland Co. (ADM) Kao LLC joint venture. This oil is metabolized differently from other oils in that it is not stored as body fat but immediately burned as energy (Nagao and Teramoto 2001; Soni *et al.* 2001). It lowered the magnitude of increase in serum and chylomicron TAG levels as compared with TAG in a single administration study in humans; thus it is considered to reduce postprandial hypertriglyceridemia (Matsuo and Tokimitsu 2001). DAG has a similar caloric value and absorption rate as TAG but resynthesis of TAG in the small intestine epithelial cells is different when DAG or TAG are ingested. DAG is considered to be effective in preventing obesity and, possibly, in moderating lifestyle-related diseases. DAG prevented body fat accumulation, especially in visceral fat, in a double-blind controlled study. The serum profiles and anthropometric parameters (body weight, body mass index, waist circumference and thickness) were obviously improved by consuming DAG as cooking oil in free-living subjects (Yasukawa and Yasunaga 2001). DAG has received GRAS status from the US FDA, and it is expected that future application of DAG in various food products will improve the health of the general public.

2.8.2 *Margarine and shortening*

Margarine was first produced in 1869 by a French chemist to meet the butter shortage during the industrial revolution. The traditional form of the product is stick margarine. Other forms, including spreadable, polyunsaturated and low-fat margarines, have been developed to satisfy the demands of convenience and nutrition. A significant recent trend is away from margarine (80% fat, as defined by the FDA's Standard of Identity) to spreads with less fat (75% to less than 5%). This trend has accelerated to a point where there are now very few full-fat margarine products available in the US (Chrysam 1996).

The most important functional properties of margarines and spreads are 'spreadability', oiliness and melting property. These properties relate to fat level and type and stability of the emulsion. Spreadability can be predicted by SFI and penetration measurement. Oil-off refers to the phenomenon when fine fat crystals no longer form a stable network to trap the liquid oil. Consistency and emulsion stability depend on the amount and type of crystallized fat. During rapid cooling, the most unstable α crystals form but they quickly transform to the β' form, which is relatively stable and consists of a very fine crystal network capable of immobilizing a large quantity of oil. These β' crystals may also transform into the most stable β form, which has a coarse and sandy texture and

from which liquid (oil) may be expelled out. Quick melting at body temperature and the consequent cooling sensation is the desired quality and is related to the melting profile of the fat as well as emulsion formation (Chrysam 1996).

Most table spreads in the US are formulated with soybean oil. Palm oil, lauric fat, and even partially hydrogenated marine oils are commonly used in such products in Europe. Blending of unmodified oils with oils hydrogenated to various degrees allows the production of margarines with desirable texture. The greater the number of base stocks available, the greater is the flexibility to produce a wide range of products and the higher the tolerance to processing conditions. A study of procedures for designing suitable margarine from various stocks was conducted by Cho and co-workers (1993).

Other ingredients used in margarines are dairy products, emulsifiers, preservatives, flavors, vitamins and colors. The processing of margarine includes emulsification, chilling, working, resting and packaging (Chrysam 1996). The ingredients are emulsified before being fed into a swept-surface heat exchanger. The mass emerging from the cooling tubes is a partially solidified mass and it is further crystallized in the working unit. Texture of the product is further modified in the resting tube before the margarine is packaged.

Shortening contains 100% fat of vegetable or animal source and is used in frying, cooking, baking and other confectionary items. It can be in plastic and semi-solid or pourable fluid form, or in encapsulated powder, pellet or flake form. It is produced by formulating a blend, solidifying and plasticizing the blend, and packaging and tempering. The β' form crystals are preferred for both margarine and shortening products. The large number of minute air bubbles, incorporated in the shortening, improve the leavening of baked foods. A more in-depth discussion of the science and technology of shortening has been presented by Metzroth (1996).

2.8.3 *Mayonnaise and salad dressing*

The official definition (FDA Standard of Identity) describes mayonnaise as a semi-solid food prepared from vegetable oil (no less than 65%), egg yolk and vinegar. Most mayonnaise in the US contains 75–82% oil which is usually soybean oil. Other salad oils that have undergone winterization (including partially hydrogenated soybean oil) can also be used in mayonnaise. The production of mayonnaise is partly an art due to the difficulty of producing the o/w emulsion in which the dispersed phase is seven times more than the continuous phase. Egg solids and processing conditions play critical roles in mayonnaise quality.

Salad dressings were developed as an alternative to mayonnaise. The standard of identity requires that salad dressing contain not less than 30% vegetable oil, vinegar, not less than 4% egg yolk, and is thickened by starch. The oils used in salad dressing are selected using the same criteria as for mayonnaise.

The quality of mayonnaise and salad dressing is determined by the physical and oxidative stability of its lipid components. Phase separation is caused by emulsion breakdown due to mechanical shock, agitation or extreme temperatures. Oxidation of vegetable oil and egg lipid is another form of degradation of mayonnaise or salad dressing. Because the quality of oil plays a major role in the flavor stability of these products, only the best quality oil should be used in product formulation. Another class of dressing is pourable as opposed to spoonable products (mayonnaise and Kraft's Miracle Whip). The standard for this type of product is undefined, except for French dressing (Krishnamurthy and Witte 1996). Pourable dressing can be in two different finished forms; one phase or two phases depending upon whether the product is homogenized. The oil used in these products is predominantly soybean oil in the US. Canada and Europe may use different oils for such products, depending on the availability of vegetable oil in that specific region.

References

- Abidi, S.L., List, G.R. and Rennick, K.A. (1999) Effect of genetic modification on the distribution of minor constituents in canola oil. *J. Am. Oil Chem. Soc.*, **76**, 463–467.
- Almonor, G.O., Fenner, G.P. and Wilson, R.F. (1998) Temperature effect on tocopherol composition in soybeans with genetically improved quality. *J. Am. Oil Chem. Soc.*, **75**, 591–596.
- Basu, H.N. and Norris, M.E. (1996) Process for production of esters for use as a diesel fuel substitute using a non-alkaline catalyst. US Patent 5,525,126.
- Brekke, O.L. (1980a) Oil degumming and soybean lecithin, in *Handbook of Soy Oil Processing and Utilization* (eds D.R. Erickson, E.H. Pryde, O.L. Brekke, T.L. Mounts and R.A. Falb), AOCS Press, Champaign, IL, pp. 71–88.
- Chang, C.J., Chang, Y., Lee, H., Lin, J. and Yang, P. (2000) Supercritical carbon dioxide extraction of high-value substances from soybean oil deodorizer distillate. *Ind. Eng. Chem. Res.*, **39**, 4521–4525.
- Chen, Q., Shi, H. and Ho, C. (1992) Effect of rosemary extract and major constituents on lipid oxidation and soybean lipoxygenase activity. *J. Am. Oil Chem. Soc.*, **69**, 999–1002.
- Cho, F., DeMan, J.M. and Allen, O.B. (1993) Application of simplex-centroid design for the formulation of partially interesterified canola/palm blends. *J. Food Lipid*, **1**, 25–52.
- Chrysam, M.M. (1996) Margarines and spreads, in *Bailey's Industrial Oil and Fat Products, Edible Oil and Fat Products: Products and Application Technology* (ed Y.H. Hui), 5th edn, Vol 3, John Wiley & Sons, Inc, New York, NY, pp. 65–114.
- Clark, J.P. and Frandsen, S.S. (1998) Phytochemicals from vegetable oil deodorizer distillate, in *Proc. World Conf. Oilseed Edible Oils Process* (eds S.S. Koseoglu, K.C. Rhee and R.F. Wilson), AOCS Press, Champaign, IL, Vol 1, pp. 135–138.
- Connor, W.E. (2000) Importance of *n*-3 fatty acids in health and disease. *Am. J. Clin. Nutr.*, **71**, 171S–175S.
- Coppin, E.A. and Pike, O.A. (2001) Oil stability index correlated with sensory determination of oxidative stability in light-exposed soybean oil. *J. Am. Oil Chem. Soc.*, **78**, 13–18.
- Daniels, R.S. (1989) Fertilizer process. Can. Pat. 1,256,449.
- De Greyt, W. and Kellens, M. (2000) Refining practices, in *Edible Oil Processing* (eds W. Hamm and R.J. Hamilton), Sheffield Academic Press, Sheffield, UK, pp. 79–128.

- Dijkstra, A.J. (1992) Degumming, refining, washing and drying fats and oils, in *Proc. World Conf. Oilseed Technology and Utilization* (ed T.A. Applewhite), AOCS Press, Champaign, IL, pp. 138–151.
- Dolde, D., Vlahakis, C. and Hazebroek, J. (1999) Tocopherols in breeding lines and effects of planting location, fatty acid composition, and temperature during development. *J. Am. Oil Chem. Soc.*, **76**, 349–355.
- Dupont, J., White, P.J., Carpenter, M.P., Schaefer, E.J., Meydani, S.N., Elson, C.E., Woods, M. and Gorbach, S.L. (1990) Food uses and health effects of corn oils. *J. Amer. Coll. Nutr.*, **9**, 438–470.
- Emken, E.A. (1984) Nutrition and biochemistry of trans and positional fatty acid isomers in hydrogenated oils. *Annu. Rev. Nutr.*, **4**, 339–376.
- Emken, E.A., Adlof, R.O., Rohwedder, W.K. and Gulley, R.M. (1989) Incorporation of *trans*-8- and *cis*-8-octadecenoic acid isomers in human plasma and lipoprotein lipids. *Lipids*, **24**, 61–69.
- Erickson, D.R. (1995a) Neutralization, in *Practical Handbook of Soybean Processing and Utilization* (ed D.R. Erickson), AOCS Press, Champaign, IL, pp. 184–202.
- Erickson, D.R. (1995b) Bleaching/adsorption treatment, in *Practical Handbook of Soybean Processing and Utilization* (ed D.R. Erickson), AOCS Press, Champaign, IL, pp. 203–217.
- Erickson, M.D. (1995c) Interesterification, in *Practical Handbook of Soybean Processing and Utilization* (ed D.R. Erickson), AOCS Press, Champaign, IL, pp. 277–296.
- Erickson, D.R. and Erickson, M.D. (1995) Hydrogenation and base stock formulation procedures, in *Practical Handbook of Soybean Processing and Utilization* (ed D.R. Erickson), AOCS Press, Champaign, IL, pp. 218–238.
- Fatemi, S.H. and Hammond, E.G. (1980) Analysis of oleate, linoleate, and linolenate hydroperoxides in oxidized ester mixtures. *Lipids*, **15**, 379–385.
- Federal Register (2001) 40 CFR Part 63. National Emission Standards for Hazardous Air Pollutants (NESHAP): Solvent Extraction for Vegetable Oil Production; Final Rule. Thursday, April 12, 2001.
- Fehr, W.R., Welke, G.A., Hammond, E.G., Duvick, D.N. and Cianzio, S.R. (1992) Inheritance of reduced linolenic acid content in soybean genotypes A16 and A17. *Crop Sci.*, **32**, 903–906.
- Ferrari, R.A., Schulte, E., Esteves, W., Bruhl, L. and Mukherjee, K.D. (1996) Minor constituents of vegetable oils during industrial processing. *J. Am. Oil Chem. Soc.*, **73**, 587–592.
- Formo, M.W. (1979) Physical properties of fats and fatty acids, in *Bailey's Industrial Oil and Fat Products* (ed D. Swern), 4th edn, Vol 1, John Wiley and Sons, New York, NY, pp. 177–232.
- Frankel, E.N. (1985) Chemistry of autooxidation: Mechanism, products and flavor significance, in *Flavor Chemistry of Fats and Oils* (eds D.B. Min and T.H. Smouse), AOCS Press, Champaign, IL, pp. 1–37.
- Frankel, E.N. (1998) *Lipid Oxidation*, The Oily Press Ltd, Dundee, Scotland.
- Fritsche, K.L. and Johnson, P.V. (1988) Reduced growth and metastasis of a transplantable syngenic mammary tumor (410.4) by dietary alpha-linolenic acid. *J. Am. Oil Chem. Soc.*, **65**, 509.
- Geller, D.P. and Goodrum, J.W. (2000) Rheology of vegetable analogs and triglycerides. *J. Am. Oil Chem. Soc.*, **77**, 111–114.
- Golbitz, P. (2000) *Soya & Oilseed Blue Book*, Soyatech, Inc. Bar Harbor, ME.
- Gunstone, F.D. (2001) Soybeans dominate global oilseed. *INFORM*, **12**, 737–740.
- Gunstone, F.D. and Pollard, M.R. (2001) Vegetable oils with fatty acid composition changed by plant breeding or by genetic modification, in *Structured and Modified Lipids* (ed F.D. Gunstone), Marcel Dekker, Inc., New York, NY, pp. 155–184.
- Haas, M.J. and Scott, K.M. (1996) Combined nonenzymatic-enzymatic method for the synthesis of simple alkyl fatty acid esters from soapstock. *J. Am. Oil Chem. Soc.*, **73**, 1393–1401.
- Haas, M.J., Bloomer, S. and Scott, K. (2000) Simple, high-efficiency synthesis of fatty acid methyl esters from soapstock. *J. Am. Oil Chem. Soc.*, **77**, 373–379.
- Halvorsen, J.D., Mammel, W.C. Jr. and Clements, L.D. (1993) Density estimation of fatty acids and vegetable oils based on their fatty acid composition. *J. Am. Oil Chem. Soc.*, **70**, 875–880.

- Harp, T.K., and Hammond, E.G. (1998) Stereospecific analysis of soybean triacylglycerols. *Lipids*, **33**, 209–216.
- Hastert, R.C. (1996) Hydrogenation, in *Bailey's Industrial Oil and Fat Products, Edible Oil and Fat Products: Processing Technology* (ed Y.H. Hui), 5th edn, Vol 4, John Wiley & Sons, Inc., New York, NY, pp. 213–300.
- Hegsted, D.M., Ausman, L.M., Johnson, L.A. and Dallal, G.E. (1993) Dietary fat and serum lipids: an evaluation of the experimental data. *Am. J. Clin. Nutr.*, **57**, 875–883.
- Hernandez, E. (2001) Latest developments in refining by adsorption and filtration of specialty oils with soluble silicates, in *Abstracts: 92nd AOCS Annual Meetings and Expo.*, AOCS Press, Champaign, IL, S98.
- Hicks, K.B. and Moreau, R.A. (2001) Phytosterols and phytostanols: Functional food cholesterol busters. *Food Tech.*, **55**, 63–67.
- Hollingsworth, P. (2001) Margarine: The over-the-top functional food. *Food Tech.*, **55**, 59–62.
- Hoy, C. and Xu, X. (2001) Structured triacylglycerols, in *Structured and Modified Lipids* (ed F.D. Gunstone), Marcel Dekker, Inc., New York, NY, pp. 209–239.
- Judd, J.T., Clevidence, B.A., Muesing, R.A., Wittes, J., Sunkin, M.E. and Podczasy, J. (1994) Dietary *trans* fatty acids: Effects on plasma lipids and lipoproteins of healthy men and women. *Am. J. Clin. Nutr.*, **59**, 861–868.
- Jung, M.Y., Yoon, S.H. and Min, D.B. (1989) Effect of processing steps on the contents of minor compounds and oxidation of soybean oil. *J. Am. Oil Chem. Soc.*, **66**, 118–120.
- Kamal-Eldin, A. and Andersson, R. (1997) A multivariate study of the correlation between tocopherol content and fatty acid composition in vegetable oils. *J. Am. Oil Chem. Soc.*, **74**, 375–380.
- Kellens, M. (2000) Oil modification processes, in *Edible Oil Processing* (eds W. Hamm and R.J. Hamilton), Sheffield Academic Press, Sheffield, UK, pp. 129–173.
- Kemeny, Z., Recseg, K., Henon, G., Kovari, K. and Zwobada, F. (2001) Deodorization of vegetable oils: Prediction of *trans* polyunsaturated fatty acid content. *J. Am. Oil Chem. Soc.*, **78**, 973–979.
- Knowlton, S., Kostows, C.M. and Kelly, E.F. (1999) Functional performance of genetically modified high stearate soybean oils, *90th American Oil Chemists' Society Meeting Abstract*, Orlando, FL., AOCS Press, Champaign, IL, S30.
- Kock, M. (1983) Oilseed pretreatment in connection with physical refining. *J. Am. Oil Chem. Soc.*, **60**, 198–202.
- Kok, L.L., Fehr, W.R., Hammond, E.G. and White, P.J. (1999) Trans-free margarine from highly saturated soybean oil. *J. Am. Oil Chem. Soc.*, **76**, 1175–1181.
- Konishi, H., Neff, W.E. and Mounts, T.L. (1995) Oxidative stability of soybean oil products obtained by regioselective chemical interesterification. *J. Am. Oil Chem. Soc.*, **72**, 1393–1398.
- Krishnamurthy, R.G. and Witte, V.C. (1996) Cooking oils, salad oils, and oil-based dressings, in *Bailey's Industrial Oil and Fat Products, Edible Oil and Fat Products: Products and Application Technology* (ed Y.H. Hui), 5th edn, Vol 3, John Wiley & Sons, Inc., New York, NY, pp. 193–223.
- Kwon, T.W., Snyder, H.E. and Brown, H.G. (1984) Oxidative stability of soybean oil at different stages of refining. *J. Am. Oil Chem. Soc.*, **61**, 1843–1846.
- Lau, F.Y., Hammond, E.G. and Ross, P.F. (1982) Effect of randomization on the oxidation of corn oil. *J. Am. Oil Chem. Soc.*, **59**, 407–411.
- Law, M.R. (2000) Plant sterol and stanol margarines and health. *Western J. Med.*, **173**, 43–47.
- Lee, I., Fatemi, S.H., Hammond, E.G. and White, P.J. (1995) Quantitation of flavor volatiles in oxidized soybean oil by dynamic headspace analysis. *J. Am. Oil Chem. Soc.*, **72**, 539–546.
- List, G.R. (1989) Commercial manufacture of lecithin, in *Lecithins: Source, Manufacture & Uses* (ed B.F. Szuhaj), AOCS Press, Champaign, IL, pp. 145–161.
- List, G.R., Emken, E.A., Kwolek, W. F., Simpson, T.D. and Dutton, H.J. (1977) “Zero *trans*” margarines: Preparation, structure, and properties of interesterified soybean oil-soy trisaturate blends. *J. Am. Oil Chem. Soc.*, **54**, 408–413.

- List, G.R., Mounts, T.L. and Lanser, A.C. (1992) Factors promoting the formation of nonhydratable soybean phosphatides. *J. Am. Oil Chem. Soc.*, **69**, 443–446.
- List, G.R., King, J.W., Johnson, J.H., Warner, K. and Mounts, T.L. (1993) Supercritical CO₂ degumming and physical refining of soybean oil. *J. Am. Oil Chem. Soc.*, **70**, 473–476.
- List, G.R., Pelloso, T., Orthoefer, F., Chrysam, M. and Mounts, T.L. (1995) Preparation and properties of zero *trans* soybean oil margarines. *J. Am. Oil Chem. Soc.*, **72**, 383–384.
- List, G.R., Mounts, T.L., Orthoefer, F. and Neff, W.E. (1996) Potential margarine oils from genetically modified soybeans. *J. Am. Oil Chem. Soc.*, **73**, 729–732.
- List, G.R., Neff, W.E., Holliday, R.L., King, J.W. and Holser, R. (2000) Hydrogenation of soybean oil triglycerides: Effect of pressure on selectivity. *J. Am. Oil Chem. Soc.*, **77**, 311–314.
- List, G.R., Pelloso, T., Orthoefer, F., Warner, K. and Neff, W.E. (2001) Soft margarines from high stearic acid soybean oils. *J. Am. Oil Chem. Soc.*, **78**, 103–104.
- Litchfield, C. (ed.) (1972) Distribution of fatty acids in natural triglyceride mixtures, in *Analysis of Triglycerides*, Academic Press, New York, NY, pp. 233–264.
- Liu, H. and White, P.J. (1992a) Oxidative stability of soybean oils with altered fatty acid composition. *J. Am. Oil Chem. Soc.*, **69**, 528–532.
- Liu, H. and White, P.J. (1992b) High temperature stability of soybean oils with altered fatty acid composition. *J. Am. Oil Chem. Soc.*, **69**, 533–537.
- Liu, K. (1999) Soy oil modification: Products and applications. *INFORM*, **10**, 868–878.
- Lutton, E.S., Mallery, M.F. and Burgers, J. (1962) Interesterification of lard. *J. Am. Oil Chem. Soc.*, **39**, 233–235.
- Matsuo, N. and Tokimitsu, I. (2001) Metabolic characteristics of diacylglycerol. *INFORM*, **12**, 1098–1102.
- Merrill, A.H. Jr. and Schmelz, E. (2001) Sphingolipids: metabolism-based inhibitors of carcinogenesis produced by animals, plants, and other organisms, in *Handbook of Nutraceuticals and Functional Foods* (ed R.C. Wildman), CrC Press, New York, NY, pp. 377–392.
- Metzroth, D.J. (1996) Shortening: science and technology, in *Bailey's Industrial Oil and Fat Products, Edible Oil and Fat Products: Products and Application Technology* (ed Y.H. Hui), 5th edn, Vol 3, John Wiley & Sons, Inc., New York, NY, pp. 115–160.
- Miller, L.A. and White, P.J. (1988) High temperature stabilities of low-linolenate, high-stearate and common soybean oils. *J. Am. Oil Chem. Soc.*, **65**, 1324–1326.
- Morad, N.A., Mustafa Kamal, A.A., Panau, F. and Yew, T.W. (2000) Lipid specific heat capacity estimation for fatty acids, triacylglycerols, and vegetable oils based on their fatty acid composition. *J. Am. Oil Chem. Soc.*, **77**, 1001–1005.
- Moulton, K.J. and Mounts, T.L. (1990) Continuous ultrasonic degumming of crude soybean oil. *J. Am. Oil Chem. Soc.*, **67**, 33–38.
- Mounts, T.L., Abidi, S.L. and Rennick, K.A. (1996) Effect of genetic modification on the content and composition of bioactive constituents in soybean oil. *J. Am. Oil Chem. Soc.*, **73**, 581–586.
- Nagao, T. and Teramoto, T. (2001) Physiological action of diacylglycerol. *Rinsho Eiyo*, **99**, 414–418.
- National Oilseed Processors Association (1993) Yearbook and Trading Rules (1993–1994), Washington, DC, p. 86.
- Neff, W.E. and List G.R. (1999) Oxidative stability of natural and randomized high-palmitic and high-stearic acid oils from genetically modified soybean varieties. *J. Am. Oil Chem. Soc.*, **76**, 825–831.
- Nelson, A.I., Wijeratne, W.B., Yeh, S.W., Wei, T.M. and Wei, L.S. (1987) Dry extrusion as an aid to mechanical expelling of oil from soybeans. *J. Am. Oil Chem. Soc.*, **64**, 1341–1347.
- Normen, L., Dutta, P., Lia, A. and Andersson, H. (2000) Soy sterol esters and β -sitostanol ester as inhibitors of cholesterol absorption in human small bowel. *Am. J. Clin. Nutr.*, **71**, 908–913.
- Nouredдини, H., Teoh, B.C. and Clements, L.D. (1992) Viscosities of vegetable oils and fatty acids. *J. Am. Oil Chem. Soc.*, **69**, 1189–1191.
- Ohnishi, M. and Fujino, Y. (1982) Sphingolipids in immature and mature soybeans. *Lipids*, **17**, 803–810.

- Orthofer, F.T. (1996) Vegetable oils, in *Bailey's Industrial Oil and Fat Products, Edible Oil and Fat Products: General Applications* (ed Y.H. Hui), 5th edn, Vol 1, John Wiley & Sons, Inc., New York, NY, pp. 19–44.
- Ozawa, Y., Sato, H., Nakatani, A., Mori, O., Hara, Y., Nakada, Y., Akiyama, Y. and Morinaga, Y. (2001) Chemical composition of soybean oil extracted from hypocotyl-enriched soybean raw material and its cholesterol lowering effects in rats. *J. Oleo Sci.*, **50**, 217–223.
- Pagliero, C., Ochoa, N., Marchese, J. and Mattea, M. (2001) Degumming of crude soybean oil by ultrafiltration using polymeric membranes. *J. Am. Oil Chem. Soc.*, **78**, 793–796.
- Penk, G. (1986) Practical experience with the Alcon Process, in *Proc. World Conf. Emerging Technologies in the Fats and Oil Industry* (ed A.R. Baldwin), AOCS Press, Champaign, IL, pp. 38–45.
- Perkins, E.G. (1995a) Composition of soybeans and soybean products, in *Practical Handbook of Soybean Processing and Utilization* (ed D.R. Erickson), AOCS Press, Champaign, IL, pp. 9–28.
- Perkins, E.G. (1995b) Physical properties of soybeans, in *Practical Handbook of Soybean Processing and Utilization* (ed D.R. Erickson), AOCS Press, Champaign, IL, pp. 29–38.
- Pickard, M.D., Jones, T.J. and Tyler, R.T. (1996) By-products utilization, in *Bailey's Industrial Oil and Fat Products, Vol 4: Edible Oil and Fat Products: Processing Technology* (ed Y.H. Hui), 5th edn, Vol 4, John Wiley & Sons, Inc., New York, NY, pp. 603–630.
- Pryde, E.H. (1980a) Composition of soybean oil, in *Handbook of Soy Oil Processing and Utilization* (eds D.R. Erickson, E.H. Pryde, O.L. Brekke, T.L. Mounts and R.A. Falb), AOCS Press, Champaign, IL, pp. 13–31.
- Pryde, E.H. (1980b) Physical properties of soybean oil, in *Handbook of Soy Oil Processing and Utilization* (eds D.R. Erickson, E.H. Pryde, O.L. Brekke, T.L. Mounts and R.A. Falb), AOCS Press, Champaign, IL, pp. 33–47.
- Rabelo, J., Batista, E., Cavaleri, F.W. and Meirelles, A.J.A. (2000) Viscosity prediction for fatty systems. *J. Am. Oil Chem. Soc.*, **77**, 1255–1261.
- Raghuveer, K.G. and Hammond, E.G. (1967) The influence of glyceride structure on the rate of autoxidation. *J. Am. Oil Chem. Soc.*, **44**, 239–243.
- Ramamurthi, S., McCurdy, A.R. and Tyler, R.T. (1998) Deodorizer distillate: A valuable byproduct, in *Proc. World Conf. Oilseed Edible Oils Process* (eds S.S. Koseoglu, K.C. Rhee, and R.F. Wilson), AOCS Press, Champaign, IL, Vol 1, pp. 130–134.
- Raman, L.P., Cheryan, M. and Rajagopalan, N. (1996) Deacidification of soybean oil by membrane technology. *J. Am. Oil Chem. Soc.*, **73**, 219–224.
- Reske, J., Siebrecht, A. and Hazebroek, J. (1997) Triacylglycerol composition and structure in genetically modified sunflower and soybean oils. *J. Am. Oil Chem. Soc.*, **74**, 989–998.
- Rihani, D.N. and Doraiswamy, L.K. (1965) Estimation of heat capacity of organic compounds from group contributions. *Ind. Eng. Chem. Fundam.*, **4**, 17–21.
- Rodenbush, C.M., Hsieh, F.H. and Viswanath, D.S. (1999) Density and viscosity of vegetable oils. *J. Am. Oil Chem. Soc.*, **76**, 1415–1419.
- Sato, H., Ito, K., Sakai, K., Morinaga, Y., Sukegawa, E., Kitamura, T., Shimasaki, H. and Itakura, H. (2001) Effects of soybean-germ oil on reducing serum cholesterol level. *J. Oleo Sci.*, **50**, 649–656.
- Schneider, M. (1986) Phospholipids, in *Proc. World Conf. Emerging Technologies in the Fats and Oils Industry* (ed A.R. Baldwin), AOCS Press, Champaign, IL, pp. 160–164.
- Seger, J.C. and van de Sande, R.L.K.M. (1990) Degumming – theory and practice, in *World Conference Proc. Edible Fats and Oils Processing: Basic Principles and Modern Practices* (ed D.R. Erickson), AOCS Press, Champaign, IL, pp. 88–93.
- Shen, N., Fehr, W., Johnson, L. and White, P. (1997) Oxidative stabilities of soybeans with elevated palmitate and reduced linolenate contents. *J. Am. Oil Chem. Soc.*, **74**, 299–302.
- Shimada, Y., Nakai, S., Suenaga, M., Sugihara, A., Kitano, M. and Tominaga, Y. (2000) Facile purification of tocopherols from soybean oil deodorizer distillate in high yield using lipase. *J. Am. Oil Chem. Soc.*, **77**, 1009–1013.

- Shintani, D.S. and DellaPenna, D. (1998) Elevating the vitamin E content of plants through metabolic engineering. *Science*, **282**, 2098–2100.
- Sipos, E.F. and Szuhaj, B.F. (1996a) Soybean oil, in *Bailey's Industrial Oil and Fat Products, Edible Oil and Fat Products: Oils and Oilseeds* (ed Y.H. Hui), 5th edn, Vol 2, John Wiley & Sons, Inc., New York, NY, pp. 497–602.
- Sipos, E.F. and Szuhaj, B.F. (1996b) Lecithins, in *Bailey's Industrial Oil and Fat Products, Edible Oil and Fat Products: General Applications* (ed Y.H. Hui), 5th edn, Vol 1, John Wiley & Sons, Inc., New York, NY, pp. 311–396.
- Soni, M.G., Kimura, H. and Burdock, G.A. (2001) Chronic study of diacylglycerol oil in rats. *Food Chem. Toxicol.*, **39**, 317–329.
- Stern, R., Hillion, G., Gateau, P. and Guibet, J.C. (1986) Preparation of methyl and ethyl esters from crude vegetable oils and soap stock, in *Proc. World Conference Emerging Technologies in the Fats and Oils Industry* (ed A.R. Baldwin), AOCS Press, Champaign, IL, pp. 420–422.
- Subramanian, S., Nakajima, M., Yasui, A., Nabetani, H., Kimura, T. and Maekawa, T. (1999) Evaluation of surfactant-aided degumming of vegetable oils by membrane technology. *J. Am. Oil Chem. Soc.*, **76**, 1247–1253.
- Sumner, C.E., Jr., Barnicki, S.D. and Dolfi, M.D. (1995) Process for the production of sterol and tocopherol concentrates. US Patent 5424457.
- Sundram, K., Khor, H.T., Ong, A.S.H. and Pathmanathan, R. (1989) Effect of dietary palm oils on mammary carcinogenesis in female rats induced by 7,12-dimethylbenz(a)anthracene. *Cancer Res.*, **49**, 1447–1451.
- Teberikler, L., Koseoglu, S. and Akgerman, A. (2001) Selective extraction of phosphatidylcholine from lecithin by supercritical carbon dioxide/ethanol mixture. *J. Am. Oil Chem. Soc.*, **78**, 115–119.
- Tekin, A. and Hammond, E.G. (1998) Factors affecting the electrical resistivity of soybean oil. *J. Am. Oil Chem. Soc.*, **75**, 737–740.
- Tekin, A. and Hammond, E.G. (2000) Factors affecting the electrical resistivity of soybean oil methyl ester. *J. Am. Oil Chem. Soc.*, **77**, 281–283.
- USDA–NASS (2000) Agricultural Statistics 2000, <http://www.usda.gov/nass/pubs/agr00/acro00.htm>.
- Vesper, H., Schmelz, E.M., Nikolova-Karakashian, M.N., Dillehay, D.L., Lynch, D.V. and Merrill, A.H. Jr. (1999) Sphingolipids in food and the emerging importance of sphingolipids to nutrition. *J. Nutr.*, **129**, 1239–1250.
- Vlahakis, C. and Hazebroek, J. (2000) Phytosterol accumulation in canola, sunflower, and soybean oils: Effect of genetics, planting location, and temperature. *J. Am. Oil Chem. Soc.*, **77**, 49–53.
- Wang, T. and Briggs, J.L. Rheological and thermal properties of soybean oils with modified fatty acid compositions. *J. Am. Oil Chem. Soc.* (in press).
- Wang, T. and Hammond, E.G. (1999) Fractionation of soybean phospholipids by high-performance liquid chromatography with an evaporative light scattering detector. *J. Am. Oil Chem. Soc.*, **76**, 1313–1321.
- Wang, T. and Johnson, L.A. (2001a) Survey of soybean oil and meal qualities produced by different processes. *J. Am. Oil Chem. Soc.*, **78**, 311–318.
- Wang, T. and Johnson, L.A. (2001b) Natural refining of extruded-expelled soybean oils having various fatty acid compositions. *J. Am. Oil Chem. Soc.*, **78**, 461–466.
- Wang, T. and Johnson, L.A. (2001c) Refining normal and genetically enhanced soybean oils obtained by various extraction methods. *J. Am. Oil Chem. Soc.*, **78**, 809–815.
- Wang, T., Hammond, E.G. and Fehr, W.R. (1997) Phospholipid fatty acid composition and stereospecific distribution of soybeans with a wide range of fatty acid compositions. *J. Am. Oil Chem. Soc.*, **74**, 1587–1594.
- Wang, T., Hammond, E.G. and Fehr, W.R. (2001a) Neutral and polar lipid phase transition of soybeans with altered saturated fatty acid contents. *J. Am. Oil Chem. Soc.*, **78**, 1139–1144.
- Wang, T., Harp, T., Hammond, E.G., Burris, J.S. and Fehr, W.R. (2001b) Seed physiological performance of soybeans with altered fatty acid contents. *Seed Science Res.*, **11**, 93–97.

- Wang, T, Mentzen, W., Hammond, E.G. and Kaiser, M.S. Fatty acid methyl ester conversion from acidulated soapstock. *J. Am. Oil Chem. Soc.* (Submitted).
- Weihrauch, J.L. and Gardner, J.M. (1978) Sterol content of foods of plant origin. *J. Amer. Diet Assoc.*, **73**, 39–47.
- Wendel, A. (1995) Lecithin, in *Kirk-Othmer Encyclopedia of Chemical Technology* (ed M. Howe-Grant), 4th edn, Vol 15, John Wiley & Sons, New York, NY, pp. 192–210.
- White, P.J. and Miller, L.A. (1988) Oxidative stabilities of low-linolenate, high-stearate and common soybean oils. *J. Am. Oil Chem. Soc.*, **65**, 1334–1338.
- Wilson, R.F. (1999) Alternatives to genetically modified soybean – the Better Bean Initiative. *Lipid Technol.*, **10**, 107–110.
- Winters, R.L. (1990) Deodorizer distillate, in *Proc. World Conf. Edible Fats and Oils Processing, Basic Principles and Modern Practices* (ed D.R. Erickson), AOCS Press, Champaign, IL, pp. 402–405.
- Woerfel, J.B. (1995) Extraction, in *Practical Handbook of Soybean Processing and Utilization* (ed D.R. Erickson), AOCS Press, Champaign, IL, pp. 65–92.
- Wolf, F.R. and Knowlton, S. (1999) Edible applications of high oleic soybean oil, 90th American Oil Chemists' Society Meeting Abstract, AOCS Press, Champaign, Illinois, S24.
- Wu, Y. and Wang, T. (2001) Phospholipid class and fatty acid compositions of modified soybeans, 92nd AOCS Annual Meeting and Expo. *INFORM Supplement*, S97.
- Wu, H., Weng, X., Qiu, O. and Li, L. (2001) Extraction of tocopherol from soybean oil deodorizer. *Shanghai Daxue Xuebao-Ziran Kexueban*, **7**, 331–333.
- Yasukawa, T. and Yasunaga, K. (2001) Nutritional functions of dietary diacylglycerols. *J. Oleo Sci.*, **50**, 427–432.