VEGETABLE OILS IN FOOD TECHNOLOGY: Composition, Properties and Uses

FRANK D. GUNSTONE,
Editor

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Composition, Properties and Uses

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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, tocols, 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

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Contents

1 Production and trade of vegetable oils

Frank D. Gunstone

1.1 Extraction, refining and processing

Most vegetable oils are obtained from beans or seeds, which generally furnish two valuable commodities—an oil and a protein-rich meal. Seed extraction is achieved by pressing and/or by solvent extraction. Oils such as palm and olive, on the other hand, are pressed out of the soft fruit (endosperm). Seeds give oils in different proportions. Using figures for 2000/01, world average oil yields are: soybean (18.3%); rapeseed (38.6%); sunflower (40.9%); groundnut (40.3%); cottonseed (15.1%); coconut (62.4%); palmkernel (44.6%); sesame (42.4%); linseed (33.5%); average for all oilseeds (25.8%). In addition, yields from palm fruit (45–50%), olive (25–30%) and corn (about 5%) are as indicated.

Some oils, such as virgin olive oil, are used without further treatment but most are refined in some measure before use. The refining processes remove undesirable materials (phospholipids, monoacylglycerols, diacylglycerols, free acids, colour and pigments, oxidised materials, flavour components, trace metals and sulfur compounds) but may also remove valuable minor components which are antioxidants and vitamins such as carotenes and tocopherols. These processes must therefore be designed to maximise the first and to minimise the second. Some of the useful minor components can be recovered from side streams to give valuable products such as phospholipids, free acids, tocopherols, carotenes, sterols and squalene. Because of the changes that occur, it is always important to note whether compositional data relate to crude or refined oil. Details of the levels of these in the various seed oils are given in appropriate chapters in this volume (see also Gunstone 2000). Extraction and refining processes have been described by Fils (2000) and by De Greyt and Kellens (2000) respectively. Hamm (2001) has discussed the major differences in extraction and refining procedures between Europe and North America as a consequence of the size of the industrial plant and of the differing oilseeds to be handled.

With only a limited number of oils and fats available on a commercial scale, it is not surprising that these are sometimes inadequate to meet the physical, nutritional, and chemical properties required for use in food products. Over a century or more, lipid technologists have designed and used procedures for overcoming the limitations of a restricted range of natural products. In particular, they have sought to modify the fatty acid composition of their lipids, knowing that such changes will influence the physical, nutritional, and

Table 1.1 Methods of changing fatty acid composition and physical, nutritional and chemical properties thereby

Technological solutions
Blending
Distillation
Fractionation
Hydrogenation
Interesterification with chemical catalysts
Interesterification with specific lipases
Enzymic enhancement
Biological solutions
Domestication of wild crops
Oils modified by conventional seed breeding
Oils modified by (intra-species) genetic engineering
Lipids from unconventional sources (micro-organisms)

chemical properties. These have been classified (Gunstone 1998 and 2001) into technological and biological procedures according to the procedures listed in Table 1.1.

The procedures most relevant to this book are fractionation, hydrogenation, and modification of fatty acid composition, either by conventional seed breeding or by genetic engineering; examples are detailed in appropriate chapters. For example, the usefulness of both palm oil and palmkernel oil are greatly extended by fractionation. Hydrogenation is applied mainly in one of two ways. A very light hydrogenation is applied, particularly to soybean oil and rapeseed oil, to reduce the level of linolenic acid in these oils and to extend shelf life. This is called brush hydrogenation. More extensive, but still partial, hydrogenation is applied to unsaturated liquid oils to produce semi-solid fats that can be used in margarines and spreads. As a consequence of this process, the levels of polyunsaturated fatty acids are markedly reduced, saturated acid content rises slightly, and there is a considerable rise in monounsaturated acids, including some with *trans* configuration. The *trans* acids have higher melting points than their *cis* isomers, thereby contributing to the desired increase in solid acids. Unfortunately these changes have undesirable nutritional consequences.

In the following chapters, examples are cited where fatty acid composition has been modified by biological methods—both traditional and modern. Well-known examples include low-erucic acid rapeseed oil (canola oil) and high-oleic sunflower oil, but attempts to develop oils with modified fatty acid are being actively pursued in many counties—in both academic and industrial laboratories—and substantial developments are likely in the next five to ten years. Some of have been described by the author (Gunstone 2001) and others are cited in the following chapters of this book.

1.2 Vegetable oils—production, disappearance and trade

World production of oils and fats—currently about 117 million tonnes per annum—comes from vegetable and animal sources. *Oil World* publications* recognise 17 commodity oils, of which four are of animal origin. The remainder are from vegetable sources and the following chapters of this book cover all these except castor oil, which is used solely for industrial purposes. The statements made in this section are supported by the detailed information in the accompanying Tables.

Of the total production of oils and fats, about 80% is used for food purposes (which will be described here in appropriate chapters), 6% is used in animal feed, and the remaining 14% provides the basis of the oleochemical industry (Gunstone and Hamilton 2001).

Within the sources of vegetable oils it is useful to distinguish three different types:

- *Byproducts*. Cotton and corn are grown primarily for fibre and for cereal respectively and the oil is a byproduct. Soybean can also be included in this category because it yields two products—oil and meal—which represent approximately18% and 79% respectively of the dried bean. The demand for soybeans is driven sometimes by one of these and sometimes by the other. It could also be argued that peanuts (groundnuts) should also be included, since only about one half of the crop is crushed (for oil and meal) and the rest is consumed as nuts.
- *Tree crops*. Palm, palmkernel, coconut and olive oils are obtained from trees that have to be planted and mature before they give a useful crop. Once this stage is reached, the trees continue to provide crops for 25–30 years, in the case of palm, and longer than that for olive. These crops cannot be changed on a yearly basis.
- *Annual crops*. The third category are annual crops such as rape, sunflower and linseed. Appropriate decisions have to be made annually by the farmer or planter concerning which crops to grow. The choice is usually between oilseed crops and cereals, and the decision is based on agricultural and economic factors.

Another distinction that is sometimes made is between oilseed crops and those vegetable oils which come from the endosperm (soft fleshy fruit). Palm and olive belong to this category.

Most of the crops are produced annually at harvest time, which comes late in the calendar year in the northern hemisphere and early in the calendar year in the

* *Oil World*, ISTA Mielke GmbH of Hamburg, Germany, produce weekly, monthly, annual, and occasional issues devoted to the production and use of 12 oilseeds, 17 oils and fats, and 10 oil meals.

Table 1.2 Production, exports and imports (million tonnes) of 10 oilseeds and of 17 oils and fats in selected countries in 2000/01

		Oilseeds			Oils and fats		
	Population*	Production	Exports	Imports	Production	Exports	Imports
World	6133	306.9	64.7	64.7	117.1	37.7	37.7
Malaysia	23	3.4	–	0.7	13.6	11.5	0.4
Argentina	37	29.6	5.9	–	5.3	4.5	–
Canada	31	10.7	6.3	0.8	2.2	1.1	0.4
Australia	19	2.9	1.8	–	0.9	0.5	0.2
US	286	85.1	28.2	0.8	15.7	2.9	1.9
Brazil	173	38.7	12.8	0.6	5.5	1.4	0.3
Indonesia	215	5.1	–	1.5	8.9	5.6	–
China	1263	47.8	0.9	14.4	15.8	0.2	2.9
India	1025	20.8	0.2	–	6.7	0.2	5.9
EU-15	377	14.6	0.7	20.5	15.2	2.6	5.2

*Millions.

southern hemisphere. However, some equatorial crops like palm and coconut are harvested through all the twelve months of the year, though there is some minor seasonal variation in quantity.

In discussing the trade in oilseed, oils and fats, and oil meals in geographical terms it is useful to divide countries/regions into four categories. These are discussed below and illustrated in Table 1.2.

- Countries with small populations that produce large amounts of oilseeds/oils and fats are the world's largest exporters of these commodities and dominate world trade. Examples include Malaysia, Argentina, Canada and Australia.
- Countries with large populations that produce large amounts of oilseeds/oils and fats. These countries need to feed their own large populations but are still significant exporters. Examples are the US, Brazil and Indonesia.
- Countries with very large populations which, despite local production, are still major importers. China and India and other highly populated counties in Asia belong to this category.
- Finally there are countries/regions which are essentially traders. They produce, consume, import, and export these commodities. EU-15 is the biggest example but Hong Kong (as was) and Singapore, by virtue of their geographical closeness to the world's largest importer (China) and exporter (Malaysia), are also significant traders.

Table 1.3 shows the annual average production of 17 oils and fats for selected five-year periods from 1976/80 with forecasts up to 2016/20 taken from a revised *Oil World* publication in 2002. That is a period of forty years. There has been a

Table 1.3 Annual average production of 17 oils and fats in selected five-year periods from 1976/80 with forecasts up to 2016/20

	1976/80	1986/90	1996/00	2006/10	2016/20
World total	52.65	75.66	105.06	165.65	184.77
Soybean oil	11.23	15.28	23.14	33.60	41.12
Cottonseed oil	2.83	3.64	4.00	5.35	6.51
Groundnut oil	3.01	3.70	4.55	5.72	6.38
Sunflowerseed oil	4.21	7.25	9.11	12.43	16.97
Rapeseed oil	3.01	7.51	12.64	17.72	22.69
Sesameseed oil	0.51	0.64	0.70	0.86	0.96
Corn oil	0.83	1.35	1.91	2.49	3.16
Olive oil	1.68	1.80	2.47	2.75	2.98
Palm oil	3.69	9.22	18.72	31.43	43.36
Palmkernel oil	0.46	1.21	2.34	3.84	5.28
Coconut oil	2.85	3.07	3.01	3.70	4.55
Butter	5.60	6.35	5.81	6.93	7.99
Lard	4.25	5.17	6.38	7.93	9.14
Fish oil	1.13	1.53	1.25	1.18	11.59
Linseed oil	0.79	0.73	0.70	0.81	0.97
Castorseed oil	0.32	0.40	0.46	0.71	0.78
Tallow	6.24	6.79	7.85	10.06	10.76

Source: Mielke 2002. The order of citation in the above Table is that used in the reference publication. This book does not include the four animal fats nor castor oil. The reference publication does not provide figures for cocoa butter but this has an annual production of about 1.7 million tonnes.

considerable increase in oil and fat production during that time from 53 million tonnes in 1976/80 to 105 million tonnes in 1996/2000 with 185 million tonnes expected in 20 years' time.

The production levels of virtually all the commodities have increased during the past 20 years and further increases are expected in the coming years. However they have not all increased equally; some have lost market share and four have become increasingly dominant. The latter are soybean oil, palm oil (and palmkernel oil), rapeseed oil, and sunflowerseed oil. The percentage share of world production of these oils is summarised in Table 1.4. Palm oil and palmkernel oil are combined in this Table. Although palmkernel oil is a minor oil, it is produced from the same source as palm oil and it is therefore appropriate to combine these for this discussion. In the past 20 years both palm oil and rapeseed oil have increased considerably to take up positions two and three in order of production level. It is considered that palm oil production will exceed that of soybean oil towards the end of the forty-year period.

Typical among oils which have lost market share over the past twenty years are cottonseed oil, which has fallen from 5.4 to 3.8%, groundnut oil (from 5.7 to 4.3%), and olive oil (from 3.2 to 2.3%), despite the increases in production shown in Table 1.3.

Table 1.4 Four major vegetable oils as % of total oil and fat production

	1976/80	1986/90	1999/00	2000/10	2016/20
Soybean oil	21.3	20.2	22.0	22.9	20.2
Palm and pko*	7.9	13.8	20.0	24.0	26.3
Rapeseed oil	5.7	9.9	12.0	12.1	12.3
Sunflowerseed oil	8.0	9.6	8.7	8.5	9.2

These figures are derived from Table 1.3.
*Palmkernel oil.

Annual production of oils and fats in 2000/01 is expected to be about 117 million tonnes. Given an average price range of $300–500 per tonne, this indicates a total value of $35–60 billion for the year's oils and fats production.

In Tables 1.5–1.7 attention is focused on the five years 1996/97 to 2000/01 to show the most recent trends. These double dates are 'harvest years'. The earlier date relates to the harvest of the northern hemisphere and the later figure to that of the southern hemisphere. Oils and fats come from oilseeds, fruits, and from animal sources and Table 1.5 gives figures for 10 oilseeds. Most of the seed is

Table 1.5 Global production of 10 oilseeds and of oil and meal derived from these (million tonnes) during the five-year period 1996/97 to 2000/01

	1996/97	1997/98	1998/99	1999/00	2000/01
Production	259.79	285.95	295.38	302.84	306.92
Crushing	222.60	233.36	242.34	251.99	259.27
Oil	57.39	59.73	61.78	65.30	66.80
Meal	149.96	158.63	165.58	171.46	177.63

Source: Mielke 2001.

Table 1.6 Production (million tonnes) of 12 vegetable oils during the five-year period 1996/97 to 2000/01

	1996/97	1997/98	1998/99	1999/00	2000/01
Soybean	20.96	23.18	24.60	25.30	26.66
Palm	17.57	17.10	19.36	21.26	23.38
Rapeseed	11.48	12.19	12.56	14.30	14.15
Sunflowerseed	9.11	8.44	9.28	9.57	8.87
Groundnut	4.61	4.36	4.78	4.53	4.86
Cottonseed	4.06	4.13	3.89	3.92	3.89
Coconut	3.14	3.37	2.35	3.09	3.43
Palmkernel	2.19	2.20	2.43	2.63	2.89
Olive	2.77	2.62	2.54	2.35	2.56
Corn	1.85	1.89	1.92	2.00	2.03
Sesame	0.72	0.74	0.72	0.73	0.78
Linseed	0.67	0.68	0.73	0.74	0.72

Source: Mielke 2001.
Oils are cited in decreasing order of production in 2000/01.

Table 1.7 Production, disappearance, export and imports (million tonnes) of 17 oils and fats during the five-year period 1996/97 to 2000/01

	1996/97	1997/98	1998/99	1999/00	2000/01
Production	100.14	102.03	107.51	113.44	117.12
Disappearance	99.82	102.37	106.61	112.24	117.54
Per person (kg)	17.1	17.3	17.8	18.5	19.2
Exports	32.04	33.11	34.08	35.10	37.69
Imports	31.40	33.25	33.76	35.42	37.67

Source: Mielke 2001.

crushed, but some is held back as seed for planting and some is used directly for animal feed or human food. Crushing produces oil and meal. The proportion of these varies slightly from year to year, depending on the relative amounts of the various oilseeds with their differing levels of oil.

It should be explained that 'disappearance' is a technical term. Applied to a country/region for a particular year, it is the sum of local production and imports with deduction of exports and allowance for changes in stocks during the year in question. It includes human consumption, animal feed, industrial consumption, and waste, and cannot be equated directly with dietary intake. Disappearance per person is expressed in kg/year and is available on a world basis (as in Table 1.7) or for individual countries/regions. Disappearance per person has shown a steady rise over many years. In the years between 1996/97 and 2000/01, it has risen 12% from 17.1 to 19.2 kg/year. Exports and imports are at virtually the same level and correspond to 31–32% of total production. The balance is used in the country where it is produced.

In Tables 1.8–1.19, attention is directed to the production, disappearance and imports/exports of the 12 vegetable oils described in the other chapters of this book. Each Table shows the major countries/regions involved. The figures in the following text apply to year 2000/01. They vary slightly from year to year but the major features are unlikely to change very quickly. Some major points from each Table are discussed here, but readers can derive further information through careful study of the Tables.

1.2.1 Soybean oil

Soybean oil is the oil produced in largest quantity and is second only to palm oil in traded oil (Table 1.8). There is also a large trade in soybeans but no comparable trade in palm fruits, which are extracted as soon as possible close to the point of collection. The major producers of soybean oil are the US, Brazil, Argentina, China (local beans augmented with imports), and EU-15 (mainly imported beans). Soybean oil is consumed in every country for which details

Table 1.8 Major countries/regions involved in the production, disappearance, export and imports (million tonnes) of soybean oil in 2000/01

	Total	Major countries/regions
Production	26.66	US 8.24, Brazil 4.28, Argentina 3.28, China 3.26, EU-15 2.87, India 0.75, Japan 0.71, Mexico 0.70, Taiwan 0.42, Canada 0.30, South Korea 0.22, Thailand 0.21, other 1.42
Disappearance	26.65	US 7.50, China 3.45, Brazil 3.10, India 1.94, EU-15 1.82, Mexico 0.79, Iran 0.71, Japan 0.71, Bangladesh 0.50, Taiwan 0.48, other 5.64
Exports	7.45	Argentina 3.20, Brazil 1.30, EU-15 1.07, US 0.73, Iran 0.21, Malaysia 0.18, Hong Kong 0.17, Bolivia 0.12, other 0.47
Imports	7.44	India 1.20, Iran 0.81, Bangladesh 0.49, Egypt 0.34, Morocco 0.29, former USSR 0.28, Hong Kong 0.27, China 0.24, Venezuela 0.24, Pakistan 0.21, other 3.07

Source: Mielke 2001.

are available. Disappearance is generally greatest in the producing countries with five countries/regions exceeding one million tonnes. These are the US (28%), China (13%), Brazil (12%), India (7%), and EU-15 (7%). Argentina is the biggest exporter of soybean oil (43% of total soybean oil exports). Very many countries import soybean oil with India at the head of the list with 1.20 million tonnes (16% of total soybean oil imports) in 2000/01.

1.2.2 Palm oil

Palm oil (Table 1.9) now takes second place in the list of oils produced and will probably overtake soybean oil in another 10–15 years. It is already the oil traded in largest amount, accounting for 44% of all oil and fat exports. These volumes have grown considerably in the past 20 years or so (see Table 1.4). Production and exports are dominated by two South East Asian countries. Malaysia has 51% of all palm oil production and 63% of palm oil exports; Indonesia has levels corresponding to 31% and 26% respectively. As indicated previously, Indonesia has a much larger population than Malaysia (Table 1.1), and therefore exports a lower proportion of its palm oil. Production is increasing in both countries, and, if Indonesia can avoid political unrest and economic downturn, then it is expected to overtake Malaysian production in around 10–15 years. A number of other countries produce lower levels of palm oil (Table 1.9). Palm oil is consumed in many countries and this material is important in meeting the rapidly growing demands of developing countries with increasing population and rising personal income. The main importers are India, EU-15, China and Pakistan.

1.2.3 Rapeseed/canola oil

Rapeseed/canola oil (Table 1.10) now occupies the third position in rank order of production of oils and fats. Using local seeds and/or imported seeds the oil

Table 1.9 Major countries/regions involved in the production, disappearance, export and imports (million tonnes) of palm oil in 2000/01

	Total	Major countries/regions
Production	23.38	Malaysia 11.98, Indonesia 7.33, Nigeria 0.75, Colombia 0.54, Thailand 0.53, Papua New Guinea 0.30, Ivory Coast 0.27, Ecuador 0.25, other 1.43
Disappearance	23.20	India 4.12, Indonesia 2.95, EU-15 2.50, China 1.79, Malaysia 1.50, Pakistan 1.17, Nigeria 0.87, Thailand 0.50, Egypt 0.45, Colombia 0.44, Japan 0.37, Bangladesh 0.25, Turkey 0.24, Ivory Coast 0.21, Kenya 0.21, South Korea 0.21, Saudi Arabia 0.21, South Africa 0.20, Ecuador 0.20, Myanmar 0.20, other 4.61
Exports	16.75	Malaysia 10.58, Indonesia 4.32, Papua New Guinea 0.29, Singapore 0.24, Hong Kong 0.23, other 1.09
Imports	16.64	India 4.03, EU-15 2.62, China 1.86, Pakistan 1.17, Egypt 0.53, Japan 0.38, Singapore 0.38, Hong Kong 0.25, Bangladesh 0.24, Turkey 0.24, Kenya 0.22, Myanmar 0.22, Saudi Arabia 0.22, South Africa 0.21, South Korea 0.21, other 2.86

Source: Mielke 2001.

Table 1.10 Major countries/regions involved in the production, disappearance, export and imports (million tonnes) of rapeseed oil in 2000/01

	Total	Major countries/regions
Production	14.15	China 4.53, EU-15 3.68, India 1.60, Canada 1.30, Japan 0.93, Central Europe 0.62, Mexico 0.37, US 0.32, Pakistan 0.24, Bangladesh 0.15, Australia 0.15, other 0.25
Disappearance	14.28	China 4.59, EU-15 3.34, India 1.67, Japan 0.95, US 0.76, Central Europe 0.67, Canada 0.60, Mexico 0.42, Pakistan 0.26, former USSR 0.25, other 0.77
Exports	1.65	Canada 0.79, EU-15 0.36, Hong Kong 0.17, US 0.12, other 0.21
Imports	1.64	US 0.54, Hong Kong 0.26, China 0.13, former USSR 0.13, other 0.58

Source: Mielke 2001.

is produced mainly in China, EU-15, India, Canada, and Japan. Only 12% of the oil is then exported, mainly from Canada which accounts for 48% of all rapeseed oil exports. The major importer is the US. There is also a strong trade in the seeds which is not covered by these figures.

1.2.4 Sunflowerseed oil

Sunflowerseed oil (Table 1.11) is the last member of the group of four major oils and fats. It maintains its share at about 9% of the total but has achieved very variable levels over the past five years (Table 1.4). It is available as oil of differing fatty acids composition detailed in Chapter 5, but these are taken

Table 1.11 Major countries/regions involved in the production, disappearance, export and imports (million tonnes) of sunflower seed oil in 2000/01

	Total	Major countries/regions
Production	8.87	Former USSR 2.40, EU-15 2.04, Argentina 1.60, Central Europe 0.70, Turkey 0.47, US 0.37, India 0.25, China 0.22, South Africa 0.29, other 0.53
Disappearance	9.17	EU-15 2.08, former USSR 1.98, Central Europe 0.76, India 0.72, Turkey 0.54, Argentina 0.54, South Africa 0.37, Algeria 0.23, China 0.21, US 0.16, Mexico 0.16, other 1.42
Exports	2.37	Argentina 1.18, former USSR 0.53, US 0.24, EU-15 0.16, Central Europe 0.11, other 0.16
Imports	2.39	India 0.45, Algeria 0.23, EU-15 0.17, Mexico 0.16, Egypt 0.15, Iran 0.14, Central Europe 0.13, other 0.96

Source: Mielke 2001.

together in the data presented here. The major producers are the former USSR, EU-15, and Argentina. About 27% of the oil is exported, mainly from Argentina.

1.2.5 Groundnut (peanut) oil

Only about 53% of groundnuts (Table 1.12) are crushed, the balance being used in other ways. There is very little trade in the oil. It is produced and used mainly in China and India, which together account for 71% of total production and usage. Minor quantities of the oil are produced and used in several African countries.

1.2.6 Cottonseed oil

Cottonseed oil (Table 1.13) is another oil traded only to a small extent. China is the major producer and user (about 29%) with India, the US, the former USSR, Pakistan, Brazil and Turkey providing lower levels.

Table 1.12 Major countries/regions involved in the production, disappearance, export and imports (million tonnes) of groundnut oil in 2000/01

	Total	Major countries/regions
Production	4.86	China 2.38, India 1.06, Nigeria 0.32, Sudan 0.16, Senegal 0.16, other 0.78
Disappearance	4.87	China 2.38, India 1.07, Nigeria 0.32, Sudan 0.16, EU-15 0.15, US 0.13, Myanmar 0.13, other 0.53
Exports	0.27	Senegal 0.11, Argentina 0.06, other 0.10
Imports	0.27	EU-15 0.15, other 0.12

Source: Mielke 2001.

Table 1.13 Major countries/regions involved in the production, disappearance, export and imports (million tonnes) of cottonseed oil in 2000/01

	Total	Major countries/regions
Production	3.89	China 1.12, India 0.45, US 0.40, former USSR 0.36, Pakistan 0.35, Brazil 0.20, Turkey 0.19, other 0.82
Disappearance	3.94	China 1.12, India 0.49, former USSR 0.38, US 0.35, Pakistan 0.35, Turkey 0.21, Brazil 0.17, other 0.87
Exports	0.20	US 0.05, Brazil 0.03, other 0.12
Imports	0.20	Canada 0.04, India 0.03, other 0.13

Source: Mielke 2001.

Table 1.14 Major countries/regions involved in the production, disappearance, export and imports (million tonnes) of coconut oil in 2000/01

	Total	Major countries/regions
Production	3.43	Philippines 1.47, Indonesia 0.80, India 0.44, other 0.72
Disappearance	3.30	EU-15 0.81, US 0.46, India 0.46, Philippines 0.32, Indonesia 0.17, Malaysia 0.11, Mexico 0.11, other 0.86
Exports	2.05	Philippines 1.17, Indonesia 0.63, other 0.25
Imports	2.09	EU-15 0.79, US 0.54, Malaysia 0.11, China 0.10, other 0.55

Source: Mielke 2001.

1.2.7 Coconut oil

Coconut oil (Table 1.14) has a very uneven record in terms of its production. This is a consequence of climatic and political instability in the countries where it is produced. Production at 3.4 million tonnes is mainly in the Philippines (43%), Indonesia (23%) and India (13%). The Philippines and Indonesia are the major exporters, while EU-15 and the US are the major importers. Coconut oil is an important lauric oil with significant food and non-food uses. It competes with palmkernel oil as the other major lauric oil.

1.2.8 Palmkernel oil

Palmkernel oil (Table 1.15) is available at a slightly lower level than coconut oil but production is increasing steadily with that of palm oil, and it is expected that one day production will exceed that of coconut oil. Malaysia and Indonesia are the major producers and exporters, with EU-15 and the US again the major importing countries.

1.2.9 Olive oil

Olive oil (Table 1.16), produced at a level of around 2.6 million tonnes, has a long history going back to pre-biblical times. It is produced and consumed

Table 1.15 Major countries/regions involved in the production, disappearance, export and imports (million tonnes) of palmkernel oil in 2000/01

	Total	Major countries/regions
Production	2.89	Malaysia 1.54, Indonesia 0.77, Nigeria 0.19, other 0.39
Disappearance	2.81	Malaysia 0.90, EU-15 0.49, Nigeria 0.19, US 0.18, Indonesia 0.15, other 0.90
Exports	1.43	Malaysia 0.67, Indonesia 0.63, other 0.14
Imports	1.42	EU-15 0.51, US 0.19, other 0.72

Source: Mielke 2001.

Table 1.16 Major countries/regions involved in the production, disappearance, export and imports (million tonnes) of olive oil in 2000/01

	Total	Major countries/regions
Production	2.56	Spain 1.01, Greece 0.44, Italy 0.35, Turkey 0.21, Syria 0.18, Tunisia 0.16, other 0.21
Disappearance	2.70	EU-15 1.88, US 0.20, Syria 0.12, Turkey 0.10, other 0.40
Exports	0.55	Italy 0.15, Tunisia 0.13, Spain 0.11, other 0.16
Imports	0.55	US 0.20, Italy 0.11, other 0.24

Source: Mielke 2001.

Table 1.17 Major countries/regions involved in the production, disappearance, export and imports (million tonnes) of corn oil in 2000/01

	Total	Major countries/regions
Production	2.04	US 1.16, EU-15 0.21, Japan 0.11, other 0.56
Disappearance	2.06	US 0.70, EU-15 0.25, Turkey 0.11, Japan 0.10, other 0.90
Exports	0.80	US 0.49, EU-15 0.13, other 0.18
Imports	0.80	EU-15 0.17, Turkey 0.09, Libya 0.08, Saudi Arabia 0.06, other 0.40

Source: Mielke 2001.

mainly in Mediterranean countries, but demand is increasing in other countries in Northern Europe and in the US as a consequence of strong marketing of this oil. Olive oil is considered to be an essential ingredient of the healthy Mediterranean life style.

1.2.10 Corn oil

Corn oil (Table 1.17) is available at about 2 million tonnes each year with about 40% being traded. The US is the major producer, consumer and exporter of this oil, with EU-15 involved at a lower level.

Table 1.18 Major countries/regions involved in the production, disappearance, export and imports (million tonnes) of sesame oil in 2000/01

	Total	Major countries/regions
Production	0.78	China 0.23, India 0.15, Myanmar 0.09, other 0.31
Disappearance	0.78	China 0.22, India 0.15, Myanmar 0.09, other 0.32
Exports	0.03	
Imports	0.03	

Source: Mielke 2001.

Table 1.19 Major countries/regions involved in the production, disappearance, export and imports (million tonnes) of linseed oil in 2000/01

	Total	Major countries/regions
Production	0.72	EU-15 0.20, China 0.16, US 0.13, other 0.23
Disappearance	0.73	China 0.20, EU-15 0.14, US 0.10, India 0.07, other 0.22
Exports	0.14	EU-15 0.06, US 0.04, other 0.04
Imports	0.14	China 0.04, other 0.10

Source: Mielke 2001.

1.2.11 Sesame oil

Sesame oil (Table 1.18) is a minor oil with interesting properties (see Chapter 11). Production at a little below 0.8 million tonnes is mainly in China, India and Myanmar (Burma). Consumption is largely confined to these same countries.

1.2.12 Linseed oil

Linseed oil (Table 1.19) is unusual among these oils in that its production has hardly changed over the past 20 years. Its main use is as an industrial oil based on its high unsaturation, but increasingly it is consumed as a food oil. It is used as flaxseed by those who recognise the dietary importance of *n*-3 acids or as linola. The latter has a modified fatty acid composition which puts it in the linoleic acid-rich group of seed oils. There is a substantial trade in the seeds as well as in the oil. Details of countries/regions involved in production, consumption, and trading are given in Table 1.19.

1.3 Some significant factors

In considering the production and trade in vegetable oil the following significant factors have to be noted.

Imports into China and India. Through the operation of the market, the production of oils and fats and their disappearance remain approximately in

Table 1.20 Disappearance of oils and fats in China and in India in the five-year period 1996/97 to 2000/01, along with imports of seeds into China and oil into India*

	1996/97	1997/98	1998/00	1999/00	2000/01
China					
Disappearance	14.37	15.10	15.79	17.04	18.47
Seed imports	2.37	3.29	6.43	13.70	14.42
India					
Disappearance	9.41	9.69	10.87	11.72	12.42
Oil imports	1.98	2.18	4.47	5.26	5.86

Source: Mielke 2001.
*All figures in million tonnes.

balance. Shortfalls and surpluses from year to year affect stocks and prices with consequent adjustment of supply and demand. Demand has increased steadily over many years, partly through the increase in population and more through increase in income, leading to increased consumption of fat and of animal protein. The latter, in turn, increases the demand for seed meal, which is sourced mainly from oilseeds. A dominant market factor at the present time is the rapidly increasing demand for oils and fats in the developing countries and especially in the two most populous countries—China and India. Table 1.20 shows the increased disappearance of oils and fats in these two countries in the past five years. In China that demand has been met mainly by the imports of large volumes of soybeans and rape seeds, followed by local extraction. This meets the internal need for both oils and fats and for seed meal. Over five years, disappearance of oils and fats in China has risen by 28.5% and the import of seed has increased over sixfold. India has followed a different route and has greatly increased its imports of oils, particularly palm oil. In the same five years, disappearance in India has increased 32% and oil imports have risen almost threefold.

Trade in oilseeds and in fats. This book is devoted to vegetable oils and information on the production, disappearance and exports/imports has been presented and discussed. For palm oil, olive oil and corn oil, these data give a good picture of the situation but for the remaining oils which are extracted from oilseeds this provides only a partial picture. There is also a trade in the seeds. It is not appropriate to give figures for these here, but this situation has to be remembered when considering the movements of oils and fats and their original source.

Oleochemical demands. This book is concerned with the source and composition of vegetable oils for use in the food industry, but it must not be forgotten that some 14% of total oils and fats are used in the oleochemical industry. The fats most in demand for this purpose (including some that are not considered in this book) are the two lauric oils (coconut and palmkernel), tallow, palm (especially palm stearin), linseed and castor. In addition, most vegetable oils find some

oleochemical use. This is particularly true for the production of biodiesel which is usually the methyl esters of the most readily available oil. This will be soybean oil or tallow in the US, rapeseed oil in Europe, palm oil in Malaysia and waste (frying) oil in Japan. It is likely that the demand of these esters as solvents and as biodiesel will increase considerably. At present (2001) the cost of mineral oil is high and the prices of vegetable oils are low and these commercial pressures add to the environmental arguments for some limited replacement of mineral oil by a vegetable alternative. Some of these issues are elaborated in a recent book by Gunstone and Hamilton (2001).

1.4 Predictions for the twenty-first century

James Fry of LMC International (Oxford and New York) has examined changes in the production and demand for oils and fats in the past quarter century (1976–2000) and made projections for the twenty-first century (Fry 2001). Between 1976 and 2000, consumption in oils and fats increased at an average rate of 3.7%, equivalent to a doubling every 20 years or so. For animal and marine fats, the increase was only 1.4% and for vegetable oils 4.5%. The four major oils have increased at average rates of 8.3% for palm oil, 7.3% for rapeseed oil, 4.5% for sunflower oil, and 4.1% for soybean oil. These increases result from a combination of higher yields and of larger areas devoted to their production, as detailed in Table 1.21. The very large increase in palm oil has come mainly from the increase in area, and only to a minor extent from a rise in yield, while the three oilseed crops show significant increases in yield as well as in area under cultivation.

Extrapolation of figures for the past 40 years over the next 100 produces ridiculous conclusions with population increasing sixfold to 36 billion, consumption per person of oils and fats increasing to a world average of 110 kilos per annum, and world production of 4 billion tonnes in 2100! More reasonably, it is now widely accepted that population will level out half-way through the century at around 10 billion, and Fry has made other assumptions about growth

Table 1.21 Trend rates in growth of output (%) over the period 1975–1999 in terms of area and yield for the four major vegetable oils

Vegetable oil	Output	Area	Yield
Soybean	3.5	2.2	1.3
Palm	8.2	7.3	0.9
Rapeseed	7.1	4.4	2.4
Sunflower seed	5.5	4.2	1.2

Source: Fry 2001.

in personal GDP and the link between income and fat consumption. On this basis, he has calculated the production of total oils and fats and of vegetable oils and disappearance on a world basis and for the four major countries/regions—the US, EU-15, China and India (Table 1.22). Fry does not expect dietary consumption to reach these high levels. In the second half of the century, levels of oils and fats used for oleochemical purposes, including the preparation of methyl esters for use as biofuels, are expected to rise considerably.

In Table 1.23, the areas which must be cultivated with oil-bearing plants to meet these requirements are reported on the basis of an annual increase in yield of 1.50%. On this basis, the present yield of 0.59 tonnes/hectare will increase to 2.03 tonnes/hectare or 4.41 times, and the required area of cultivation increase from 156 to 352 million hectares (2.26 times) by the end of the century. Corresponding figures are also given for lower (1.25%) and higher (1.75%) average annual increases.

Table 1.22 Predicted total (million tonnes) and per capita consumption (kg per annum) of oils and fats on a global basis and for selected countries/regions throughout the century

	2000	2020	2040	2060	2080	2100
Total	114	219	364	542	736	971
Vegetable oils	92	190	328	498	685	914
Population (billions)	6.08	7.90	9.23	9.99	10.18	10.35
Consumption per person						
World	19	28	39	54	72	94
US	52	68	85	100	113	124
EU-15	47	62	77	90	102	112
China	13	28	49	74	99	122
India	12	21	33	48	66	84

Source: Fry 2001.

Table 1.23 Area under oilseed cultivation (million hectares) and yield (tonnes/hectare) under three different assumptions for annual increase in oilseed yield

	2000	2020	2040	2060	2080	2100
Estimated annual increase in oil seed yield of 1.25%						
Area	156	252	340	403	432	450
Oil yield	0.59	0.75	0.96	1.24	1.59	2.03
Estimated annual increase in oil seed yield of 1.50%						
Area	156	240	308	347	355	352
Oil yield	0.59	0.79	1.06	1.43	1.93	2.60
Estimated annual increase in oil seed yield of 1.75%						
Area	156	228	279	300	291	275
Oil yield	0.59	0.83	1.17	1.66	2.35	3.33

Source: Fry 2001.

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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

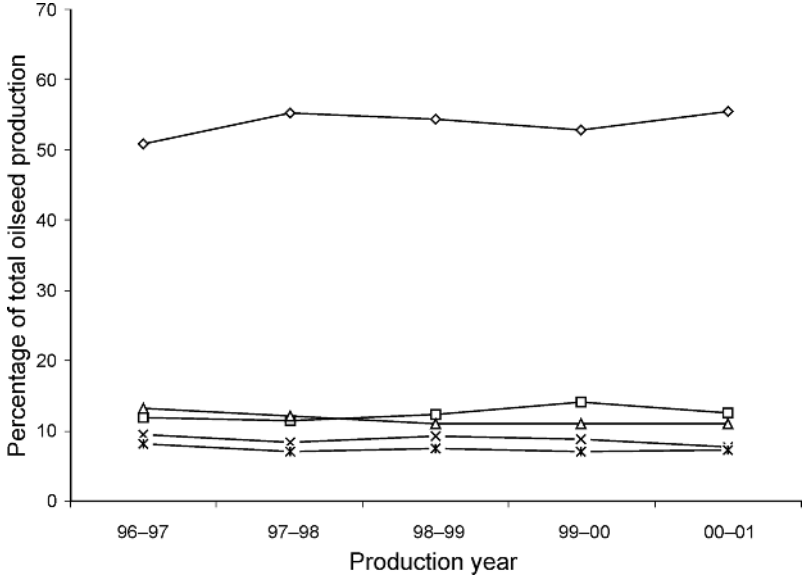

Figure 2.1 Five major oilseeds as a percentage of total worldwide oilseed production for the period 1996/97 to 2000/01 (Gunstone 2001), based on ten major oilseeds. Key: —◇—, Soybean; —□—, Rapeseed/Canola; —△—, Cottonseed; —×—, Sunflower; —✱—, Peanut.

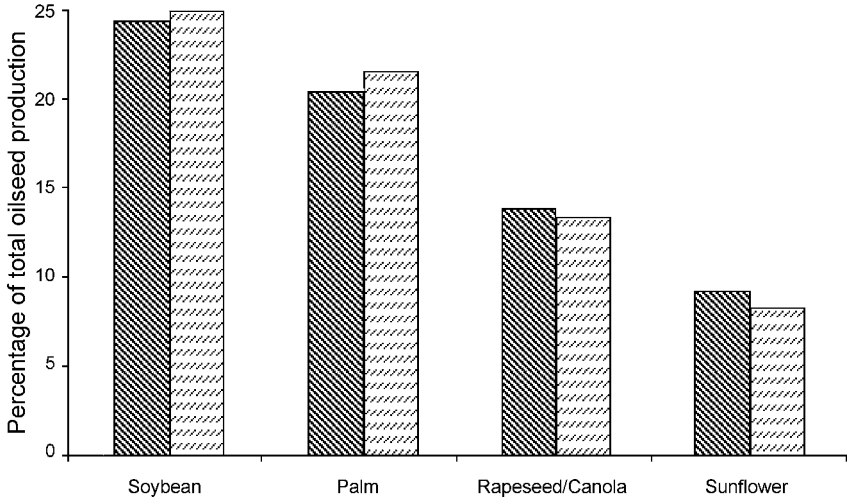

Figure 2.2 Four major oils as a percentage of total worldwide oil production for the period 1999/2000 to 2000/01 (Gunstone 2001), based on 17 commodity oils and fats. Key: ▨, 99–00; ▨, 00–01.

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

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

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	

[a]The values of each row with different letters are significantly different at 5%.
[b]Percentages 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 (70ºC) 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 CO_2 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

	Tocopherols		Sterols		Squalene	
Processing step	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 (Hernadez 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.

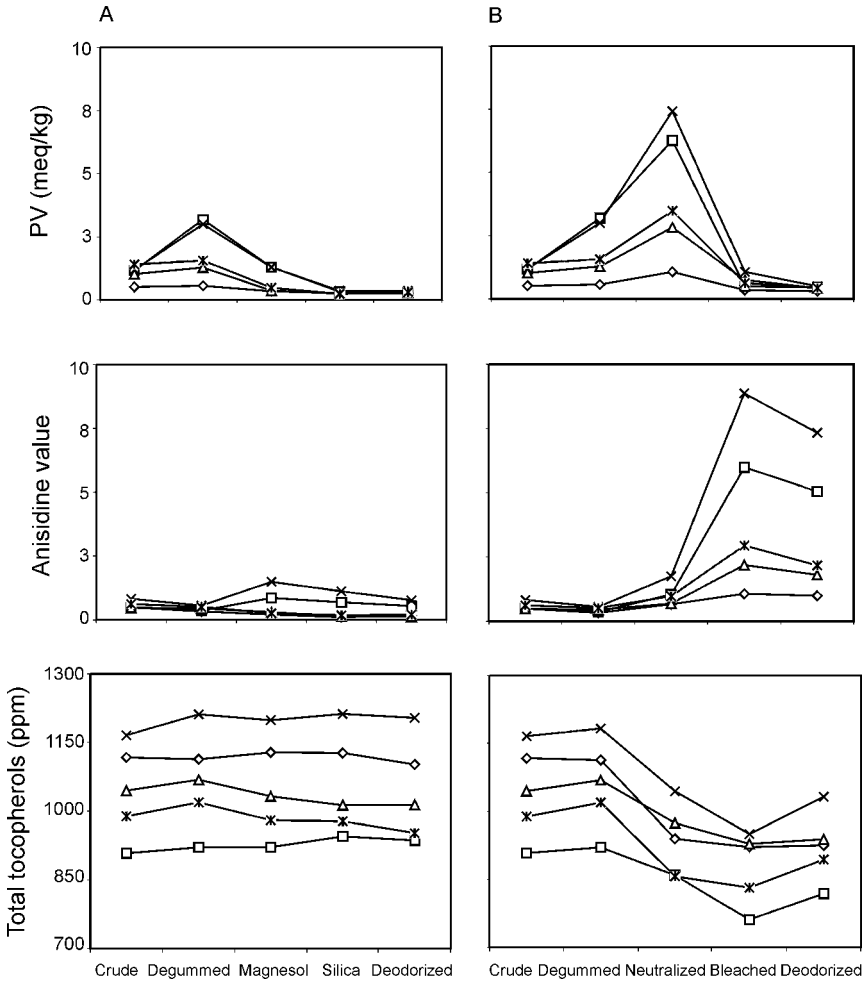

Figure 2.3 Oxidation and tocopherol retention during modified (A) and conventional (B) refining of various types of soybean oils. Key: —◇—, high-oleic acid soybean oil (HO); —□—, low-linolenic acid soybean oil (LLL); —△—, lipoxygenase-free soybean oil (LOX); —×—, low-saturated fatty acid soybean oil (LS); —✳—, 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 CO_2 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).

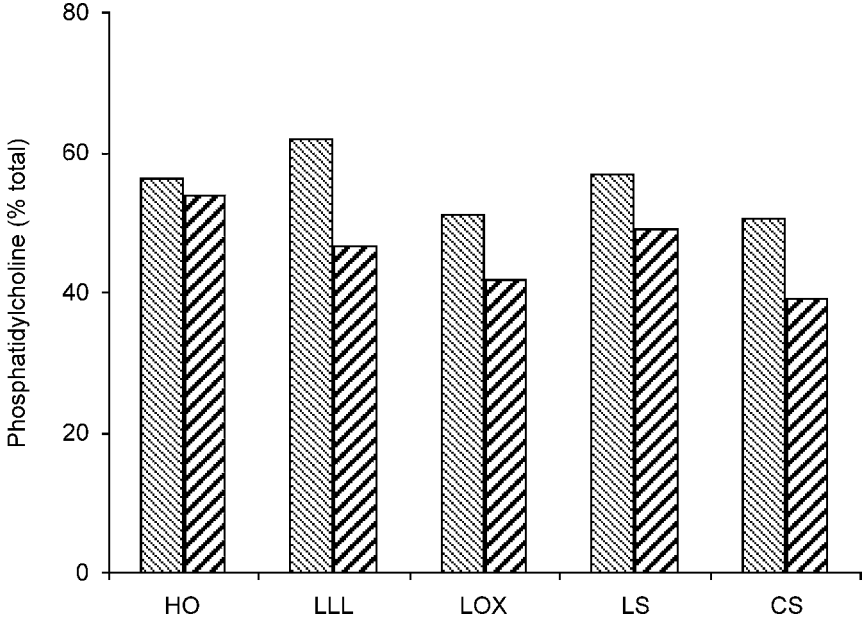

Figure 2.4 Phosphatidylcholine content of lecithin recovered from extruded-expelled (E-E) and solvent extracted (S-E) soybean oils. Abbreviations: HO, high-oleic acid soybean oil; LLL, low-linolenic acid soybean oil; LOX, lipoxygenase-free soybean oil; LS, low-saturated fatty acid soybean oil; and CS, 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 CO_2 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:

$$\text{Linolenic} \longrightarrow \text{Linoleic} \longrightarrow \text{Oleic} \longrightarrow \text{Stearic}$$

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

			SFC (%, at °C)			
	Iodine Value	M.P. (°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 trisaturate 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

	Composition (%)					
Type	16:0	18:0	18:1	18:2	18:3	Reference
Commodity	11	4	23	54	8	
Low saturates	3	1	31	57	9	Liu 1999
	4	3	28	61	3	Reske *et al*. 1997
High-palmitic	25	4	16	44	10	Neff and List 1999
	23	5	21	47	4	Shen *et al*. 1997
High-stearic	9	26	18	39	8	Neff and List 1999
	11	21	63	1	3	Knowlton *et al*. 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 *et al*. 1992
	15	6	32	45	2	Fehr *et al*. 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).

$$\rho = \mathrm{b} + \mathrm{m}T$$

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:

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

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 Noureddini and co-workers (1992). The relationship was expressed as

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

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

$$\mu = \mathrm{A}\mathrm{e}^{(Ea/\mathrm{R}T)}$$

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^0_{pi},

$$C^0_p \text{ (mix)} = \Sigma x_i C^0_{pi}$$

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,

$$\text{Correction factor (F)} = -0.2836 - 0.0005(\text{MW} - 850)$$
$$C_p\text{(estimated for oil)} = C_p\text{(calculated for mixed fatty acid)} + \text{F}$$

The accuracy of Morad's estimation method was determined to be ±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		
			Melting point (°C)	
Name	Melting point (°C)	Composition*	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

[a]IV = 132.6, [b]IV = 130.2, [c]IV = 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).

$$\begin{aligned}\Delta \text{ cholesterol } &= 2.10(\Delta \text{ saturates}) - 1.16(\Delta \text{ polyunsaturates}) \\ &\quad + 0.06(\Delta \text{ dietary cholesterol})\end{aligned}$$

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 ºC. 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.

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3 Palm oil

Siew Wai Lin

3.1 Introduction

The oil palm (*Elaeis guineensis jacquin*) originated from South Africa. It was introduced to East Asia as an ornamental plant, planted at the Bogor Botanical Garden Java (Indonesia) in 1884. The descendants spread to different parts of the world as the *Deli duras* and were utilised for D × P seed production. This is the main palm material grown in Malaysia and Indonesia. The Malaysian Palm Oil Board (MPOB), formerly known as PORIM, has the largest collection of oil palm germplasm in the world. The present planting material is mainly *dura* × *pisera* (D × P) (*tenera*). Commercial plantings in Malaysia have been based on this D × P material as it gives the highest oil yield per bunch (22.5–25.5%). Another species of oil palm, *Elaeis oleifera,* originates from Central and South America. Its oil is more unsaturated, but the oil to bunch ratio is extremely low, making it uneconomical to plant on a commercial scale.

The oil palm is the most efficient oil-producing plant, with about 4.5 tonnes of oil per hectare per year (Robbelen 1990). The palm bears fruit in the third year of planting in the field, and continues for about 25 years. Two types of oil are obtained from the oil palm fruit: palm oil from the mesocarp and kernel oil from the kernel inside the nut (see Chapter 6). Fruit bunches are harvested regularly throughout the year, following harvesting standards set by the plantations. They are then transported to the palm oil mills where crude oil and palmkernels are produced by mechanical and physical extraction processes. Oil quality is maintained by careful harvesting of fruits at the optimum stage of ripeness, minimal handling of fruits during transportation, and proper processing conditions during oil extraction.

3.2 Composition and properties of palm oil and fractions

3.2.1 Palm oil

Palm oil has a balanced fatty acid composition in which the level of saturated fatty acids is almost equal to that of the unsaturated fatty acids (Table 3.1). Palmitic acid (44–45%) and oleic acid (39–40%) are the major component acids along with linoleic acid (10–11%) and only a trace amount of linolenic acid. The low level of linoleic acid and virtual absence of linolenic acid make the

Table 3.1 Fatty acid and triacylglycerol composition of palm oil

	Malaysian (1981)[a]		Malaysian (1990)[b]		Brazilian (1993)[c]	
	Mean	Range (215 samples)	Mean	Range (244 samples)	Mean	Range (73 samples)
Fatty acids % by wt						
12:0	0.2	0.1–1.0	0.2	01–0.4	0.2	Tr–2.6
14:0	1.1	0.9–1.5	1.1	1.0–1.4	0.8	Tr–1.3
16:0	44.0	41.8–46.8	44.1	40.9–47.5	39.0	31.9–57.3
16:1	0.1	0.1–0.3	0.2	0–0.4	0.03	Tr–0.4
18:0	4.5	4.2–5.1	4.4	3.8–4.8	5.0	2.1–6.4
18:1	39.2	37.3–40.8	39.0	36.4–41.2	43.2	33.8–47.5
18:2	10.1	9.1–11.0	10.6	9.2–11.6	11.5	6.4–14.8
18:3	0.4	0–0.6	0.3	0–0.6	0.4	Tr–0.7
20:0	0.4	0–0.7	0.2	0–0.4	0.01	Tr–0.3
Triacylglycerols by carbon number						
C_{46}	0.8	0.4–1.2	1.2	0.7–2.0		NA
C_{48}	7.4	4.7–10.8	8.1	4.7–9.7		NA
C_{50}	42.6	40.0–45.2	39.9	38.9–41.6		NA
C_{52}	40.5	38.2–43.8	38.8	37.1–41.1		NA
C_{54}	8.8	6.4–11.4	11.4	10.3–12.1		NA
C_{56}	ND	ND	0.6	0.5–0.8		NA
Iodine value	53.3	51.0–55.3	52.1	50.1–54.9	58.0	50.3–62.9
SMP (°C)	36.0	32.3–39.0	36.7	33.0–39.0	NA	NA

Sources: [a]Tan *et al.* 1981; [b]Siew et al. 1990; [c]Tavares and Barberio 1995.
ND = not detectable.
NA = not available.

oil relatively stable to oxidative deterioration. Malaysian palm oil has a narrow compositional range, as indicated from several surveys carried out between 1977 and 1997. Early surveys of crude and refined palm oils were recorded by Chin and co-workers in 1982 on 215 samples, and by Tan and Oh (1981a). King and Sibley (1984) carried out a survey on oils collected from different geographical locations (Malaysia, Ivory Coast, Nigeria, Papua New Guinea, Solomon Island and Sumatra). In terms of fatty acid composition, iodine values (IV), and slip melting points, there are generally no major differences between the oils obtained from the different locations. The iodine values range from 50 to 55.

Brazilian palm oil appears to be more unsaturated, containing an average of 43.2% oleic and 11.5% linoleic acids with an iodine value of 58 (Table 3.1). The range is wider and iodine values vary from 50–63 (Tavares and Barberio 1995). These oils are likely to be of different oil palm variety. Elias and Pantzaris (1997) considered that the oils reported by Tavares and Barberio were rather

Table 3.2 Fatty acid composition of palm oil from *E. guineensis*, *E. oleifera* and their hybrids

Fatty acids (wt %)	*E. guineensis* (Eg)	*E. oleifera* (Eo)		Eg × Eo	
		Mean	Range[a]	Mean	Range[a]
12:0	0.3	–	–	–	–
14:0	1.2	0.2	0.1–0.3	0.5	0.1–0.5
16:0	44.3	18.7	14.4–23.0	32.2	22.4–44.7
16:1	–	1.6	NA	0.2	NA
18:0	4.3	0.9	0.6–1.8	3.2	1.6–4.9
18:1	39.3	56.1	55.8–64.0	51.8	36.9–60.1
18:2	10.0	21.1	16.2–22.5	10.8	8.8–16.8
Others	0.6	1.0	NA	0.9	NA
Iodine value	55.0	85.0	NA	67.5	NA

NA = not available.
Source: Rajanaidu *et al*. 2000; [a]Rajanaidu *et al*. 1985.

unusual, in that the ranges for palmitic acid (32–57%) and oleic acid (34–47%) were exceptionally wide. They concluded that the oil in the survey consisted of 'mixtures of oil of *Elaies oleifera* with various proportions of stearin'. This is apparent from the high levels of palmitic acid noted at the maximum end of the range (57.3%), and from the fact that the authors had already rejected 26 out of 99 samples as being adulterated. It is of interest to mention here that oils from *Elaeis oleifera* (South American palm) have oleic acid content as high as 55–64% and linoleic acid from 16–23% (Rajanaidu *et al*. 1985). *Elaeis oleifera*, also known as *Elaeis melanococca*, can be easily hybridised with *Elaeis guineensis*, producing oil with characteristics which are between those of the parent oils (Table 3.2). The composition of oil from the Nigerian population of *E. guineensis* shows considerable larger variation when compared with the commercial oils planted. Palmitic acid ranges from 27 to 55%, oleic acid from 28 to 56%, and linoleic acid from 6.5 to 18%. These materials provide oil palm breeders with genetic material for developing new palms with the required specifications such as high-oleic acid, carotenes or tocopherols.

The TAG profile of palm oil has been characterised by carbon-number gas chromatography (Table 3.1). The TAG of palm oil consists of C_{46} to C_{56} molecules in a near normal distribution, the major TAGs being of C_{50} and C_{52}. These carbon numbers represent the number of carbon atoms in the three acyl chains and exclude the glycerol carbon atoms. A more detailed profile of the TAGs is seen in Table 3.3. Palm oil has high contents of disaturated (POP and PPO) and monosaturated (POO and OPO) TAGs. Analysis of the 2-position of the TAGs by pancreatic lipase hydrolysis reveals the fatty acids at this position to be mainly unsaturated (oleic) (Tan 1979).

The polymorphic behaviour of a fat is determined to a large extent by the fatty acids within the TAGs. Fats which are composed of fatty acids predominantly of

Table 3.3 Triacylglycerol (TAG) composition of palm oil products

TAG (Wt %)	Palm oil[a]		Palm olein (IV < 60)[b]		Palm olein (IV 60–64)[b]		Palm olein (IV 65–67)[b]		Stearin IV 38.0	Stearin IV 45.8	Stearin IV 11
	Mean	Range	Mean	Range	Mean	Range	Mean	Range			
OLL	0.5	0.2–0.9	0.05	0.5–0.6	0.7	0.6–0.8	0.8	0.7–0.8	0.3	0.5	0.1
PLL	2.5	1.3–3.4	2.8	2.3–3.2	3.4	3.2–3.7	3.7	3.3–4.1	1.8	2.3	0.4
MLP	0.6	0.2–1.0	0.6	0.5–0.7	0.7	0.6–0.8	0.6	0.6–0.7	0.4	0.5	–
OLO	1.7	1.3–2.3	2.3	1.7–2.6	2.6	2.2–3.0	3.0	2.3–3.3	1.3	1.7	0.2
PLO	9.9	9.0–11.2	11.8	10.9–13.0	13.6	12.9–14.9	15.4	15.0–17.3	7.1	8.4	1.7
PLP	9.5	6.5–11.0	9.9	9.6–10.2	9.8	9.0–10.2	8.4	7.9–9.7	8.3	9.4	3.5
OOO	4.3	3.3–6.6	4.5	4.2–5.2	5.1	4.6–6.1	6.1	5.0–6.8	2.3	2.7	3.8
POO	22.8	20.5–26.2	26.8	25.1–29.0	30.2	28.4–32.5	34.5	33.4–35.7	16.7	18.4	5.0
POP	29.0	27.1–31.0	26.6	23.4–29.4	19.1	16.1–20.7	12.8	9.0–17.0	29.8	30.9	13.6
PPP	5.4	0.7–7.2	ND	ND	ND	ND	ND	ND	18.6	12.5	59.6
SOO	2.5	1.0–3.6	3.3	3.0–3.9	4.2	3.4–6.9	4.5	3.9–6.3	–	–	–
POS	5.1	4.6–5.9	4.7	3.9–5.2	3.6	2.9–4.8	2.5	1.9–3.5	4.8	5.4	2.4
PPS	1.0	0.1–1.8	0.07	0.1–0.3	0.2	0.1–0.3	0.2	0.1–0.3	3.6	2.7	8.0
SOS	0.5	0.1–1.4	0.16	0.2–0.6	0.4	0.2–0.5	0.2	0.1–0.4	0.6	0.6	–
Diacylglycerols (wt %)	4.9	3.0–7.6	5.3	4.7–6.1	6.4	5.6–6.9	7.1	6.2–8.6	4.5	4.0	1.1

ND = not detectable.
[a]Tan *et al.* 1997.
[b]Siew and Chong 1998.
[c]Siew, unpublished.
Symbols such as PLO refer to all the triacylglycerols with these three acyl chains.

a single chain length are most likely to be stable in the β form (DeMan, 1992). Palm oil, containing C_{16} and C_{18} acids in most of its glycerol esters, is highly stable in the β′ form.

Palm oil is unique among vegetable oils in having a significant amount of saturated acids (10–15%) at the 2-position of its TAGs. The appreciable amounts of disaturated (POP and PPO) and monosaturated (POO, OPO and PLO) are apparent as high-melting and low-melting fractions in the differential scanning calorimetry (DSC) thermograms (Figure 3.1). The oil can be easily separated into two products, palm olein and palm stearin. Figure 3.2 shows the products obtained from multiple fractionations of palm oil. A wide range of fractions

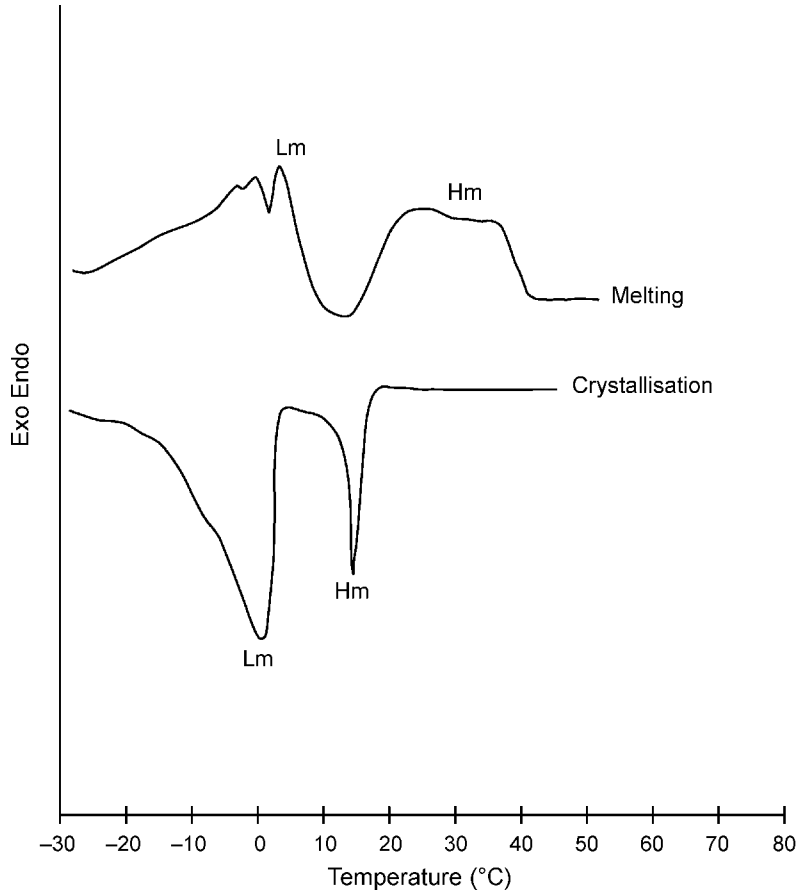

Figure 3.1 DSC melting and crystallisation thermograms of palm oil. For melting thermogram, sample was cooled to −30°C at rate of 40°C/min, held for 10 mins and heated to 80°C at 5°C/min; for cooling thermogram, sample was melted to 80°C and cooled to −30°C at 5°C/min. Lm: low melting fraction, Hm: high melting fraction.

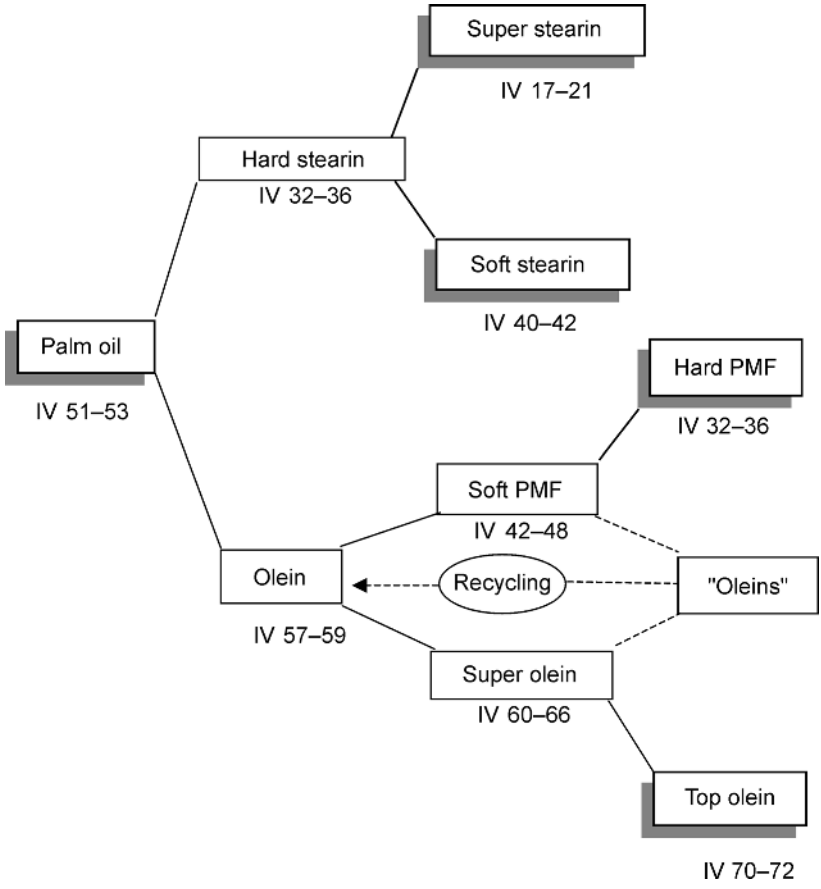

Figure 3.2 Dry multiple fractionation of palm oil (adapted with permission from Deffense, 1995).

with different properties to suit requirements of the food industry is available through dry fractionation.

3.2.2 Palm oleins

Palm oil, a semi-solid at ambient temperature (25–30°C), may be fractionated into a liquid fraction (olein) and a more solid fraction (stearin). The olein contains higher levels of oleic (39–45%) and linoleic acids (10–13%) compared to the oil (Table 3.4). Palm olein remains clear at ambient temperature of 25°C. Further fractionation of the olein produces a more unsaturated fraction, often called super-olein or double fractionated olein. These have higher levels of oleic and linoleic acids, ranging from 43–49% and 10–15% respectively, resulting in

Table 3.4 Fatty acid and triacylglycerol composition of palm olein

	Palm olein (IV < 60)[a]		Super olein (IV > 60)[b]		Top olein
	Mean	Range	Mean	Range	(IV 70–72)[c]
Fatty acid composition (wt %)					
12:0	0.3	0.2–0.4	0.3	0.2–0.4	–
14:0	1.1	0.9–1.2	1.0	0.9–1.1	1.0
16:0	40.9	36.8–43.2	35.4	30.1–37.1	28.8
18:0	4.2	3.7–4.8	3.8	3.2–4.3	2.5
18:1	41.5	39.8–44.6	45.1	43.2–49.2	52.0
18:2	11.6	10.4–12.9	13.4	10.7–15.0	14.6
18:3	0.4	0.1–0.6	0.3	0.2–0.6	0.4
20:0	0.4	0.3–0.5	0.3	0.0–0.4	0.2
Iodine value	56.8	55.6–61.9	61.9	60.1–67.5	70–72
Slip melting point (°C)	21.5	19.2–23.6	15.1	12.9–16.6	NA
Triacylglycerols by carbon number (wt %)					
C_{44}	0.1	0.0–0.5	ND	ND	NA
C_{46}	0.8	0.4–1.4	0.2	0.1–0.2	NA
C_{48}	3.3	2.4–3.9	1.9	1.7–2.6	NA
C_{50}	39.5	37.9–40.9	30.8	23.0–34.2	NA
C_{52}	42.7	41.9–43.7	53.4	50.2–59.6	NA
C_{54}	12.8	11.8–13.5	13.6	11.6–15.9	NA
C_{56}	0.7	0.5–1.1	0.2	0.1–0.4	NA

ND = not detectable.
NA = not available.
[a]Siew *et al*. 1990.
[b]Tang *et al.* 1995.
[c]Deffense 1995.

iodine values of 60–67 (Tang *et al.* 1995) and with lower cloud points of about 2–5°C. In contrast, oleins with IV of less than 60 have cloud point of 6–10°C. As the iodine value increases, the cloud point decreases, though not linearly. A cloud point of below 0°C can only be obtained with an olein of iodine value above 70. The palmitic acid content should be below 35%, preferably below 31%, for palm olein to remain clear at 10°C. Fractions with iodine above 70 and a cloud point of −4°C (Deffense 1995) are described as top-oleins. This olein can satisfy the cold test in which the oil must remain clear after 5.5 h at 0°C.

The differences in TAG composition between olein with iodine value not exceeding 60 and those above 60 are detailed in Table 3.3. The major differences are for levels of PLO (mean values of 11.8% and 13.6% respectively), POO (26.8% and 30.2%), and POP (26.6% and 19.1%). Stated in another way, SUU glycerol esters rise from 44.7 to 51.4% and SUS glycerol esters fall from 42.0 to 33.6% (S = saturated and U = unsaturated acyl chains). The ratio of POP/POO

Table 3.5 Nucleation behaviour of three palm oleins

IV of olein	POP/POO ratio	Nucleation test (11°C)
59.3 ± 3.0	0.89 ± 0.24	<1 h
61.4 ± 2.9	0.83 ± 0.22	1–6 h
63.6 ± 2.8	0.56 ± 0.20	>6 h

Source: Siew 2000.

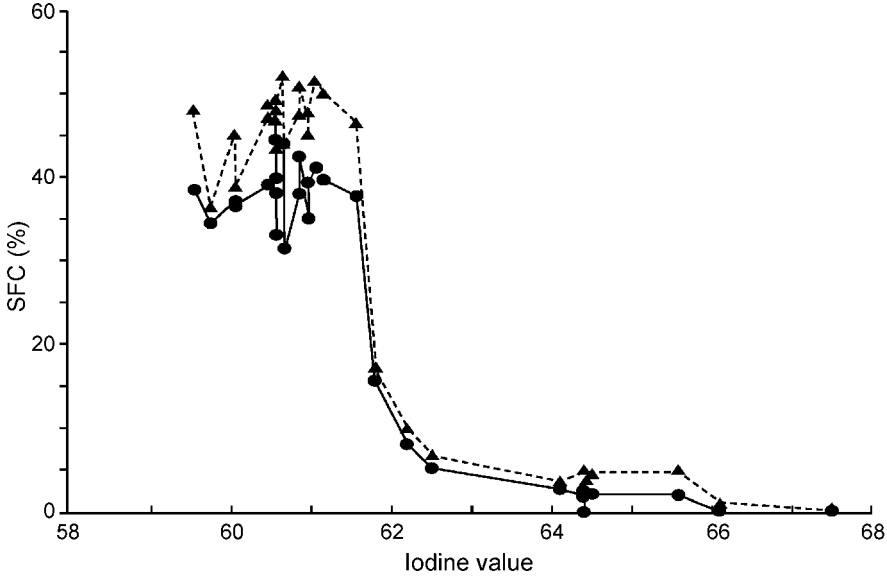

Figure 3.3 Solid fat content of palm superolein in relation to iodine value. Key: ——, SFC at 5°C; - - - -, SFC at 2.5°C (Tang *et al*. 1995, with permission from MPOB).

influences the crystallisation of palm oil as shown in Table 3.5. Figure 3.3 shows the quite remarkable change in SFC which happens in palm oleins at an iodine value around 62.

Saturated TAGs such as PPP, MPP and PPS are the seeds of crystallisation (Mohd Zaki *et al*. 1997). Other crystallisation inducers are diacylglycerols such as dipalmitoylglycerol. Siew and Ng (1996a) found high concentrations of 1,3-dipalmitoylglycerol in crystals obtained from palm olein by tempering the olein through a alternating temperature cycle of 28°C and 10°C. It is notable that diacylglycerols are preferentially distributed into the olein phase during fractionation. A higher concentration of diacylglycerols is found in more unsaturated oleins.

The content of unsaturated acids in superolein is about 59% compared to only 53% in the single fractionated olein. Figure 3.3 shows the solid fat content of the olein in relation to the iodine value (Tang *et al*. 1995). It is clear that in

order to remain clear at lower temperatures, the iodine value of olein has to be 62 and above.

3.2.3 Palm stearin

Palm stearin, the harder fraction of palm oil, contains the more saturated fatty acids and TAGs. The comprehensive survey of fractionated products of palm oil (Tan and Oh 1981b) indicated a wider compositional range for stearin, in contrast to olein (Table 3.6). The wide iodine value range (21–49) is reflected in the slip melting points (44–56°C). The palmitic acid content of the stearins varies from 47–74%, while oleic acid ranges from 15–37%. The authors found that the distribution was rather skewed and did not compute mean values. A later survey (Siew *et al.* 1990) showed a palmitic acid content in the range of 49–68% and oleic content of 24–34%. Samples in the 1981 survey were from dry, detergent and solvent processes, while samples from the later survey were generally dry fractionated types. Due to the higher cost of operations, detergent and solvent, fractionations are no longer popular processes.

Table 3.6 Fatty acid and triacylglycerol composition of palm stearin

	Stearin[a]	Soft stearin[a]	Palm mid fraction[b]
Fatty acid composition (wt %)			
12:0	0.1–0.6	0.1	0–0.3
14:0	1.1–1.9	1.1	0.8–1.4
16:0	47.2–73.8	49.3	41.4–55.5
16:1	0.05–0.2	0.1	–
18:0	4.4–5.6	4.9	4.7–6.7
18:1	15.6–37.0	34.8	32.0–41.2
18:2	3.2–9.8	9.0	3.6–11.5
18:3	0.1–0.6	0.2	0–0.2
20:0	0.1–0.6	0.4	0–0.6
Iodine value	21.6–49.4	46.7	34.5–54.8
SMP °C	44.5–56.2	47.7	24.3–44.9
Triacylglycerols (by carbon number)			
C_{46}	0.5–3.3	1.2	0–1.6
C_{48}	12.2–55.8	15.3	1.4–11.3
C_{50}	33.6–49.8	42.7	45.5–73.9
C_{52}	5.1–37.3	33.4	19.4–42.0
C_{54}	tr–8.4	7.4	1.7–8.5
C_{56}	ND	ND	0–0.9

[a]Tan and Oh 1981b; [b]Tan *et al.* 1981.
ND = not detectable.
tr = trace.

A much harder stearin is also available with as much as 79% palmitic acid. This stearin has a tripalmitoylglycerol (PPP) content of 60% and is used as hard stock for soft margarines and in infant fat formulas. Advances in crystalliser designs, cooling programs and filtration technology have enabled a wider range of stearins to be produced. Another stearin, produced from a second fractionation of the olein, is called palm mid-fraction (Figure 3.2). This oil contains high C_{50} (POP) TAG (Table 3.6) and is utilised in manufacture of a cocoa butter equivalent. Tan and co-workers (1981) characterised palm mid-fractions and proposed the following specifications: ratio of $C_{50}/C_{48} + C_{54}$ 4 minimum, C_{52} TAGs content 43% maximum, iodine value 32–55, and slip melting point 23–40°C. The iodine value and slip melting point ranges, though representative of mid-fractions, were too wide to represent good quality palm mid-fractions. Palm mid-fraction is often refractionated by a solvent process to enrich the POP esters further. Dry fractionation processes are now available which can produce high quality palm mid-fractions (Tan 2001). The use of high-pressure membrane filtration has helped to improve the quality of palm mid-fractions. Products of iodine value around 33–35, previously only available through solvent fractionation, can now be produced from dry fractionation processes.

3.3 Physical characteristics of palm oil products

3.3.1 Palm oil

Palm oil is a semi-solid at room temperature (28°C), the melting point range being from 32–40°C. The slip melting point method is commonly adopted for measuring this parameter. By the DSC method the fat melts completely at 39–40°C, when heated at 5°C/min, from an oil cooled rapidly to −40°C at 5°C/min. The slip melting point is affected by the content of free fatty acids and diacylglycerols. Thus crude oils have slightly higher slip melting point than refined oils.

The solid fat content of a fat determines its applications and usage. As an oil with saturated and unsaturated fatty acids in roughly equal proportions, solids exist from 50°C down to 10°C (Table 3.7). At a temperature of 10°C, the solid content amounts to about 50%, reducing to half of this at 20°C. The variation between samples arises from differences in fatty acid and TAG compositions, as well as in the levels of diacylglycerol in the oil. Siew and Ng (1999) observed that 10% of added diacylglycerol reduces the solids content by 20%.

The melting and crystallisation characteristics of the oil can be followed using the DSC technique (Figure 3.1). Both the melting and cooling thermograms show two main endotherms/exotherms representative of the high and low melting fractions of the oil. From these thermograms, it is clear that palm oil is an excellent oil for fractionation. Suitable cooling programs produce oleins

Table 3.7 Physical properties of palm oil and its fractions

No. of samples	Palm oil[a] 244		Palm olein[a] 238		Super olein[b] 32		Palm stearin[a] 205		Palm mid fraction[c] 39		Palm mid fraction[d]	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	soft	hard
Refractive index	1.4548	1.4544–1.4550 (at 50°C)	1.4589	1.4589–1.4592 (at 40°C)	1.4634	1.4631–1.4641 (at 30°C)	1.4493	1.4482–1.4501 (at 60°C)	NA	NA	NA	NA
Apparent density (g/ml)	0.8899	0.8896–0.8910 (at 50°C)	0.8972	0.8969–0.8977 (at 40°C)	0.9046	0.9042–0.9054 (at 30°C)	0.8822	0.8813–0.8844 (at 60°C)	NA	NA	NA	NA
Solid fat content by nuclear magnetic resonance												
Temperature (°C)												
10	53.7	46.1–60.8	38.3	23.9–45.5	17.5	0–26.3	76.0	49.5–84.1	10	52.7–90.6	75.0	95.0
15	39.1	33.4–50.8	19.9	10.7–25.9	0.9	0–9.0	68.9	37.2–79.0	15	40.0–85.0	64.0	93.0
20	26.1	21.6–31.3	5.7	0.0–9.0			60.2	25.2–71.2	20	10.3–73.1	45.0	90.0
25	16.3	12.1–20.7	2.1	0.0–4.3			50.6	15.8–63.5	25	0–24.9	11.0	78.0
30	10.5	6.1–14.3					40.4	11.2–55.0	30	0–20.2		47.0
35	7.9	3.5–11.7					34.3	7.2–46.6	35	0–15.3		6.0
40	4.6	0.0–8.3					28.1	6.1–38.0	40	0–7.8		
45							22.4	1.0–32.2				
50							12.5	0.0–21.3				
55							0.6	0.0–9.1				

Source: [a]Siew *et al.* 1992; [b]Tang 1995; [c]Tan *et al.* 1981; [d]Deffense 1995.
NA = not available.

and stearins of different compositions to suit market requirements. The fact that palm oil crystallises in the β′ form helps in the fractionation and filtration process as large crystals are formed, enabling easy filtration.

Other physical characteristics such as refractive index and apparent density of the oil are as given in Table 3.7.

3.3.2 Palm olein

Palm olein, being the liquid fraction of palm oil, is clear at a room temperature of 28°C. Its clarity depends on iodine value, TAG composition, and diacylglycerol content. Table 3.8 shows the cold stability of palm olein in relation to its iodine value (Nor Aini *et al*. 1993). The clarity of the olein can be significantly affected by the diacylglycerol content as shown in Table 3.9. Diacylglycerols derived from palm oil affect the cold stability of palm olein. While dipalmitoylglycerol (PP) causes rapid crystallisation of the olein, other diacylglycerols such as palmitoyl oleoylglycerol (PO) and dioleoylglycerol (OO) do not significantly affect cold stability. The physical characteristics of palm olein are closely related to its chemical composition.

Solid fat contents are low, 37% at 10°C for normal olein and only 17% for super oleins (Table 3.7). At 25°C, most oleins are completely liquid. Super oleins fall into two categories. Those with iodine value below 61.5 have higher solids of 40–52% at 2.5°C and 31–42% at 5°C and those with iodine values exceeding 61.5 have much lower solids of 0.5–17% at 2.5°C and 0–16% at 5°C. (Tang *et al*. 1995), Improved cold stability can thus be expected with such oils.

Cooling and melting thermograms of palm olein are illustrated in Figures 3.4 and 3.5. In contrast to the thermograms of palm oil, those for palm olein reveal only a single broad crystallisation peak. This exotherm is generally sharper in

Table 3.8 Cold stability of palm olein at 5–20°C

	Single fractionated palm olein			Double fractionated palm olein			
Iodine value	56	58	62	60	62	65	67
Cloud point (°C)	8.3	6.3	3.5	4.5	4.0	2.0	1.5
Temperature (°C)							
5	< 3 h	< 3 h	< 3 h	< 3 h	< 3 h	< 5 h	< 5 h
						< 1 d	
10	< 3 h	< 3 h	> 5 h	< 3 h	1 d	< 2 d	1 d
			< 1 d				
15	< 3 h	< 3 h	> 1 d	< 1 d	< 4 d	< 7 d	< 5 d
20	> 5 h	> 5 h	> 20 d	< 1 d	< 4 d	> 60 d	> 60 d
	< 1 d	< 1 d					

*Time the oil remains clear (h denotes hour, d denotes day).

Source: Nor Aini and Hanirah 1996, 1997.

Table 3.9 Effect of added diacylglycerols (DAG) on the crystallisation of palm olein at 5°C

Percentage of DAG	Crystallisation time (min)						
	PDG	1,2-PP	1,3-PP	1,2-PO	1,3-PO	1,2-OO	1,3-OO
Olein IV 58.1[a]							
0.0	3.9	3.9	3.9	3.9	3.9	3.9	3.9
0.5	1.9	1.7	1.2	2.5	2.5	2.7	2.3
1.0	1.9	0.8	0.8	2.6	2.3	2.7	2.3
1.5	1.9	0.7	rt[c]	2.8	2.3	3.0	2.4
2.0	1.9	0.7	rt	3.0	2.3	3.0	2.8
2.5	1.9	0.6	rt	3.0	2.0	3.0	3.3
5.0	1.4						
7.5	1.4						
10.0	1.4						
Olein IV 62.8[b]							
0.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0
0.5	36.0	8.5	1.9	37.5	38.0	29.5	29.5
1.0	33.5	2.1	rt	37.5	38.0	29.5	29.5
1.5	17.5	1.4	rt	37.5	38.5	29.5	29.5
2.0	12.5	1.4	rt	40.5	42.0	29.5	29.5
2.5	9.0	1.4	rt	45.0	45.0	29.5	29.5
5.0	2.0						
7.5	1.3						
10.0	1.3						

[a]LSD ($P < 0.05$) 0.7; [b]LSD ($P < 0.05$)1.31; [c]rt, crystallise at room temperature (28°C); [d]PDG refers to diacylglycerols extracted from palm oil.
Source: Siew and Ng 1996b.

oleins with higher iodine values. The exotherm is shifted slightly from 2.8 to 0.2°C in moving to a more unsaturated olein, from iodine value of 56 to 65. The shift in peak temperature is minimal. In the melting thermograms for oleins of iodine value 56, 60 and 65, respectively, the change in peak temperature varies from 6.9, to 5.7, to 4.4°C, while the melting temperature changes from 24, to 15, to 13°C.

3.3.3 Palm stearin

Palm stearin, the more saturated fraction of palm oil, is more variable in composition and thus in physical characteristics. The wide range in solid fat content (Table 3.7) is consistent with the wide range in iodine value for the oil. The variation in composition allows food manufacturers a wide choice of materials for their formulations. In fact, many product formulations require some material to provide the solids required at a certain temperature range. Palm stearin can provide the required solids in blends with unsaturated vegetable oils.

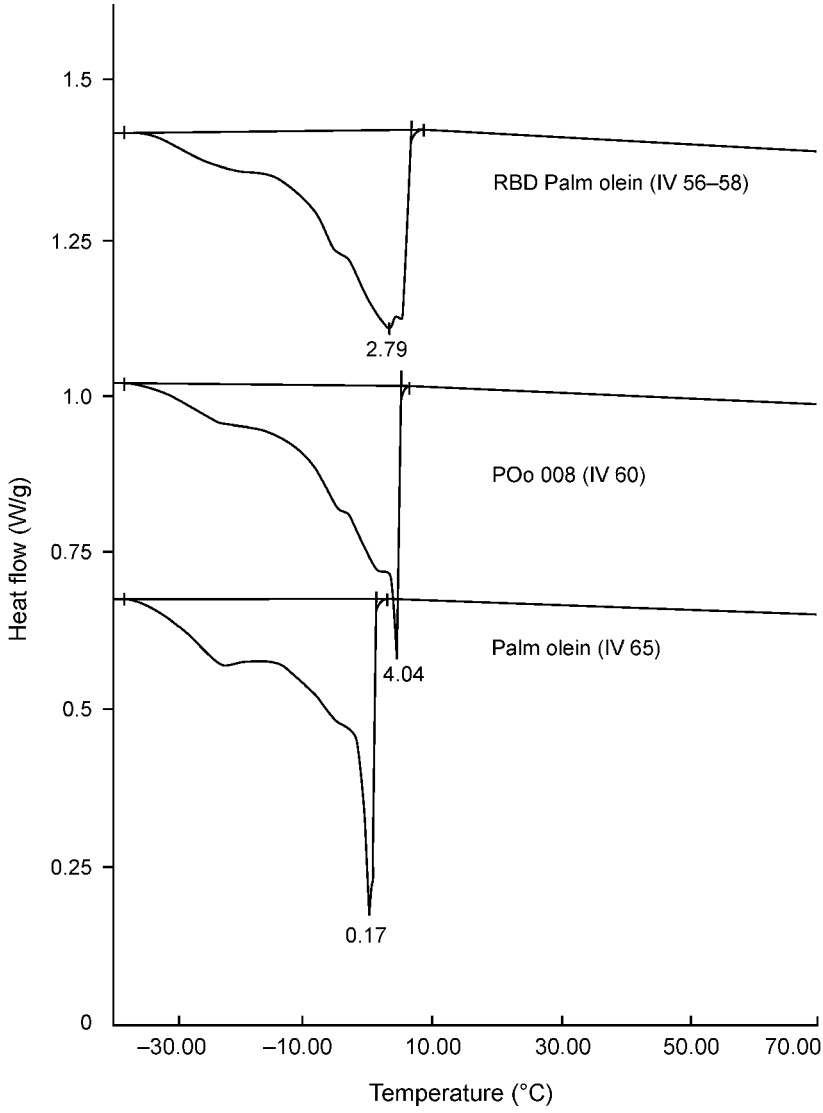

Figure 3.4 Cooling thermograms of palm oleins. Sample was melted to 80°C and cooled to −30°C at 5°C/min.

The crystallisation and melting behaviour of palm stearin depends on the composition. Figures 3.6 and 3.7 show the behaviour of different palm stearins. PMF shows crystallisation exotherms which overlap into several peaks, while its melting thermogram shows one main endotherm with a shoulder, finally melting

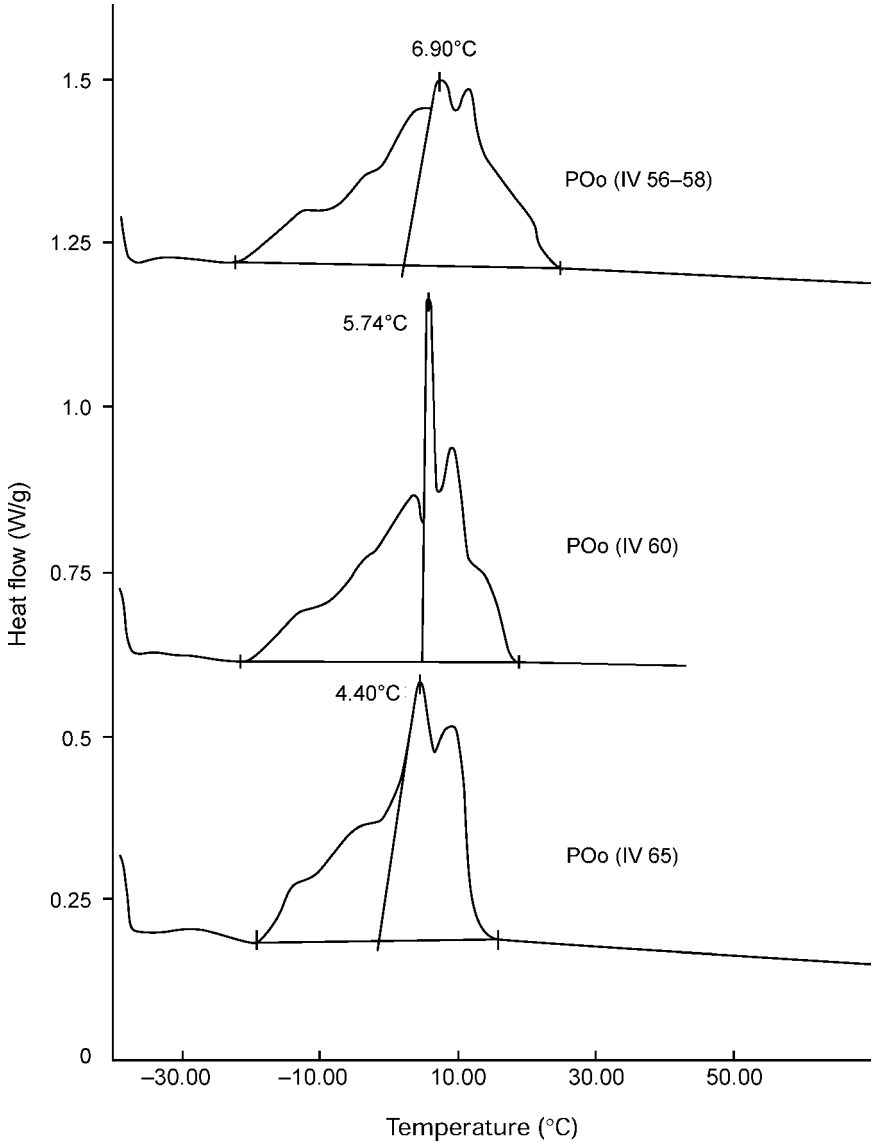

Figure 3.5 Melting thermograms of palm oleins. Sample was cooled to −30°C at rate of 40°C/min, held for 10 mins and heated to 80°C at 5°C/min.

at 31°C. The two other stearins (of iodine value 35 and 44) have different melting and crystallisation profiles, although both still have considerable proportions of the more unsaturated TAGs. Some polymorphic transformations are also observed in both stearins. A high melting fraction is also observed which results

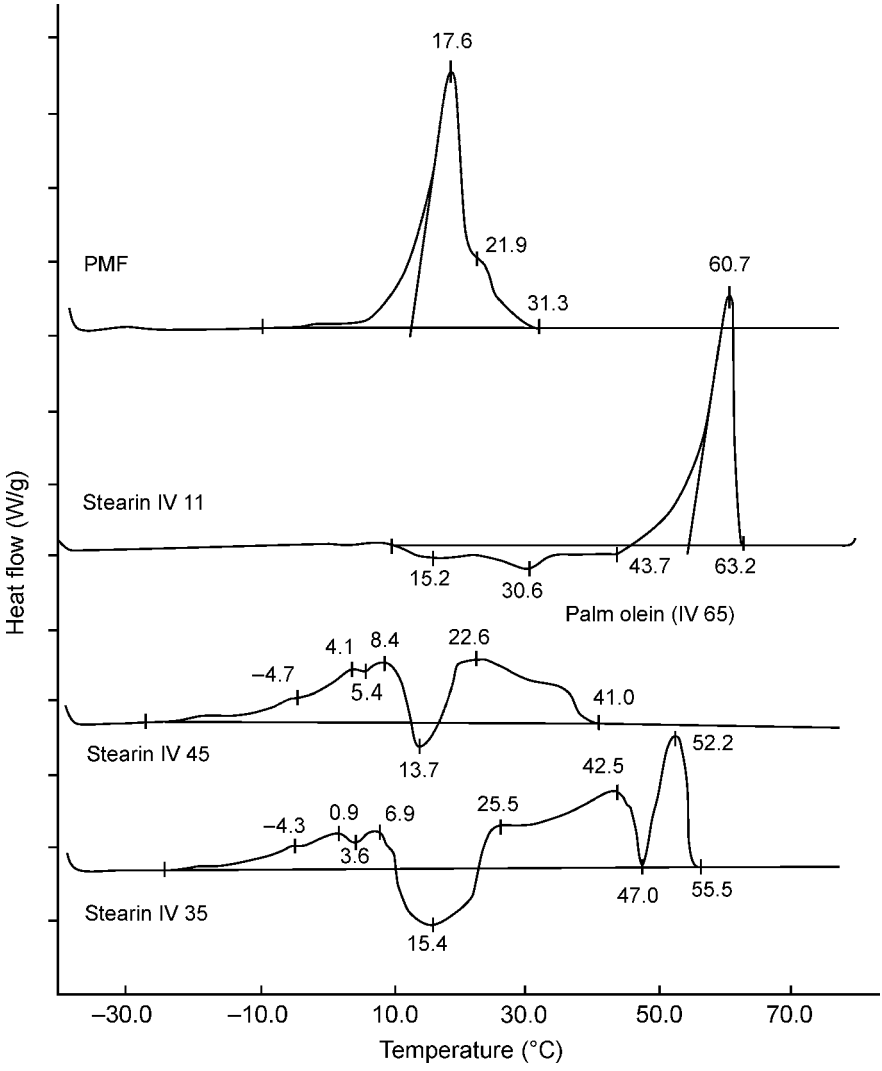

Figure 3.6 Melting thermograms of palm stearins. Sample was cooled to −30°C at rate of 40°C/min, held for 10 mins and heated to 80°C at 5°C/min.

in the oil melting at 55°C. In contrast, the hard stearin of iodine value 11 shows only one exotherm and endotherm, indicating that the lower melting fractions have been clearly removed during fractionation. It is obvious from the figures that the melting and crystallisation behaviour of palm stearins varies greatly. Understanding the properties and behaviour of different stearins enables full exploitation of usage and application in food products.

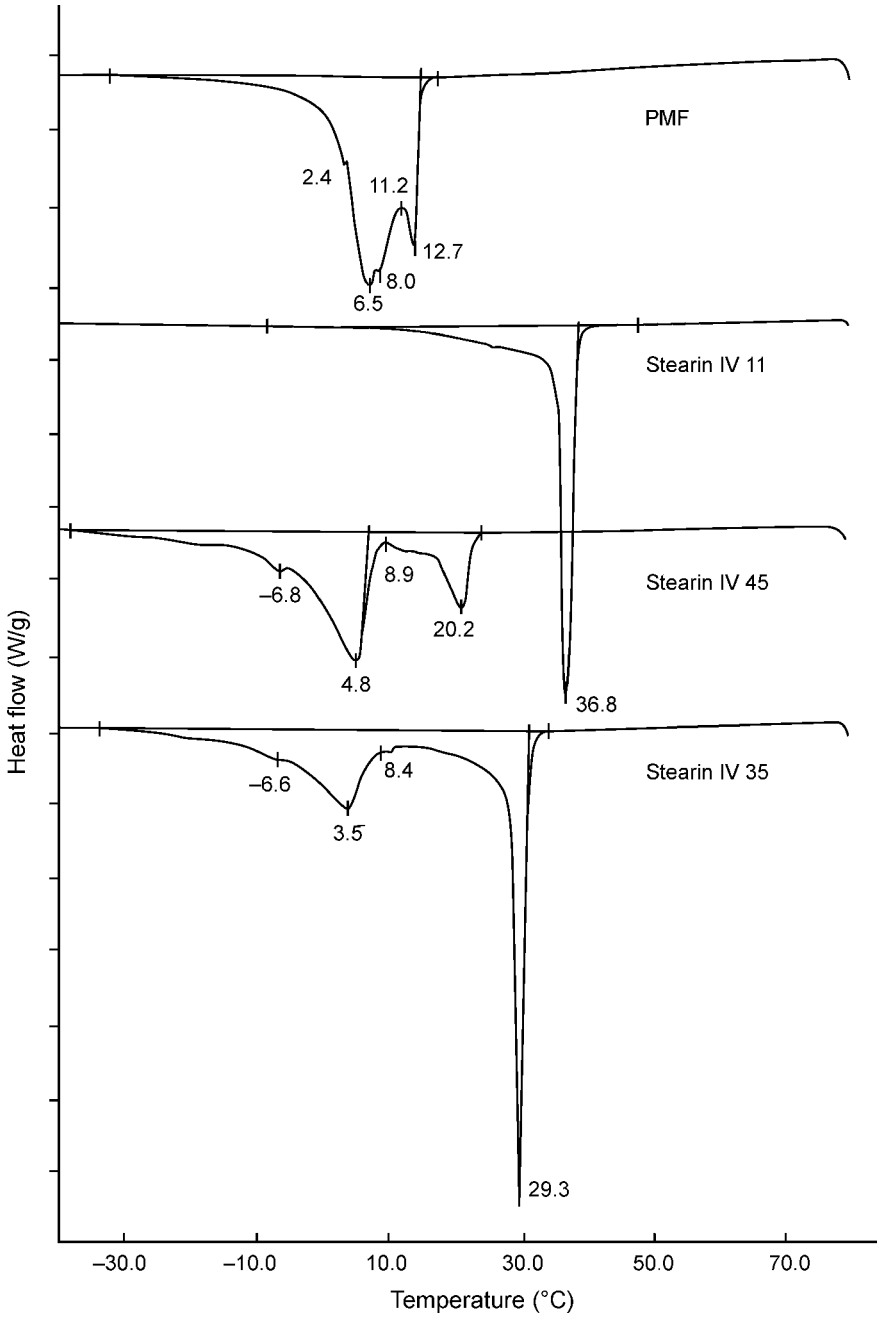

Figure 3.7 Crystallisation thermograms of palm stearins. Sample was melted to 80°C and cooled to −30°C at 5°C/min.

3.4 Minor components of palm oil products

Crude palm oil is rich in minor components such as carotenoids, tocopherols, tocotrienols, sterols, phospholipids, triterpene alcohols, squalene, aliphatic alcohols and aliphatic hydrocarbons (Goh *et al.* 1985). The major components of interest are the carotenes, tocopherols, tocotrienols, sterols and squalene (Table 3.10). Carotenes and tocopherols are antioxidants and stabilise the oil against oxidation. During refining, the bleaching and steam deodorisation processes partially remove some of these valuable components. The amounts retained in the refined oils depend on the conditions of refining.

3.4.1 Carotenes

The dark red-orange colour of oil palm fruit is due to the high concentration of carotenoids and anthocynanins. Crude palm oil, extracted commercially by sterilisation and press, contains 400–1000 ppm of carotenoids, the variation being due to process conditions, species of oil palm and level of oxidation. Carotenoids in palm oil are α-carotene, β-carotene, phytoene, phytofluene, *cis* β-carotene, *cis* α-carotene, δ-carotene, γ-carotene, ζ-carotene, neurosporene, β-zeacarotene, α-zeacarotene and lycopene (Table 3.11) (Yap *et al*. 1991, Jalani *et al*. 1997). The carotenoid profiles of the crude olein and stearin were similar to that of the crude oil. All three contained the core group of compounds: neurosporene, α-, β-, γ-carotenes and lycopene. The major components are α-carotene and β-carotene. The crude oil obtained from the tenera variety of *Elaeis guineensis*, has a carotene content of 500–700 ppm (Table 3.11), while that of *Elaeis oleifera* is about 4600 ppm. The carotene content of hybrid palms,

Table 3.10 Minor components of crude and refined palm oil

Minor components	Crude palm oil (ppm)	Refined oil (ppm)
Carotenoids (Jacobsberg 1974)	500–700	ND
Tocopherols and tocotrienols (Abdul Gapor *et al*. 1981)	600–1000	350–630
Sterols (Rossell *et al.* 1983)	326–527	NA
(Siew 1990)	210–620	70–316
Ubiquinone (Hazura *et al*. 1996)	10–80	10–70
Squalene (Goh and Gee, 1984)	200–500	NA
(Abdul Gapor 2000)	421–979	184–791
Phospholipids (Goh *et al*. 1982)	5–130	NA
Triterpene alcohols (Itoh *et al.* 1973a)	40–80	NA
Methyl sterols (Itoh *et al.* 1973b)	40–80	NA
Aliphatic alcohols (Jacobsberg 1974)	100–200	NA

ND = not detectable.
NA = not available.

Table 3.11 Composition of carotenoids in palm oil, given as % of total carotenoids

Type	*E. guineesis* (Eg)	*E. oleifera* (Eo)	Eg × Eo hybrid
Phytoene	1.27	1.12	1.83
Cis β-Carotene	0.68	0.48	0.38
Phytofluene	0.06	trace	trace
β-Carotene	56.02	54.08	60.53
α-Carotene	35.06	40.38	32.78
Cis-α-Carotene	2.49	2.30	1.37
ζ-Carotene	0.69	0.36	1.13
γ-Carotene	0.33	0.08	0.23
δ-Carotene	0.83	0.09	0.24
Neurosporene	0.29	0.04	0.23
β-Zeacarotene	0.74	0.57	1.03
α-Zeacarotene	0.23	0.43	0.35
Lycopene	1.30	0.07	0.05
(Total ppm)	500–700	4300–4600	1250-1800

Source: Jalani *et al*. 1997, Yap *et al.* 1991.

Table 3.12 Carotene content in palm oil fractions

Type of oil	ppm
Crude palm oil (*E. guineesis*, tenera)	500–700
Crude palm olein	600–760
Crude palm stearin	380–540
Residual oil from fibre	4000–6000
Second-pressed oil	1800–2400

produced from the cross of the two species, lies between those values. Second pressed oils (Table 3.12), obtained by double pressing process of palm fruits, have a much higher concentration of carotenoids (1800–2400 ppm) (Choo 1995). Physically refined oils show no trace of the carotenoids. These are either absorbed onto the bleaching earths or destroyed during thermal treatment. Carotenes preferentially segregate into the more unsaturated olein fraction, leaving little in the stearin fraction. This has important consequences for the oxidative stability of these two fractions.

Crude palm oil is consumed in some countries as a source of vitamin A. To retain these carotenes in the oil, processes are currently available to produce a red palm oil. These are either molecular distillation (Ooi *et al*. 1992) or chemical neutralisation followed by modified refining.

In crude palm oil, the carotene content provides an indication of quality as is shown by the use of DOBI, an index for determining the 'bleachability' of palm oil (Swoboda 1982). As oils from a particular oil palm species will have

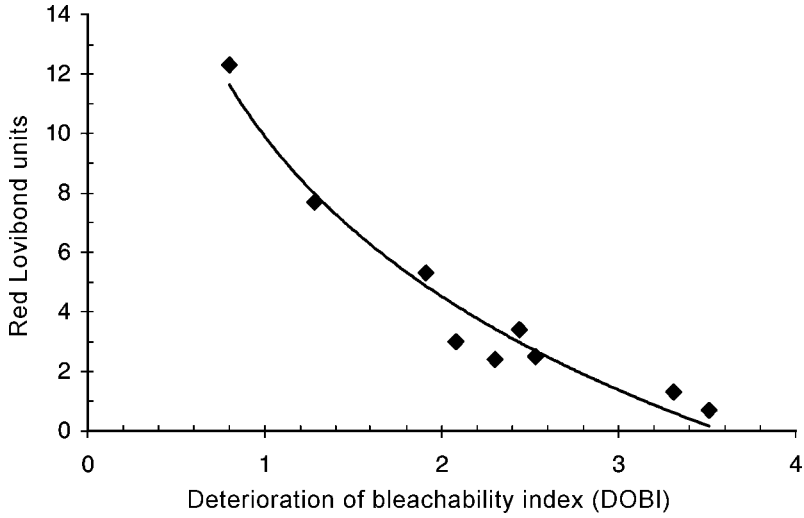

Figure 3.8 Relationship between DOBI and colour of refined oil.

carotene values within a narrow range, any dramatic lowering of carotene is due to degradation of the oil. Good quality oils not only have high carotene values, but also low secondary oxidation characteristics as measured by absorption at 269 nm. The DOBI value, which is the ratio of the absorbance at 446 nm (measurement of carotene) to 269 nm, is well correlated to the colour remaining after refining (Figure 3.8). Oils with low DOBI values, due to low carotenes and high secondary oxidation values, are difficult to refine.

Palm carotenoids provide a source of pro-vitamin A and its orange-red colour is useful as a natural pigment for food preparations, margarines, biscuits and confectionery. Besides the role of providing a source of vitamin, carotenoids are considered to have anti-carcinogenic properties.

3.4.2 Tocopherols and tocotrienols

Crude palm oil, besides being rich in vitamin A, also has a high content of vitamin E, present as tocopherols and tocotrienols (Abdul Gapor 1990; Abdul Gapor *et al.* 1988) (Table 3.13 and Table 3.14), of which 70% are tocotrienols (Hashimoto *et al.* 1980). Crude palm olein has a higher content of tocopherols and tocotrienols. Refined oils retain about 70% of the tocols, the amount varying depending on conditions of refining. Most of the loss occurs at deodorisation, and consequently palm fatty acid distillate (PFAD) has up to five to ten times the level in crude oil and PFAD is a good starting material for recovery of vitamin E. There is considerable interest in the nutritional and physiological properties of vitamin E in palm oil, particularly the tocotrienols. Table 3.14 shows the

Table 3.13 Vitamin E (total tocopherols and tocotrienols) content in palm oil products

Type of oil	Total (ppm)
Crude palm oil[a]	708–1141
Refined palm oil[a]	378–890
Crude palm olein[a]	880–1129
Refined palm olein[a]	559–902
Crude palm stearin[a]	426–552
Refined palm stearin[a]	348–381
Palm oil fatty acid distillate[b]	744–8192
Palm olein fatty acid distillate[b]	1018–7172
Palm stearin fatty acid distillate[b]	162–2408

[a]Abdul Gapor 1990.
[b]Abdul Gapor *et al*. 1988.

Table 3.14 Composition of tocopherols and tocotrienols (% of total) in palm oils and fatty acid distillate

Type of material	α-Tocopherol	α-Tocotrienol	γ-Tocotrienol	δ-Tocotrienol	Total (ppm)
Crude palm oil[a]					
E. guineesis (Eg)	21	23	45	11	600–1000
E. oleifera (Eo)	15	27	54	4	700–1500
Eg × Eo	19	28	42	11	600–1600
Palm fatty acid distillate[b]	21	16	39	24	744–8192

[a]Jalani *et al*. 1997.
[b]Abdul Gapor *et al*. 1988.

composition of tocopherols and tocotrienols in palm oils of different oil palm materials. Most of the vitamin E is in the form of γ-tocotrienols, in contrast to that of other oils where the vitamin E is mainly α-tocopherol. According to Abdul Gapor (1990) the order of antioxidant activities of tocotrienols was γ- > δ- > α-. At 200 ppm, the α-tocotrienol improves oxidative stability by a factor of 6.3. γ-Tocotrienol has twice the antioxidant effect of α-tocotrienol.

Tocotrienols have become a focus of research in recent years because of findings showing high efficacy in protecting against heart related diseases and certain cancers. The tumour protective effect of tocotrienols from palm oil was demonstrated by Nesaretnam and co-workers (1995). This effect was studied *in vitro* on human breast cancer cell lines. A tocotrienol-rich fraction (TRF) inhibited the incorporation of (^{3}H) thymidine into these cells by 50% at a concentration of 180 μg/ml. In contrast, α-tocopherols do not significantly reduce tumour growth at concentrations up to 500 μg/ml. Other evidence that palm vitamin E has anticancer properties comes from work of Guthrie and co-workers (1997) on oestrogen receptor positive MCF-7 human breast cancer cells. Guthrie showed that a combination of tamoxifen with tocotrienols was more

Table 3.15 Sterol content and composition of palm oil products

Type of oil	Cholesterol (ppm)	Campesterol (ppm)	Stigmasterol (ppm)	β-Sitosterol (ppm)	Others* (ppm)	Total sterols (ppm)
Crude palm oil[a]	2.7–13	46.4–150	26.3–65.7	120–369.5	2–21	210–620
Crude palm oil[b]	7–13	90–151	44–66	218–370	2–18	326–527
Refined palm oil[a]	1.2–5.5	15.3–65.4	8.5–36.9	45–198	0–10.5	70–316
Crude palm olein[a]	6.2–7.5	56.7–103.8	29.9–51.0	149–253	24.6–28.1	270–440
Refined palm olein[a]	2.1–2.4	25.6–30.4	12.4–23.3	67.7–11.4	nil–1.2	109–170
Palm stearin[c]	2.7–4.9	20.6–24.2	11.4–11.8	56.7–58.4	2.9–6.0	389–481
Palm fatty acid distillate[d]	11	23	14	52	–	1536–19,811

Source: [a] Siew 1990; [b]Rossell *et al*. 1983; [c]Downes 1982; [d]Abdul Gapor *et al*. 1988 (composition is expressed as percentage of total sterols).
*Mixture of Δ^5-avenasterol, Δ^7-stigmastenol, Δ^7-avenasterol.

effective than either tocotrienols and tamoxifen alone. Komiyama and Yamoka (1993) reported the effectiveness of palm tocotrienols against transplantable mice tumours.

In addition to anticancer effects, tocotrienol-rich fractions of palm oil have hypocholesterolaemic effects in humans and offer protection against heart diseases (Qureshi *et al.* 1991; Serbinova *et al.* 1993). Tocotrienols differ from tocopherols in the degree of saturation of the side chains; the prenyl side chain is considered to be responsible for the differential membrane distribution and metabolism of tocotrienols in comparison to tocopherols. Full investigations into the role and mechanisms of each tocotrienol and their interactions with other minor components, such as carotenoids, in inhibiting cancer development, as well as conferring protection against other age-related diseases, are now important areas of research.

3.4.3 Sterols, squalene and other hydrocarbons

Sterols form a major part of the unsaponifiable fraction of palm oil. The common vegetable oil sterols are also found in palm oil products. These are sitosterol, stigmasterol and campesterol, with cholesterol only a minor component. Crude palm oil contains 210–620 ppm of sterols (Table 3.15) (Siew 1990). Fractionation and refining change the content and composition of the sterols in the oil. Again, the palm fatty acid distillate is a good source of sterols, having 1500–20,000 ppm with an average of 6500 ppm (Abdul Gapor *et al.* 1988).

The C_{30} hydrocarbon squalene is present at about 200–500 ppm in crude palm oil; sesquiterpene (C_{15}) and diterpene (C_{20}) hydrocarbons are present at lower levels. Abdul Gapor and Hazrina (2000) reported squalene as high as 979 ppm in some crude oils and 791 ppm in refined oils. These levels are generally higher than that of other vegetable oils, with the exception of olive oil. Palm fatty acid distillate has 5000 ppm to 8000 ppm of squalene. Crude palm oil also has 10–80 ppm of ubiquinone 10 (Hazura *et al.* 1996).

3.5 Food applications of palm oil products

Palm oil is one of the major oils in the world oils and fats trade and detailed figures are given in Chapter 1. Almost 90% of this oil is used as edible products in many applications, such as cooking/frying oils, margarines, shortenings, vanaspati, speciality fats and spray dried products. A large variety of possible product formulations can be made with either palm oil alone or in combination with palmkernel oil/fractions or with other vegetable oils. Its composition confers oxidative stability, having very little polyunsaturated acid. Being naturally semi-solid in nature, there is little necessity for hydrogenation.

3.5.1 Cooking/frying oil

Palm olein is much used as a cooking oil, domestically and in industrial outlets. Palm oil and its fractions are accepted as frying oils for food products such as snack chips, crackers, cookies, pastries, doughnuts, fries and instant noodles. Frying, being a thermal process, results in rapid deterioration of oil. The oxidative stability of palm oil, olein, and stearin (Table 3.16) is a major advantage of the oils. Palm olein has the longest induction period—44 h at 100°C. Blending less stable vegetable oils with palm olein improves their stability (Teah 1988; Razali and Badri 1993). Improvements are seen in the reduced levels of primary and secondary oxidation products, and formation of fatty acids, volatiles and polymers. In addition, the cloud points of most vegetable oils are raised slightly by blending with palm olein (Table 3.16). Free fatty acid content is one of the parameters used for evaluating the quality of frying oils. During frying, there is less formation of free acids when palm olein is used or blended with other vegetable oils (Teah 1988). Besides this, polymer content is lower, and thus less change in viscosity is observed. Most polyunsaturated oils have to be hydrogenated for use as frying oils to reduce high polymer formation and viscosity increase during frying. An alternative approach to this problem is to blend oils. Zalewski and co-workers (1999) showed that using palm olein (iodine value 62) and rapeseed oil (50:50), or a ternary mixture of palm olein

Table 3.16 Induction period (IP) and cloud points of oils and blends

Oils and blends	Induction period (h)	Cloud point (°C)
Refined palm oil[a]	51.7	–
Refined palm olein	44.0	9.6
Refined palm stearin[a]	55.8	–
Cottonseed	11.1	−3.0
Cottonseed/palm olein	–	5.0
Groundnut	15.0	1.9
Groundnut/palm olein	21.0	2.0
Maize	9.0	−9.5
Maize/palm olein	12.0	−1.9
Olive	11.8	−10.0
Olive/palm olein	–	−10.0
Rapeseed	11.5	−5.0
Rapeseed/palm olein	16.0	0.0
Sesame	8.0	–
Sesame/palm olein	7.0	0.3
Soybean	16.0	−9.0
Soybean/palm olein	19.0	−2.2
Sunflowerseed	6	−9.5
Sunflowerseed/palm olein	7	−2.3

[a]Palm olein was added at 30% in each blend.
Source: Teah 1988.

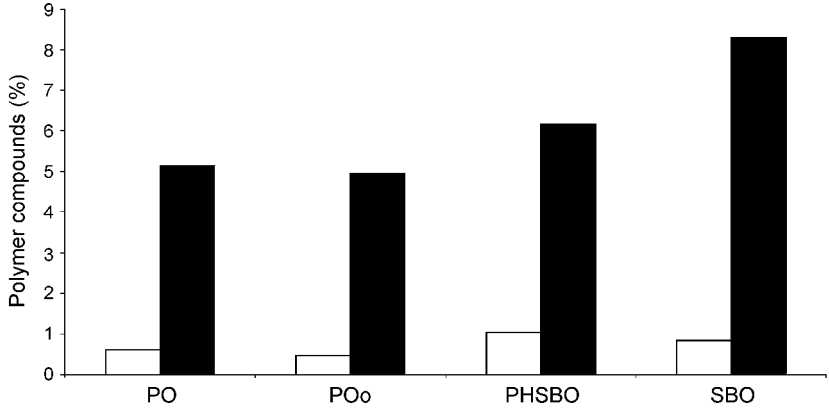

Figure 3.9 Polymer content of some frying oils (Razali and Badri 1993). PO: palm oil; POo: palm olein; PHSBO: partially hydrogenated palm olein; SBO: soyabean oil. Key: □, day 0; ■, 5th day

(iodine value 56), palm stearin (iodine value 48), and rapeseed oil (40:40:20), produced fewer polar compounds than using pure rapeseed oil. Lower anisidine values also indicate that oil stability is better with a higher level of palm oil products. Palm olein blends with rapeseed oil allow for good sensory quality of chips up to six months of storage. A palm olein/sunflower blend has proven to be very successful, as there appears to be a synergistic effect on the stability (Van Twisk and Du Plessis 1997) and on formation of polymer compounds (Figure 3.9) (Razali and Badri 1993). Due to changing consumer demand for healthy foods, the usage of high-oleic oils in frying should grow significantly. Palm olein, especially double-fractionated palm olein, fits Appelqvist's (1997) criteria of 'a healthy frying oil' in having low saturated and polyunsaturated, high monounsaturated and no *trans* acids. A comparison of potato chips fried in olein with those fried in high-oleic sunflower oil showed comparable properties after 16 weeks of storage of the chips (Razali *et al*. 1999).

In temperate countries where palm olein crystallises or turns cloudy, blending with polyunsaturated oils is an easy and simple way to obtain a clear product for the retail supermarkets. The clarity of palm olein depends on its iodine value (Table 3.8) (Nor Aini and Hanirah 1996, 1997). The time that palm olein remains clear at 20°C varies from one day for oils of iodine value of 56 to more than 60 days for double fractionated oils of iodine value 65–67.

3.5.2 Margarines and shortenings

Margarine is a flavoured product containing 80% fat blended with water, and containing vitamins and other ingredients. Initially developed to replace dairy butter, it now appears in a variety of types including regular, whipped, soft-tub, liquid, diet, spreads, low-calorie, bakery and speciality. Today's margarines

incorporate nutritional as well as functional properties and cater for the requirements of different consumers. The properties of margarines depend on the characteristics of the oil forming the major ingredient of the product. The solid fat content of the oil at a range of temperatures is an indicator of the crystallisation properties of the finished product.

Palm oil and its fractions are suitable for margarine production. It is possible to incorporate them into margarine formulations as shown by Teah and co-workers (1994), Noor Lida and co-workers (1997) and Nor Aini and Mohd Suria (2000). Figure 3.10 shows the solid fat content of margarines formulated with mixtures of palm oil and/or palmkernel oil with other vegetable oils. Tub, packet, industrial/bakery and pastry margarines can all be formulated with some palm oil and/or its fractions in the formulation. Domestic margarines in Malaysia are formulated with palm oil/palm olein or palmkernel oil with liquid oil. For table margarines, as much as 50% of palm oil can be used in the fat blend, while for palm olein, up to 60% can be used. Palm stearin, with its high PPP content, is an excellent hard stock for margarines made from liquid oils (DeMan 2000). There are several advantages in using palm stearin as a component for interesterification with liquid oils to yield a good hard stock, such as availability of oil, cheap raw material, and the removal of the need for hydrogenation. The nutritional effects of *trans* acids produced during hydrogenation are a matter of controversy. By interesterification of ternary or binary blends, it is possible to obtain suitable formulations which are free of *trans* fatty acids. In fact many

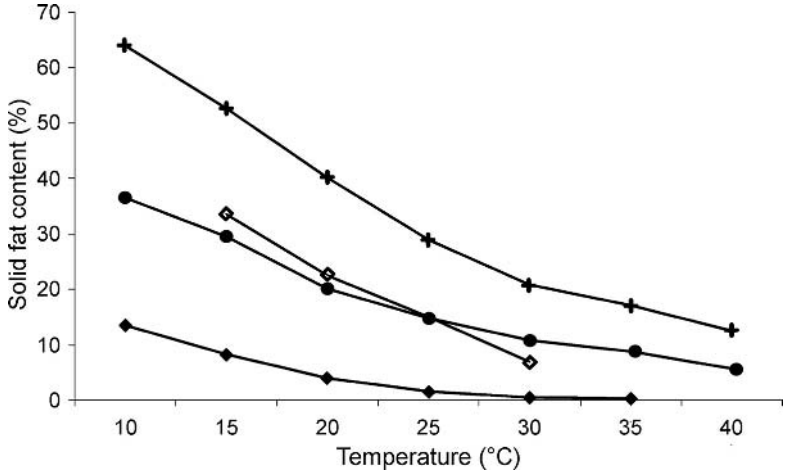

Figure 3.10 Solid fat content of margarine using palm oil products (Noorlida and Mohd Suria 1995). PO: palm oil; POo: palm olein; POs: palm stearin; RSO: rapeseed oil; PKO: palmkernel oil; SBO: soyabean oil; IE: interesterification. Key: —◆—, POo/POs/RSO (40/10/50); —◇—, IE POs/PKO (75/25); —●—, POo/POs/SBO (20/50/30); —+—, PO/POs (10/90).

Table 3.17 SFC for several *trans*-free margarines from palm oil

Blend	PS:PKOo	IE (PS:PKOo)	IE (POo:PKO)	IE (PS:PKOo:SFO)	PS:SBO
Composition	70:30	60:40	70:30	60:20:20	80:20
Slip melting point (°C)	45.5	34.3	33.3	38.5	43.3
SFC (%) wideline NMR					
10°C	56.3	31.8	NA	33.7	69.1
15°C	42.2	23.3	34.6	24.6	57.8
20°C	29.8	15.6	22.7	18.9	46.3
25°C	20.9	10.8	NA	NA	33.6
30°C	16.3	6.3	7.8	7.1	23.9
35°C	11.1	2.4	–	–	17.7
40°C	10.7	–			8.3

Source: Teah *et al*. 1994.

suitable blends can be tailor-made to suit the requirements of the consumers of different countries, using the indigenous oils of those countries along with palm oil and/or its fractions. Interesterified palm stearin (60%) and palmkernel olein (40%) result in a product with suitable properties for margarines (Table 3.17) (Teah *et al*. 1994). With a wide range of palm stearins available, it is possible to make many combinations for stick and soft margarines (Petrauskaite *et al*. 1998). A new palm-based pourable margarine has been formulated by Miskandar and Mohd Suria (1998).

Palm oil is suited for industrial margarines, having 23% solids at 20°C. Palm stearins may also be included in the formulations as shown by Teah (1994) (Table 3.17). Puff pastry margarines, based on palm stearin and palm oil or with palmkernel olein or soyabean oil, have been reported (Teah *et al*. 1982). The basic requirements for puff pastry margarines are the most demanding with regard to crystallisation. The features of a rolled-in margarine are plasticity and firmness.

Palm, palm stearin and also the hydrogenated products tend to be β′ stable (Yap *et al*. 1989a), providing the right crystal polymorph for a smooth texture in margarines. This interesting feature of the fat is utilised in production of margarines using liquid oils. Soft margarines based on hydrogenated palm olein and liquid oils, such as canola and sunflower, can incorporate high proportions of the liquid oil while still retaining the β′ form required (Table 3.18) (DeMan *et al.* 1993). Palm oil in a mixture with hydrogenated canola oil can delay the formation of β crystals from β prone hydrogenated canola oil (D'Souza *et al.* 1991, Yap *et al*. 1989b). The stick margarines, which had β′ form, had a palmitic acid content of approximately 20%. Addition of 10–12% of palm stearin or hydrogenated palm oil to liquid oils is sufficient to stabilise the product in the β′ crystals. It appears that when the higher melting fraction of a fat is comprised of TAGs that are stable in the β′, the entire fat will then crystallise in the same form

Table 3.18 The β′ polymorphic stability of liquid oils containing hydrogenated palm olein

		Drop point (°C)	SFC at 10°C	Polymorphic form after four cycles
Hydrog. olein:SFO				
IV 42.8	30:70	36.5	20.0	β′
IV 37.9	30:70	41.4	23.7	β′
IV 32.0	30:70	44.0	25.5	β′
Hydrog. olein:canola oil				
IV 42.8	40:60	35.8	26.4	β′
IV 37.9	30:70	33.0	19.6	β′
IV 32.0	20:80	30.2	12.8	β′

Source: DeMan *et al.* (1993).

(DeMan *et al.* 1992). Thus it is useful to add small amounts of palm products, especially hard palm stearin, to margarines and shortening formulations.

3.5.3 Shortenings

Shortening was the term used to described the function performed by naturally occurring solid fats, such as lard and butter, in baked foods. It is now generally applied to fat products which can affect the emulsification, lubricity, structure, aeration, flavour and heat-transfer of prepared foods. Palm oil, a semi-solid fat, is highly suited to this purpose and its tendency to form β′ crystals is an advantage as such crystals provide better aeration in batters than β forms. Unlike margarines, shortenings are entirely oils and fats (100%) though some may have small amounts of emulsifiers added. Figure 3.11 shows the solid content of palm oil products which can be incorporated with other oils to be used as shortenings. Blends of soft stearin with palm oil give products with the solid content required of a shortening.

Shortenings made from palm oil products have been studied extensively (Nor Aini *et al.* 1989, 1995; Nor Aini 1988). Softer shortenings are made from palm oil (PO), hydrogenated palm oil (HPO), palm stearin (POs), anhydrous milk fat (AMF) and butterfat (BF) and low melting milkfat fractions (Table 3.19). These shortenings display crystalline structures in the β′ polymorphic form. The yield values of these shortenings vary from 60–1120 g/cm^2 on day 15 to 70–1370 g/cm^2 on day 60. Shortenings based on hydrogenated palm oil are harder, but the plasticity and spreadability can be improved by addition of AMF. Interesterification helps to improve the creaming performances of the shortenings, as post-hardening problems which may be observed in palm based shortenings, are eliminated. Krawczyk and co-workers (1996), in reviewing the technology of low-fat spreads, reiterated the claim that products which are whipped, required 20–25% solid fat crystals, as these determine their creaming power and help to stabilise water droplets in the mixture. Again, large β crystals

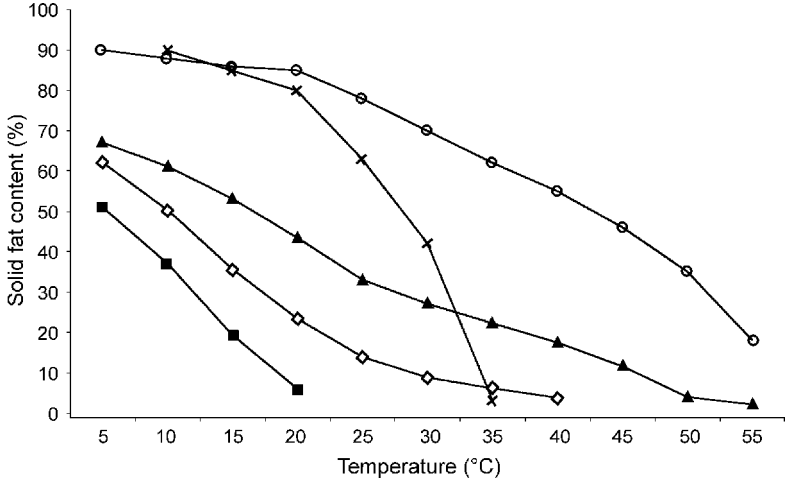

Figure 3.11 Solid fat content of palm oil products. PO: palm oil; POo: palm olein; POs: palm stearin; PMF: palm mid-fraction. Key: —◇—, PO; —■—, POo; —▲—, POs; —✕—, PMF; —○—, POs (hard).

are not desirable as they result in coarse and grainy structures. A suitable formulation for low fat spreads utilising palm in the mixture is shown in Table 3.20 (Krawczyk *et al*. 1996). A high palmitic content was also reported to be good for aeration of fat/sugar mixtures (Nor Aini *et al*. 1989). Blends of palm stearin (20–40%) with palm oil make good pastries for pies, tarts and curry puffs (Nor Aini 1992).

3.5.4 Vanaspati

Vanaspati is an all-purpose fat widely used in the Middle Eastern countries and the Indo–Pakistan subcontinent. It is a substitute of ghee, which is made from butter fat.

Hydrogenated products are readily accepted as suitable oils for the vanaspati industry. The texture of the product varies with different consumers. In India and Pakistan, graininess is a required criterion. Pakistan consumers prefer grainy crystals among liquid oil, unlike the Indian counterparts who prefer their vanaspati to be grainy, yet dry and crumbly. The product melts at 37–39°C, which is a property of palm oil. Palm oil at ambient temperatures has a semi-solid texture like that of vanaspati, and the granular consistency can be obtained through interesterification. Kheiri and Oh (1983) provided details of hydrogenated palm oil products suited for the Indian and Pakistan markets (Table 3.21). Blends of hydrogenated palm olein and palm oil have the consistency of vanaspati. Mixtures of palm stearin and palm oil with melting points up to 40°C are suited for the Middle East countries (Table 3.22).

Table 3.19 Characteristics of shortenings from palm oil products

Shortening	Slip melting point (°C)	Polymorphic form	Days of storage			
			15		60	
			Yield value	Consistency	Yield value	Consistency
PO	38.3 ± 0.4	β′	250	good consistency	300	good consistency
PO:AMF 60:40	37.3 ± 0.1	β′	60	very soft	70	very soft
HPO	41.4 ± 0.1	β′	1120	very firm	1370	very firm
HPO:AMF 80:20	40.3 ± 0.3	β′	880	slightly firm	990	slightly firm
HPO:AMF 60:40	38.4 ± 0.1	β′	640	good consistency	690	good consistency
IEPO	35.7 ± 0.2	β >>> β′	190	slightly soft	220	slightly soft
IEPO:AMF 80:20	33.8 ± 0.3	β >> β′	180	slightly soft	190	slightly soft
POs:AMF 40:60	42.6 ± 0.7	β′ > β	400	good consistency	550	good consistency
POs:SfMF 60:40	43.7 ± 0.2	β′	410	good consistency	1010	very firm
POs:SfMF 40:60	42.9 ± 0.6	β′	370	good consistency	710	slightly firm

Source: Nor Aini *et al.* 1995.

Table 3.20 Low-fat spread formula based on palm and soybean oil

	Composition (by % weight)	
Ingredients	40% fat	25% fat
Water	58.42	64.41
Other ingredients	1.58	10.58
Fat phase	–	–
Soybean oil	20.0	11.51
Hydrogenated soy oil	11.64	7.15
Refined palm oil	7.9	5.65
Distilled monoglyceride	0.35	0.35
Polyglycerol ester	–	0.25
Flavour	0.05	0.05
Antioxidant	0.058	0.038
β-Carotene	0.002	0.002

Source: Krawczyk *et al*. 1996.

Table 3.21 Binary blends of refined palm oil (PO) and hydrogenated palm olein (HPOo)

Composition (%)		Solid fat content (%)						
PO	HPOo	20°C	25°C	30°C	35°C	37°C	40°C	Melting point (°C)
100	0	28.9	19.8	11.1	9.0	–	5.9	37.4
90	10	30.8	20.8	13.0	7.3	5.2	3.6	38.7
80	20	36.1	24.1	15.1	9.5	6.5	3.4	39.5
70	30	40.2	27.3	18.0	11.3	7.8	4.7	39.8
60	40	45.0	30.7	19.5	12.6	9.3	5.1	40.5
50	50	47.9	34.3	22.6	14.7	10.4	5.7	41.3
40	60	51.0	37.3	28.7	15.5	11.2	7.9	41.4
30	70	55.6	40.4	27.2	17.9	13.1	8.2	41.9

Source: Kheiri and Oh (1983).

Table 3.22 Binary blends of refined palm oil (PO) and palm stearin (POs)

Composition (%)		Solid fat content (%)						
PO	POs	20°C	25°C	30°C	35°C	37°C	40°C	Melting point (°C)
100	0	23.0	16.0	9.8	6.9	3.1	3.1	6.3
90	10	26.2	16.9	11.9	9.4	5.6	5.6	38.3
80	20	28.2	18.5	12.2	10.1	6.2	6.2	39.0
70	30	28.7	20.9	13.1	9.5	5.9	5.9	39.5
60	40	30.0	21.7	15.3	10.5	6.8	6.8	40.2
50	50	32.4	23.8	16.5	11.7	8.0	8.0	40.7
40	60	34.0	24.7	17.4	13.4	9.5	9.5	41.5
30	70	36.4	25.1	18.2	15.1	11.5	11.5	42.0

Source: Kheiri and Oh 1983.

Trans-free vanaspati can be formulated using palm stearin with other oils (Table 3.23) (Nor Aini *et al*. 1997). Interesterification allows more palm stearin to be incorporated into the formula. Other *trans*-free formulations are obtained with ternary blends of palm oil/palm stearin/palm olein or palm oil/palm stearin/palm kernel olein (Table 3.24). These products have characteristics similar to those of hydrogenated vanaspati. Formulations for vanaspati may be varied to suit the requirements of different consumers. Incorporation of more or fewer palm oil products in the formulation generally affects the melting point property, which is a limitation for certain countries.

3.5.5 Cocoa butter equivalents (CBE)

These are fats rich in symmetrical disaturated TAGs which behave like cocoa butter in all respects, and are able to mix in all proportions with cocoa butter. The desirable characteristics of cocoa butter are due to the SOS TAGs (S = saturated) which provide suitable melting point and solid fat content to give rapid melt in the mouth and cooling sensations. Palm mid-fraction (PMF), which has high contents of POP, is easily formulated with other SOS fats for chocolate products (Berger 1981). About 70%–80% PMF with 20%–30% shea or sal stearin, or 60%–65% PMF with 20%–30% shea or sal stearin and 15%–20% illipe are suitable for plain and for milk chocolate with 15% milkfat. Compatibility of cocoa butter (CB) and CBE is affected by addition of milkfat and its fractions into the product (Sabariah *et al*. 1998). Eutectic interactions between anhydrous milkfat (AMF), CBE and CB were noticeable due to different polymorphism encountered in these fats.

Cocoa butter-like fats can also be formulated with interesterified oils. Blends suitable for butter cream fillings in biscuits may be formulated from palm stearin/palm kernel olein (25:75) or palm stearin/palm kernel olein/palm kernel oil (25:37.5:37.5) (Noor Lida *et al*. 1997).

3.5.6 Other uses

Other uses of palm oil are in snack foods, biscuits, ice-creams, salad dressings, mayonnaise, and so on. Fat plays a key role in all the above food items and formulations using palm oil products essentially replace some of the oils used traditionally. Oil suitable for ice-creams should be partly solid at 5°C and at −5°C, substantially liquid at 37°C, and have good 'melt' feel characteristics. Palm oil, with a similar solid fat content profile to butterfat, is one such oil with suitable characteristics for ice-cream formulations. Palmkernel oil is also much used in ice cream products.

Salad oils, dressings, and mayonnaise are products used for mixing vegetables, meat and other ingredients together. Mayonnaise contains vegetable oils, acidifying agents and egg yolk. The stability of the oil in the emulsion

Table 3.23 Physical characteristics of vanaspati based on direct and interesterified blends of palm stearin (Pos) with other oils

	Direct blends			Interesterified blends		
Sample	Melting point (°C)	Appearance	Consistency	Melting point (°C)	Appearance	Consistency
POs:SBO						
40:60	41.5	Wet, granular	Soft	35.9	Wet, oily, granular	Very soft
60:40	45.5	Slightly dry, granular	Slightly firm	41.5	Wet, oily, granular	Very soft
80:20	47.7	Dry, granular	Firm	45.6	Wet, oily, granular	Soft
POs:RSO						
40:60	43.6	Wet, granular	Soft	38.7	Wet, oily, smooth	Very soft
60:40	45.9	Slightly dry, granular	Slightly firm	43.4	Wet, granular	Soft
80:20	48.5	Dry, granular	Firm	45.6	Wet, oily, granular	Soft
POs:SFO						
40:60	43.8	Wet, granular	Soft	34.3	Wet, oily, granular	Very soft
60:40	45.3	Dry, granular	Slightly firm	39.3	Wet, oily, granular	Very soft
80:20	48.6	Dry, granular	Firm	45.4	Oily, granular	Soft
Vanaspati	39.0	Dry, granular	Slightly firm	38.5	Granular	Soft

Source: Nor Aini *et al*. 1997.

Table 3.24 Characteristics of vanaspati containing palm oil (PO), palm stearin (POs), palm olein (POo) and palmkernel olein (PKOo)

Sample formulation	Slip melting point (°C)	Softening point (°C)	Dropping point (°C)
PO:POs:POo 80:5:15	37.2	37.7	38.9
PO:POs:POo 80:10:10	39.2	42.2	41.2
PO:POs:POo 60:20:20	42.3	41.9	45.6
PO:POs:POo 40:30:30	46.8	43.2	47.0
PO:POs:PKOo 80:5:15	38.0	39.0	39.7
PO:POs:PKOo 80:10:10	41.2	40.9	41.9
PO:POs:PKOo 60:20:20	47.3	45.6	44.8
PO:POs:PKOo 40:30:30	48.3	46.5	44.9
Commercial sample (vanaspati)	38.5	42.6	42.7

Source: Nor Aini *et al*. 1999.

is important. Salad dressing contains oil, egg yolk, acidifying agents and other ingredients. The salad oils used in these products are usually polyunsaturated oils. Blends of palm olein with polyunsaturated oils provide greater oxidative stability, and keep better. Red palm olein, containing high carotenoids, makes a good salad dressing but is reddish in colour.

3.6 Conclusion

The unique feature of palm oil is its balanced range of saturated and unsaturated fatty acids, which allow the oil to be easily fractionated into products containing more saturated or more unsaturated TAGs. The wide range in composition and properties of palm oil and its fractions allows many possible formulations to be made, incorporating the most suitable fractions in food products. Blending and interesterification are the main processes used to produce oils with properties suitable for margarine, shortening, vanaspati and frying oils, for example. The advantages of using palm oil products include the cheap raw material, ready

availability and the low cost of processing since hydrogenation is not necessary. The high oxidative stability of the oil is partly due to the fatty acid composition, but also to the carotenoids and tocotrienols present. Processing technologies enhance natural pigments, tocopherols and tocotrienols in the refined oils, enabling the creation of products with suitable specifications as required by customers. Future research should lead to oils with higher oleic acid content, and higher carotenoid and tocotrienol levels for the health conscious market. Nutritional research, focused on the beneficial effects of vitamin E and β-carotene, has helped to enhance the perception and use of palm oil as a healthy oil.

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4 Canola/rapeseed oil

Roman Przybylski and Ted Mag

4.1 Introduction

In the past two decades, production of *Brassica* oilseeds has become second only to soybeans as a source of vegetable oil (see Chapter 1). Canola oil (low-erucic acid and low-glucosinolate rapeseed oil) is now held by some to be the best nutritional edible oil available. This oil was developed after significant improvement and modification of the original high-erucic acid rapeseed oil (HEAR). The level of erucic acid has been reduced to below 2% (and usually below 1%) of the total fatty acids. Additionally, the level of glucosinolates in the seed has been lowered to a level below 30 μmol/g, resulting in better quality meal. In this chapter, the origin, composition, properties, and utilization of both canola and HEAR oils for food purposes are discussed.

Oilseed rape species used to produce canola oil and meal are from the *Brassica* genus in the Cruciferae family. They were first cultivated in India almost 4000 years ago. Large-scale planting of rape oilseed was first reported in Europe in the thirteenth century. The *Brassica* species probably evolved from the same common ancestor as wild mustard (*Sinapis*), radish (*Raphanus*) and arrugala (*Eruca*).

Early rapeseed cultivars had high levels of erucic acid in the oil and high levels of glucosinolates in the meal. The presence of these components was considered to be a health concern. The high levels of erucic acid were blamed for producing fatty deposits in the heart, skeletal muscles and adrenals of rodents as well as impairing growth. Plant breeding programs were initiated in Canada, and in 1959 a rapeseed line (Liho) containing low levels of erucic acid was identified. A program of backcrossing and selection was conducted to transfer the low-erucic acid trait into agronomically adapted cultivars. This led to the first low-erucic acid cultivar of *B. napus* (Oro) in 1968 and the first low-erucic acid *B. rapa* cultivar (Span) in 1971. Because of health concerns associated with high levels of erucic acid, by 1974 over 95% of the rapeseed grown in Canada were low-erucic acid varieties.

Glucosinolates were also considered detrimental in rapeseed meal fed to poultry, swine and ruminants. Their hydrolyzed products, isothiocyanates and other sulfur-containing compounds, interfere with the uptake of iodine by the thyroid gland, contribute to liver disease, and reduce growth and weight gain in animals. Consequently, plant breeders realized that if rapeseed meal was to be used in animal feed, the glucosinolate content should be reduced. A Polish line with a low-glucosinolate trait (Bronowski) was identified by Krzymanski in the

late 1950s. Breeding efforts to introduce this trait into low-erucic acid lines, led by Baldur Stefansson at the University of Manitoba, resulted in the release of the world's first low-erucic, low-glucosinolate cultivar of *B. napus*, often called the double zero rapeseed. This was followed in 1977 by the release of the first low-erucic, low-glucosinolate cultivar of *B. rapa* (Candle) by Keith Downey of the National Research Council of Canada in Saskatoon. Approximately 80% of all Canadian rapeseed acreage in 1980 contained the double zero cultivars. The detailed history of the development of canola is described in a booklet entitled 'The Story of Rapeseed in Western Canada' (Saskatchewan Wheat Pool, 1974).

The name canola was registered by the Western Canadian Oilseed Crushers in 1978 and subsequently transferred to the Canola Council of Canada in 1980. The name included those cultivars containing less than 5% erucic acid in the oil and less than 3 mg/g aliphatic glucosinolates in the meal. In 1986 the definition of canola was amended to *B. napus* and *B. rapa* lines with less than 2% erucic acid in the oil and less than 30 μmol/g glucosinolates in the air-dried, oil-free meal and canola oil was added to the GRAS list of food products in the US.

It proved to be more difficult to introduce the low-erucic acid trait into European rapeseed lines because they were primarily of the winter type. This extended the time required to produce each generation, and crosses between spring low-erucic acid rapeseed (LEAR) cultivars and winter lines resulted in undesirable segregates. Nevertheless, the development of European LEAR varieties was accomplished within 15 years. European acreage of rapeseed declined during the 1970s as a result of health concerns. In 1977 the low-erucic acid trait was made mandatory in Europe. Initially the new LEAR cultivars produced lower yields and lower oil content compared to the traditional rapeseed cultivars. Subsequent plant breeding overcame these problems with European production of LEAR increasing substantially by 1984. The other rapeseed growing areas of the world, notably India and China, did not take part in the development and conversion to canola type rapeseed, and HEAR still predominates in these areas.

Canola oil produced in Canada is obtained from genetically modified seeds of *Brassica napus* and *Brassica rapa* (*campestris*). These cultivars, low in erucic acid and glucosinolates, are quite different in chemical, physical and nutritional characteristics from high-erucic acid rapeseed oil. Current Canadian plant breeding programs continue to focus on the development of oils with specific characteristics to meet consumer demands and food manufacturing practices such as lowering the content of saturated fatty acids and designing oils for specific applications.

4.2 Composition

4.2.1 Nature of edible oils and fats

Edible oils and fats are composed primarily of triacylglycerols—esters of glycerol with three molecules of fatty acids. Analysis of canola oils showed the

Table 4.1 Constituents of canola, rapeseed and soybean oils

Component	Canola	Rapeseed	Soybean
Triacylglycerols (%)	94.4–99.1	91.8–99.0	93.0–99.2
Phospholipids (%)			
Crude oil	up to 2.5	up to 3.5	up to 4.0
Water-degummed	up to 0.6	up to 0.8	up to 0.4
Acid-degummed	up to 0.1	–	up to 0.2
Free fatty acids (%)	0.4–1.2	0.5–1.8	0.3–1.0
Unsaponifiables (%)	0.5–1.2	0.5–1.2	0.5–1.6
Tocopherols (ppm)	700–1200	700–1000	1700–2200
Chlorophylls (ppm)	5–50	5–55	Trace
Sulfur (ppm)	3–25	5–35	Nil

Adapted from Mag 1990 and Ying and DeMan 1989.

triacylglycerol levels to be 94.4–99.1% of the total lipid (Mag 1990). The typical composition of canola, rapeseed and soybean oils is presented in Table 4.1.

4.2.2 Fatty acid composition of canola oil

The stigma of the erucic acid (22:1 *n*-9) in rapeseed oil has lingered, despite firm evidence that this fatty acid is more of a threat to rats than to humans. It is sufficient to say that the discovery of chain-shortening of erucic acid to oleic acid by peroxisomes was a fundamental breakthrough in the understanding of fatty acid metabolism in the past few decades. Once in the oleic acid form, the erucic acid residue is as readily catabolized by mitochondria as are palmitic and other fatty acids (Ackman 1990). The fall in the level of erucic acid in rapeseed oil resulted in a marked increase in C_{18} acids and they make up around 95% of all fatty acids present in canola oil (Table 4.2).

Plant breeders have also developed canola oil with the linolenic acid content reduced to 2% (Scarth *et al*. 1988) (Table 4.2). The storage stability of this oil showed improvement compared to regular canola oil (Przybylski *et al*. 1993b). Frying performance of this oil was improved along with better storage stability of fried products such as French fries and potato chips (Petukhov *et al*. 1999; Warner and Mounts 1993). Canola has been further genetically modified to produce oil with oleic acid content raised from 60% to 85% (Wong 1991), but field production of this oil showed that the very high content of oleic acid was hard to reproduce. The fatty acid composition of the field-produced oil is presented in Table 4.2. High-oleic acid canola oil resembles the composition of olive oil more closely than that of the regular canola oil. This oil showed improved frying stability and produced better quality fried potato chips than regular canola oil (Petukhov *et al*. 1999). Warner and Mounts (1993) found that up to 2% of linolenic acid is required in frying oils to form positive characteristic flavour in fried foods. This is due to the formation of those oxidation products from linolenic acid which are major factors in the formation of the fried food flavour.

Table 4.2 Comparison of major fatty acids in some vegetable oils (w/w%)

Fatty acid	Canola	HEAR	LLCAN	HOCAN	LTCAN	GLCO	Llflax	Soybean	SUN
10:0	–	–	–	–	0.1	–	–	–	–
12:0	–	–	–	–	38.8	–	–	–	–
14:0	0.1	–	0.1	0.1	4.1	0.1	0.1	0.1	–
16:0	3.6	4.0	3.9	3.4	2.7	4.2	6.4	10.8	6.2
18:0	1.5	1.0	1.3	2.5	1.6	3.7	4.1	4.0	4.7
20:0	0.6	1.0	0.6	0.9	0.4	1.0	0.1	–	0.2
22:0	0.3	0.8	0.4	0.5	0.2	0.5	0.1	–	0.1
24:0	0.2	0.3	0.3	0.3	0.2	0.2	0.1	–	0.1
Saturated	6.3	7.1	6.6	7.7	48.1	9.9	10.9	14.9	11.3
16:1	0.2	0.3	0.2	0.2	0.2	0.2	0.1	0.3	0.2
18:1	61.6	14.8	61.4	77.8	32.8	24.4	16.9	23.8	20.4
20:1	1.4	10.0	1.5	1.6	0.8	0.8	0.1	0.2	–
22:1	0.2	45.1	0.1	0.1	0.5	0.1	–	–	–
MUFA	62.4	69.7	63.1	79.9	34.3	25.5	17.2	24.3	20.2
18:2*n*-6	21.7	14.1	28.1	9.8	11.3	26.1	70.1	53.3	68.8
18:3*n*-3	9.6	9.1	2.1	2.6	6.3	1.3	1.8	7.6	–
18:3*n*-6	–	1.0	–	–	–	37.2	–	–	–
PUFA	31.3	23.2	30.2	12.4	17.6	64.6	71.9	60.8	68.8

Abbreviations: LLCAN – low-linolenic acid canola oil; HOCAN – high-oleic acid canola oil; GLCO – canola oil with gamma linolenic acid; LLFlax – flaxseed oil with reduced content of linolenic acid; LTCAN – canola oil with high content of lauric acid; MUFA – monounsaturated fatty acids; PUFA – polyunsaturated fatty acids.
Adapted from Ackman 1990, Vecchia 1996 and Tso *et al*. 2001.

Recently canola oil with a high content of lauric acid (39%) was developed to be used in confectionery coatings, coffee whiteners, whipped toppings and center-filling fats (Table 4.2). Further, canola oil with 40% of stearic acid is available to be used as replacement for hydrogenated fats in bread and bakery markets (Vecchia 1996). Another canola oil containing approximately 10% of palmitic acid for improved crystallization properties has been developed and canola oil for the health food market containing up to 40% of γ-linolenic acid is also available (Tso *et al.* 2001).

4.2.3 Minor fatty acids

Minor acids present in oils often differ from the major components by the location of the double bond. Generally these acids are present in canola oil in the 0.01–0.1% range, except for 16:1*n*-7 which is around 0.3%. Most of these minor fatty acids are from the *n*-7 series, rather than the more common *n*-9 isomers (Ackman 1990). A similar series of minor fatty acids was found in *B. rapa* variety Candle (Sebedio and Ackman 1981). Conjugated 18:2 fatty acids have also been found in canola oils. Some of these acids are artefacts of refining and deodorization, although some were also observed as natural components in

several oil seeds. The refining process itself is a source of artefact fatty acids due to the isomerization of one or more of the *cis* double bonds of linolenic acid. These *trans* isomers can be found in any oil containing linolenic acid after refining and deodorization, accounting for 1% or more of the parent acid (Ackman 1990; Wolff 1993).

Canola oil is the only known edible oil containing one or more fatty acid with a sulfur atom as the integral part of the molecule. The structure of the proposed molecule of this fatty acid suggests the possibility of the formation or presence of many isomers (Wijesundera and Ackman 1988).

In the sediment from industrial winterization, additional minor fatty acids and alcohols with 26 to 32 carbon atoms in the chain have been found in waxes and triacylglycerols (Przybylski *et al.* 1993a). Most of these compounds are extracted from the seed coat and can initiate sediment formation in canola oil (Hu *et al.* 1994).

4.2.4 Triacylglycerols

Triacylglycerols (TAG) are the most abundant lipid class found in canola oil. The combination of fatty acids on the glycerol moiety lead to a complex mixture with n^3 possible molecular species, where n is the number of fatty acids present in the oil.

The TAG molecular species profile represents a key to understanding the physical characteristics of the oil and also is a unique means of identification, which has been used in various instances (Rezanka and Mares 1991). The position of fatty acids on the glycerol molecule was originally found for HEAR oil to be based on saturation. Long chain acids (C_{20}–C_{24}) and saturated fatty acids are placed in the *sn*-1 and *sn*-3 positions by enzyme-controlled acylation, while unsaturated C_{18} acids, especially linoleic and linolenic, are incorporated in the *sn*-2 position (Kallio and Currie 1993; Ackman 1983). The composition of the glycerol esters in modified canola oils is presented in Table 4.3. As can easily be predicted, in high-oleic acid canola oil the most abundant triacylglycerol was triolein, while in regular canola oil four triacylglycerols were detected at almost equal amounts, namely: oleo-dilinolein, linoleo-dilinolein, triolein and linoleo-diolein.

Jáky and Kurnik (1981) investigated the concentration of linoleic acid in the *sn*-1,3 and *sn*-2 positions. They found that in HEAR oil at least 95% of the linoleic acid was concentrated in the *sn*-2 position, whereas in canola oil only 54% was in this position. The increased amounts of linoleic acid in canola oil replaced the erucic acid in the *sn*-1,3 position. Surprisingly, Kallio and Currie (1993) found that triacylglycerols with acyl carbon number (ACN) 54 and two double bonds (54:2) consisted of glycerol esters where stearic acid was present predominantly in the *sn*-2 position. Triacylglycerols with saturated acids in this position usually have a higher melting point, poor solubility, and can

Table 4.3 Composition of major triacylglycerols of canola oils (%)

Triacylglycerols	Canola (CO)	LLCO	HOCO
LnLO	7.6	1.7	1.5
LLO	8.6	11.0	1.1
LnOO	10.4	2.6	8.6
LnOP	2.1	0.5	1.1
LOO	22.5	28.4	12.7
LOP	5.7	4.2	2.2
OOO	22.4	32.8	49.5
POO	4.6	4.8	7.7
SOO	2.6	2.4	5.0
PPP	0.1	1.4	2.8
LLP	1.4	1.1	0.8
LOS	1.6	1.9	1.0
LLL	1.3	1.6	0.2
LnLL	1.4	0.0	0.3
LnLnO	1.7	0.4	0.1
Others	6.0	5.2	5.4

Abbreviations: LLCO – low-linolenic canola oil; HOCO – high-oleic canola oil; Ln – linolenic; L – linoleic; O – oleic; S – stearic; P – palmitic; Others – group of 15 triacylglycerols with contribution below 1% each. Symbols such as POS (etc) represent all glycerol ester containing these three acyl chains. Adapted from Kallio and Currie 1993.

cause problems with digestibility. Additionally, high melting triacylglycerols can stimulate/initiate sediment formation and affect the clarity of the oil (Liu *et al*. 1993).

4.2.5 Polar lipids

Sosulski and co-workers (1981) examined two classes of polar lipids (PL), the phospholipids and glycolipids, in several rapeseed cultivars including a low-erucic acid winter cultivar grown in Poland and found that phospholipids the major part (3.6% of the oil) of the total polar lipids while glycolipids contributed only 0.9%. A more recent study by Przybylski and Eskin (1991) reported changes in phospholipids during canola oil processing. Their data are presented in Table 4.4.

Significant amounts of phosphatidic acid (PA) are formed during processing as a result of hydrolysis of other phospholipids. This can be explained as the effect of phospholipases and hydrothermal treatment during the conditioning of flaked seeds. Cmolik and co-workers (1987) observed an increase in the amount of phospholipids from 0.5% to 15% during conditioning of seed flakes. It was reported that hydratable phospholipids such as the phosphatidylcholines (PC) and phosphatidylethanolamines (PE) assist the removal of non-hydratable phospholipids. Phosphatidylinositol (PI) and PA are considered to be

Table 4.4 Changes in phospholipids in canola oil during processing (%)

Oil sample	Phosphorus (mg/kg)	PC	PE	PI	PA	PS
Solvent	529.0	31.2	18.8	19.8	21.6	3.1
Expeller	242.3	34.3	16.1	18.7	20.3	4.5
Degummed	12.2	2.8	10.8	28.9	38.4	14.6

Abbreviations: PC – phosphatidylcholine; PE – phosphatidylethanolamine; PI – phosphatidylinositol; PA – phosphatidic acid; PS – phosphatidylserine.
Adapted from Przybylski and Eskin 1991.

Table 4.5 Fatty acid composition of phospholipids (w/w%)

Phospholipid	16:0	16:1	18:0	18:1	18:2	18:3	20:1
Phosphatidylcholine	8.7	0.8	1.2	55.8	30.9	1.9	0.5
Phosphatidylinositol	21.8	0.8	1.9	33.6	38.1	3.6	–
Phosphatidylethanolamine	17.7	1.8	2.0	47.7	27.3	2.7	0.5

Adapted from Sosulski *et al.* 1981 and Smiles *et al*. 1988.

non-hydratable phospholipids. These are difficult to remove during degumming. Phosphoric acid is the most effective degumming agent in terms of reducing the levels of lysophosphatidylethanolamine. Use of acids for degumming also remove the majority of iron from the oil. It should be noted that in practice, canola oil phospholipids are reduced to concentrations below 0.1% using aqueous solutions of citric acid and water (Mag *et al.* 1987). Lecithins (crude phospholipids), obtained by degumming canola oil using only water, form more stable oil in water emulsions than lecithin obtained from degumming with the acids (Smiles *et al.* 1989).

Sosulski and co-workers (1981) and Smiles and co-workers (1988) examined the fatty acid composition of the individual phospholipids in the LEAR variety from winter rapeseed cultivars (Table 4.5).

Phosphatidylcholine contained the highest amount of unsaturated fatty acids, mostly oleic and linoleic acids. The other two principal phospholipids were rich in palmitic, linoleic and linolenic acids. The presence of highly unsaturated fatty acids in phospholipids is important as these are prone to oxidation and can cause accelerated deterioration of the oil. It was also reported that phospholipids have a tendency to complex heavy metals and these complexes are stable catalysts which can initiate and stimulate oxidation (Smouse 1994).

4.2.6 Tocopherols

The main components of unsaponifiables in vegetable oils are tocopherols and sterols, present in different amounts in vegetable oils. Tocopherols are known to be very efficient natural antioxidants. Their amount in the plant is probably

related to the content of unsaturated fatty acids. Canola oil contains relatively high levels of tocopherols. The different tocopherols have different antioxidant activity *in vitro* and *in vivo*. In the food system the antioxidant activity of the tocopherol isomers decreases in the following order: $\delta > \gamma > \beta > \alpha$ (Kamal-Eldin and Appelqvist 1996). Tocopherols are about 250 times more effective than BHT (Burton and Ingold 1989). Lipid peroxy radicals react with tocopherols several orders of magnitude faster than with other lipids. A single molecule of tocopherol can protect about 10^3 to 10^6 molecules of polyunsaturated fatty acids (PUFA) in the living cell. This explains why the ratio of tocopherols to PUFA in the cells is usually 1:500 and still sufficient protection is provided (Patterson 1981). Though less potent than carotenoids, these components are also effective as singlet oxygen quenchers. A single molecule of tocopherol can react with up to 120 molecules of singlet oxygen (Bowry and Stocker 1993). The high potency of tocopherols as antioxidants and quenchers arises from their ability to be transformed from the oxidized form back into the active structure by other molecules, such as ascorbic acid and glutathione (Tapel 1968).

Plastochromanol-8 is a derivative of γ-tocotrienol which has a longer side chain. This compound was detected in canola and flax oils and its antioxidative activity was established to be similar to α-tocopherol (Zambiazi 1997).

The composition of tocopherols in some common vegetable oils compared to canola oil is summarized in Table 4.6.

Canola oil contains mostly α- and γ-tocopherol, with the amount of the latter twofold higher. The content of tocopherols in refined, bleached and deodorized (RBD) oils is reduced by processing, mainly by extraction, refining and deodorization. The lowest content of tocopherols was found in cold pressed canola oil. However, when the temperature of pressing was increased, the amount of

Table 4.6 Tocopherols in selected vegetable oils (mg/kg)

Oil	α	β	γ	δ	P-8	Total
HEAR	268	–	426	–	97	790
Canola	272	–	423	–	75	770
LLCanola	150	–	314	7	47	517
HOCanola	226	–	202	3	42	473
HOLLCanola	286	–	607	8	83	983
Soybean	116	34	737	275	–	1162
Sunflower	613	17	19	–	–	649
Corn	134	18	412	39	–	603
LLFlax	26	–	213	9	130	377

Abbreviations: HEAR – high-erucic acid rapeseed; LLCanola – canola oil with low content of linolenic acid; HOCanola – canola oil with high content of oleic acid; LLFlax – flax oil with low content of linolenic acid; P-8 – Plastochromanol-8.
Adapted from Zambiazi 1997, Normand 1998.

Table 4.7 Fatty acid composition of esterified sterols in canola oil

	Contribution (%)	
Fatty acid	Sterol esters	Canola oil
14:0	3.1	0.1
16:0	17.5	3.6
18:0	18.4	1.5
18:1	30.9	60.2
18:2	20.5	21.6
18:3	7.6	9.6
20:0	0.8	0.4
22:1	1.2	0.2

Adapted from Gordon and Miller 1997.

tocopherols in oil doubled. Solvent extracted oils contain about the same level of tocopherols as hot pressed oils. The largest portion of these compounds is removed during the deodorization step in oil processing (Willner 1997).

4.2.7 Sterols

Sterols are present in canola oil as free sterols and esterified sterols in equal amounts (Ackman 1983; Evershed *et al.* 1987). The fatty acid composition of esterified sterols fraction in canola oil in Table 4.7 is presented.

The fatty acid distribution in esterified sterols differs from that of canola oil: the sterol esters contain higher levels of palmitic and stearic acids. In canola oil, sitosterol and campesterol are equally distributed in the esterified and free sterol fractions. Twice the amount of brassicasterol was found in free sterols than in esterified sterols. The total amount of sterols in rapeseed and canola oils ranges from 0.7 to 1.0%.

The composition of major sterols in common vegetable oils is presented in Table 4.8. Brassicasterol is a major sterol in rapeseed and canola oils and as it is unique to brassica oils it is often used to detect adulteration of other oils with rapeseed/canola oils (Strocchi 1987; Ackman 1990). Sterols are affected by processing and about 40% of these components can be removed from the oil during deodorization. Refining also causes changes in the chemical structure of sterols (Kochar 1983; Marchio *et al*. 1987).

Since the structure of phytosterols resembles that of cholesterol, these compounds may be involved in similar oxidative reactions. Recently, Przybylski and Eskin (1991) found some oxidation products formed from plant sterols during the storage of fried food products. Similar oxidation products were found in soybean oil and wheat flour (Nourooz-Zadeh and Appelqvist 1992). Because of health concerns associated with cholesterol oxidation products, the potential health risks of phytosterol oxidation products are now receiving serious attention.

Table 4.8 Proportions of major sterols in selected vegetable oils (%)

Sterol	HEAR	CAN	LLCAN	HOCAN	HOLLCAN	SOY	SUN	Corn
Cholesterol	0.4	0.1	0.1	0.1	0.1	0.3	0.1	0.1
Brassicasterol	13.2	13.8	12.2	10.8	16.2	–	–	–
Campesterol	34.4	27.6	31.2	33.9	28.8	18.1	7.5	17.2
Stigmasterol	0.3	0.5	0.2	0.8	0.1	15.2	7.5	6.3
β-Sitosterol	47.9	52.3	51.3	48.7	50.9	54.1	58.2	60.3
Δ^5-Avenasterol	2.1	1.9	1.9	1.8	2.1	2.5	4.0	10.5
Δ^7-Avenasterol	1.6	1.1	1.1	1.9	0.8	2.0	4.0	1.1
Δ^7-Stigmasterol	2.1	2.3	2.1	2.1	2.3	1.4	7.1	1.8
Total (g/kg)	8.8	6.9	6.3	7.1	6.9	4.6	4.1	9.7
Esterified (g/kg)	4.5	4.2	4.0	4.4	4.2	5.8	2.1	5.6

Adapted from Ackman 1990, Strocchi 1987, Zambiazi 1997, and Gordon and Miller 1997.
Abbreviations as in Table 4.2.

Table 4.9 Chlorophyll pigments in canola oil during processing (mg/kg)

Oil after	Chlor *a*	Pheo *a*	Pheo *b*	Pyro *a*	Pyro *b*
Expeller	6.27	4.48	1.79	5.37	0.67
Extraction	1.88	3.31	1.34	16.57	3.13
Expeller + extraction	1.79	5.55	1.34	9.76	1.43
Degumming	0.27	7.16	1.07	9.40	1.84
Alkaline refining	0.22	6.27	1.12	9.13	1.79
Bleaching	–	0.56	0.32	0.21	0.25

Abbreviations: Chlor = chlorophyll; Pheo = pheophytin; Pyro = pyropheophytin.
Adapted from Suzuki and Nishioka 1993.

4.2.8 Pigments

Pigments present in canola cause undesirable colour in the oil. They promote photo-oxidation as well as inhibit catalysts used for hydrogenation. Chlorophylls without phytol, such as chlorophyllides and pheophorbides, may have nutritional effects because of their photo-toxicity which may be followed by photosensitive dermatitis (Endo *et al.* 1992). A bleaching step is necessary during oil processing to remove chlorophyll, chlorophyll derivatives, and other colour bodies. Changes in chlorophylls during canola oil processing are summarized in Table 4.9.

During processing chlorophyll completely decomposes to derivatives that are more difficult to remove during bleaching. This necessitates the use of higher amounts of activated bleaching earth to achieve complete removal of all chlorophyll derivatives (Suzuki and Nishioka 1993). The type and content of chlorophylls and their derivatives in the seed are the main factors defining the quality of extracted canola oil, and have an effect on the quality of the processed oil. The composition and content of these pigments is related to the maturity of the seed (Table 4.10). In fully matured seed, the amount of

Table 4.10 Changes during canola seed maturation (mg/kg) in composition and content of chlorophylls

	Time to maturity (days)					
Chlorophylls	35	27	20	14	6	0
Chlorophyll a	19.5	23.4	27.2	58.7	41.9	82.4
Chlorophyll b	22.2	22.1	15.8	27.3	54.1	17.1
Pheophytin a	43.1	39.8	40.9	10.1	1.1	0.0
Pheophytin b	8.5	7.4	11.3	2.0	0.0	0.0
Pheophorbides a	2.2	1.7	0.6	1.5	0.0	0.0
Pyropheophytin	1.2	2.3	2.5	0.0	0.0	0.0
Methylpheophorbide	3.2	3.5	1.8	0.5	3.0	0.5
Total amount (mg/kg)	1239	906	463	48	8	4

Adapted from Ward *et al*. 1994.

chlorophylls observed was only 4 mg/kg, while in physiologically matured seed, 35 days before maturity, an amount 1239 mg/kg was found. At maturity, only chlorophyll a and b were present while all possible isomers/derivatives were observed at other stages of maturation (Table 4.10).

In addition to chlorophyll pigments, carotenoids were also found in canola oil. The content of carotenoids in crude canola oil was reported to be around 130 ppm with 90% xanthophylls and 10% of carotenes. During refining and bleaching, the amount of carotenoids was reduced to 10 ppm (Drozdowski *et al*. 1987).

4.2.9 Trace elements

The proposed Codex standard for edible low-erucic acid rapeseed gives the maximum levels permitted for iron, copper, lead and arsenic. While these metals are found in other edible oils and are present naturally in the seed, nevertheless further quantities can also be introduced during handling and processing. Diosady and co-workers (1983) and Elson and co-workers (1979) examined the effect of processing on trace elements in canola oils. It is evident from the data in Table 4.11 that processing reduces the amount of toxic and damaging trace elements, particularly lead, iron and sulfur. Phosphorus and calcium form salts which are insoluble in the oil and can be readily removed during the degumming process.

Sulfur in canola oil is in the form of organic compounds as the decomposition products of glucosinolates. Although these sulfur components occur in trace quantities, they poison catalysts used for hydrogenation as well as giving a characteristic odour to the oil. Recent developments in analytical methods for sulfur determination revealed that soybean, sunflower and even coconut oils all contain sulfur at the level of 2–10 mg/kg. Only *Brassica* oils contain significant quantities of divalent sulfur components. Crude canola oils may contain 15–35 mg/kg of sulfur, while in RBD canola oils the amount of

Table 4.11 Content of mineral elements in canola oils (mg/kg)

Oil sample	Phosphorus	Iron	Calcium	Sulfur	Zinc	Lead
Crude oil	1190.0	3.52	296.0	6.5	2.4	0.24
Degummed with water (WDG)	222.0	1.32	169.0	1.2	2.1	–
Phosphoric acid (PDG)	117.2	0.63	34.8	1.5	–	–
Bleached						
WDG	0.21	0.23	5.6	–	–	–
PDG	0.19	0.59	4.1	0.87	–	–
Deodorized						
WDG	0.25	–	–	0.25	–	0.07
PDG	0.22	–	–	0.38		

Adapted from Diosady *et al.* 1983 and Elson *et al.* 1979.

sulfur compounds is reduced to 9 mg/kg or lower (Wijesundera *et al*. 1988). Sulfur components may also improve the stability of the oil. Some of these components can act as antioxidants and protect the oil from autoxidation by complexing hydroperoxy radicals with the sulfur to form stable compounds. These compounds can also inactivate catalysts involved in oxidative processes, such as metals (Barnard *et al*. 1958).

4.2.10 Commercial crude oil, refined and deodorized oil

Typical chemical composition of crude, refined and deodorized canola oils is presented in Table 4.12. The deodorized oil data represents the oil quality as it is used as a food ingredient. The data are based on Canadian experience.

Table 4.12 Typical chemical analysis data of crude and refined, bleached and deodorized (RBD) canola oil

Parameter	Crude oil	RBD
Free fatty acids (%)	0.3–1.2	0.03
Phosphorus (mg/kg)	300–500	<2
Water degummed	120–200	–
Acid-water degummed	10–40	–
Chlorophyll (mg/kg)	4–30	<0.025
Sulfur (mg/kg)	2–15	<1
Iron (mg/kg)	0.5–1.5	<0.2
Copper (mg/kg)	<0.2	<0.02
Nickel (mg/kg)	–	<0.3
Peroxide value (me/kg)	0.5–3.0	0 (freshly deodorized)
Anisidine value	1–3	<2
Colour, Lovibond	–	<1.5 Red/10 Yellow
Moisture (%)	<0.3	–
Flavour	–	bland

Adapted from T. Mag (unpublished data).

The values for crude oil compare closely with those of other commercial oils, such as soybean oil, produced according to good extraction practice. An exception is the presence of chlorophylls and sulfur compounds that can be higher in canola oil than in most other commodity oils. The deodorized oil data reflect good refining practice and are similar to the data obtained with other deodorized commodity oils processed for food applications.

4.2.11 Oxidative stability

The stability of canola oil is limited mostly by the presence of linolenic acid, chlorophyll and its decomposition products and other minor components with high chemical reactivity, such as trace amounts of fatty acids with more than three double bonds. These highly unsaturated fatty acids can be formed during refining and bleaching (Chapman *et al*. 1994). The presence of 7–11% of linolenic acid in the triacylglycerols of canola oil places it in a similar category to soybean oil with respect to flavour and oxidative stability. The deterioration of flavour as the result of auto- and photo-oxidation of unsaturated fatty acids in oils and fats is referred to as oxidative rancidity.

The solubility of oxygen in oil is about 3–5 times greater than in water. The amount of oxygen present in oil, dissolved during manipulation, is sufficient to oxidize the oil to a peroxide value of around 10 (Przybylski and Eskin 1988; Labuza 1971).

The rate of oxidation of fats and oils is affected by the oxygen partial pressure, access of oxygen, the degree of unsaturation of fatty acids, and the presence of light, heat, antioxidants and pro-oxidants such as copper, iron, and pigments. The best stability of oil was achieved when the presence of iron and copper was below 0.1 and 0.02 ppm, respectively (Smouse 1994).

The degradation of oils and fats due to light exposure is primarily a photo-catalyzed oxidation. During photo-oxidation, singlet oxygen is generated by transformation of light energy to a sensitizer which activates oxygen. Singlet oxygen is an extremely reactive specie of oxygen—1500 times more reactive than normal oxygen—and reacts with double bonds of unsaturated fatty acids to form peroxides or free radicals. Typical photosensitizers are chlorophylls and their decomposition products formed during maturation of seed and processing, heme compounds, and polycyclic aromatic hydrocarbons (Smouse 1994). It has been found that chlorophyll degradation products are more active as photosensitizers than chlorophyll itself (Usuki *et al*. 1984).

4.3 Physical and chemical properties

The properties of canola oil are governed by components present in the oil and described by the general parameters for vegetable fats and oils. Selected physical properties for canola oil in comparison to HEAR oil are shown in Table 4.13.

Table 4.13 Some physical properties of canola and HEAR oil

Parameter	Canola	HEAR
Relative density (g/cm^3; 20°C/water at 20°C)	0.914–0.917	0.907–0.911
Refractive index (n_D 40°C)	1.465–1.467	1.465–1.469
Crismer value	67–70	80–82
Viscosity (kinematic at 20°C, mm^2/sec)	78.2	84.6
Cold test (15 h at 4°C)	Passed	Passed
Smoke point (°C)	220–230	226–234
Flash point, open cup (°C)	275–290	278–282
Specific heat (J/g at 20°C)	1.910–1.916	1.900–1.911
Saponification number	188–192	168–181
Iodine value	110–126	97–108

Abbreviations: HEAR – High-erucic acid rapeseed oil.

4.3.1 Relative density

Typical values for the specific gravity of canola oil are presented in Table 4.13. Ackman and Eaton (1977) indicated that a different ratio between eicosenoic (20:1) and C_{18} polyunsaturated fatty acids could be a major factor in changing the relative density of canola oil. Noureddini and co-workers (1992a) described the relationship between temperature and density of vegetable oils including canola. As for other liquids, the density for vegetable oils is temperature-dependent and decreases in value when the temperature increases. The same authors also developed an equation to calculate density from the fatty acids composition.

4.3.2 Viscosity

Viscosity measures relative thickness or resistance of oil to flow. The viscosity of refined, bleached and deodorized (RBD) canola oil is higher than for soybean oil. Lang and co-workers (1992) and Noureddin and co-workers (1992b) found that the viscosity of canola and other vegetable oils was affected by temperature, similarly to other liquids. They derived an equation to calculate viscosity in the temperature range from 4–100°C. The viscosity of HEAR oil is significantly higher than that of canola oil.

4.3.3 Smoke and flash point

The smoke point is the temperature at which a fat or oil produces a continuous wisp of smoke. This provides a useful indicator of its suitability for frying and 200°C is often specified as the minimum by regulations (Table 4.13).

The flash point defines the temperature at which the decomposition products formed in heated frying oils can be ignited. This temperature ranges from 275–330°C for different oils and fats (Table 4.13). An increase in the content of

unsaturated fatty acids usually causes a decrease in the flash and smoke points (Arens 1977).

4.3.4 Cold test

The cold test measures the resistance of oil to formation of sediment at 0°C or 4°C (Table 4.13). Sediment formation is usually caused by compounds with a high melting point. These are mainly waxes and triacylglycerols with long-chain saturated fatty acids (Przybylski *et al*. 1993a). The formation of haze in canola oil is not common, but may occur occasionally (Mag 1990). Oils produced from seeds grown in dry/drought conditions develop sedimentation more easily and this may be related to the higher content of saturated fatty acids formed as a response to drought stress conditions (Przybylski *et al*. 1993a).

4.3.5 Crismer value

The Crismer value (CV) measures the miscibility of an oil in a standard solvent mixture, composed of *t*-amyl alcohol, ethyl alcohol, and water in volume proportion 5:5:0.27 (Table 4.13). This parameter was a specification criterion used for international trade, mostly in Europe. However, it is rarely used today. Values are generally characteristic, within a narrow limit, for each kind of oil. The miscibility of oil is related to the solubility of the glycerol esters and is affected mainly by the unsaturation and chain length of the constituent fatty acids.

4.3.6 Saponification number

The saponification number is defined as the weight of potassium hydroxide, in milligrams, needed to saponify one gram of fat. This parameter is inversely proportional to the molecular weight of the fat. In other words, the higher the molecular weight the lower is the saponification value. Replacement of long-chain fatty acids such as erucic acid in rapeseed oil by C_{18} fatty acids increases the saponification numbers from 168–181 to 188–192 due to the reduction in molecular weight (Table 4.13).

4.3.7 Iodine value

The iodine value (IV) indicates the degree of unsaturation of a fat or oil. It is defined as the number of grams of iodine absorbed by 100 grams of fat. The higher value for canola oil is due in part to the replacement of erucic acid with unsaturated C_{18} acids, mainly oleic acid, together with a slight increase in the contribution of linoleic and linolenic acids (Table 4.13). The iodine value can also be calculated from fatty acid composition using specific factors for each

Table 4.14 Melting characteristics of palmitic and several C_{18} acids

Fatty acid	Melting point (°C)
Palmitic	64.5
Stearic	69.6
Oleic (*cis* 9)	13.2
Elaidic (*trans* 9)	43.7
Octadecenoic (*cis* 6)	28.6
Linoleic (all-*cis* 9, 12)	−5.1
Linolenic (all-*cis* 9, 12, 15)	−11.2

Adapted from Mag 1990.

unsaturated fatty acid (Kyriakidis and Katsiloulis 2000). It is claimed that this method provides more accurate data.

4.3.8 Melting characteristics, polymorphism and crystal properties

Canola oil has a homogeneous chain-length fatty acid composition with 95% being contributed by C_{18} fatty acids (Ackman 1990). Reducing the erucic acid content has a marked effect on the melting characteristics and the type of crystal formed when the oil is hydrogenated. Hydrogenation of canola oil is used to form products used in the formulation of shortenings and margarines. With increasing degree of hydrogenation, the fatty acid composition becomes more homogeneous. This results in a tendency to form β-crystals on solidification which are undesirable in margarine and shortenings. *Trans* isomers formed in hydrogenation have higher melting points than *cis* fatty acids (see Table 4.14, D'Souza *et al*. 1991) and these serve to introduce greater variety in the fatty acid composition of the hydrogenated oils, so reducing the β-crystallization tendency of the oil.

4.4 Major food uses

4.4.1 Standard canola/rapeseed oil

In describing canola/rapeseed oil food uses, the Canadian experience is significant for a number of reasons. The first reason is that canola/rapeseed was originally developed and introduced commercially in Canada, and considerable experience in using canola oil in edible oil products has accumulated. Secondly, canola, after its introduction, rapidly became the most important oilseed crop and the most heavily used edible oil in Canada, as documented below. The third reason is that the Canadian edible oil products market demands a large variety of high-quality products, which led edible oil producers to develop many uses for canola oil and to find applications especially suited for it.

Usage of canola oil in Canada has grown from the early years after its introduction to about 68% of the edible vegetable oil consumed in 2000. It has been at this level for the past decade. Thus, in 1992, 1993, 1994, 1995 and 1999 the corresponding percentages were 63, 68, 73, 72 and 68%, respectively (adapted from Canadian Oilseed Processors Association [COPA] Monthly Statistics for Feb 1993, 1994, 1995, 1996, 2000 and 2001). Most of the oil (probably > 70%) is used in liquid, that is, non-hydrogenated form.

The products in which the liquid oil are used are salad oils and salad dressings, as the liquid oil component in margarine formulations, and in household and baking shortenings.

Very lightly hydrogenated canola oil (IV about 90) and more highly hydrogenated canola oil (IV lower than 90) are used for frying and in margarine and shortenings.

4.4.1.1 Salad oil, salad dressings, mayonnaises and cooking oil uses

Canola oil is a 'natural' salad oil. This means that it remains clear (no sedimentation) at refrigeration temperatures (3–5°C). No 'winterization' or fractionation is required, except in some instances when, because of seed growing conditions, the oil may contain waxes and traces of other high-melting material (see Section 4.3.4). These compounds may crystallize over time and create appearance problems in clear bottles. Experience has shown that it is only necessary to remove these compounds for the most demanding markets. They present no health hazard and are not sufficiently concentrated to affect emulsion stability when the oil is used in mayonnaise and other emulsified salad dressings.

Canola oil is used either alone or, increasingly in some markets, as a component in salad oil blends. Such blended salad oils are generally designed to achieve a certain fatty acid composition for nutritional reasons. Canola oil contributes low saturated fat and some linolenic acid as part of the desirable nutritional features of such blends.

Canola oil is also used as cooking oil and for pan-frying. It is not recommended for deep-frying because its moderately high polyunsaturated fatty acid content makes it unsuitable.

In all these applications, canola oil gained favour in the 1980s and 1990s in many areas of the world, such as North America and many European countries. This was because of its low content of saturated fatty acids compared to all other competing oils in these applications. Further, its high content of oleic acid and its moderate content of linoleic acid has made canola oil even more competitive in food applications. Linoleic acid consumption is recognised as being too high in diets that are high in the use of soybean, sunflower and corn oils, as in most industrially developed countries. Its linolenic acid content gives canola oil a nutritional advantage over sunflower and corn oils.

The low total polyunsaturation of canola oil (about 30% versus 58% for soybean oil) along with the high content of monounsaturates (about 60% versus

25% for soybean oil) are the main factors in the good flavour stability of this oil, despite the presence of linolenic acid. Additional minor, but important, reasons why canola oil has better oxidative stability than soybean oil are:

- a larger percentage of its linolenic acid content is in the *sn*-2 position in the triacylglycerols than is the case with soybean oil; this confers somewhat greater resistance of linolenic acid to oxidation,
- the presence of some sulfur compounds, which can act as antioxidants (see also Section 4.2).

The detailed fatty acid compositions of canola, soybean, sunflower, corn (maize), and flax oils, as well as some specialty canola oils and HEAR oil are given in Table 4.2.

4.4.1.2 Frying fats

Large amounts of canola oil are used as a lightly hydrogenated (IV about 90) oil that acts as a stable but pourable frying fat. Canola oil is uniquely able to combine good stability with pourability because of its fatty acid composition.

Its low total polyunsaturation requires relatively little hydrogenation to reduce linolenic acid and linoleic acid to values that are low enough to confer good frying stability. During this process very little stearic acid is formed. Coupled with the low original content of saturates of only about 6%, an oil of good stability yet still pourable at room temperature is obtained. Table 4.15 contains the fatty acid composition and the solid fat indices (representative values) of lightly hydrogenated canola oil with 2% residual linolenic acid and IV of about 90 along with the fatty acid composition of the non-hydrogenated oil. Data for soybean oil are also included to show the difference in fatty acid composition, especially in the amount of saturates and polyunsaturates, and the difference in the solid fat content of these two lightly hydrogenated oils. The figures show the advantage of canola oil in respect to oxidative stability due to the much lower total polyunsaturation and the advantage in respect to pourability due to the

Table 4.15 Fatty acid compositions and solid fat indices of lightly hydrogenated canola and soybean oil (residual 18:3 content, 2%)

	Fatty acid composition (w/w %)						Solid fat index at °C			
IV	16:0	18:0	18:1	18:2	18:3	*Trans*	10.0	21.1	26.7	33.3
Canola										
115	4	2	61	22	9	0	none			
90	4	4	79	9	2	25	2–3	0	0	0
Soy										
130	11	4	25	53	7	0	none			
95	11	7	54	25	2	15	8	4	0	0

Adapted from T. Mag (unpublished data).

much lower solid fat present at 10°C and 21.1°C (room temperature). Because of its suitability this type of oil is heavily used for both small-scale frying in restaurants and in large industrial frying operations. A negative aspect of the hydrogenated canola frying fat is the somewhat higher concentration of *trans* isomers compared to soybean oil.

The lightly hydrogenated canola oil of IV 90, or slightly lower to produce a frying fat containing only about 1% linolenic acid, has also been shown (Teasdale 1966) to be useful as a very stable salad oil after winterization. A very significant advantage is that this 'stabilized' salad oil is obtained in a yield of about 95% and has a 12 h cold test, compared to lightly hydrogenated winterized soybean oil at a yield of 70–80% and a 6 h cold test. This type of product based on soybean oil is being used in some areas of the world, and seems to be expanding. It was very popular in the US in the 1960s but was discontinued because of the low fractionation yields.

It is important to note that lightly hydrogenated canola oil, such as that listed in Table 4.15, does not contribute significantly to the crystal matrix of fat products in which it is used. In this respect it is similar to the use of liquid canola oil, that is, it can be used in products such as margarine and shortenings without contributing to β-crystallization problems.

Canola oil is also used in more highly hydrogenated forms to produce very stable frying fats that are essentially free of any significant amounts of polyunsaturates, but with high amounts of oleic and elaidic acids and moderate amounts of saturates. Examples of more highly hydrogenated canola oils are given in Table 4.16, especially the oils in the IV range from 82 to 72. These oils are very low in polyunsaturation, containing only 0–2% linoleic acid. They are especially suitable when a stable, but relatively firm, fat is needed, such as in donut frying. In frying applications, the problem with β-crystallization leading to formation of a grainy texture and mouth feel, are usually not important, unless the deep-fried foods are stored for some time. In these cases, large fat crystals may become visible at the food surface, which is undesirable. Blends with hydrogenated soybean oil, hydrogenated cottonseed oil, or palm oil are used to control β-crystallization problems. Additional methods that are useful for

Table 4.16 Fatty acid compositions and solid fat indices of more highly hydrogenated canola oils (%)

	Fatty acid composition						Solid fat indices at °C				
IV	16:0	18:0	18:1	18:2	18:3	*Trans*	10.0	21.1	26.7	33.3	40.0
82	4	5	87	2	<1	32	18	5	0	0	0
77	4	9	84	<1	<1	35	25	11	6	0	0
72	4	13	81	0	0	44	35	17	10	3	0
68	4	18	76	0	0	48	53	34	27	13	1
62	4	25	70	0	0	46	65	53	48	33	12

Adapted from T. Mag (unpublished data).

suppressing β-crystallization are discussed below in connection with margarine products.

In Canadian practice, only selectively hydrogenated canola oil is used. The practical reason is that the somewhat higher content of *trans* isomers makes the more highly hydrogenated oil more resistant to β-crystallization than would be the case with a non-selectively hydrogenated canola oil. When the *trans* isomer content must be minimized in a canola oil product, liquid canola oil or very lightly hydrogenated canola oil is used, as shown in Table 4.15.

4.4.1.3 Soft (tub) margarine

In Canada and in many other countries in which margarine is consumed, soft, or tub margarine is now predominant. Consumption of hard (stick) margarine has decreased significantly in the past two decades. Further, a significant proportion of soft margarine in many countries is of the zero *trans* isomer type and no hydrogenated oil is used. Palm/palmkernel oil-based hard fat blends with a suitable solid fat content profile are used to provide the crystalline fat component. Only about 6–10% of the total fat is required to supply the necessary crystalline fat phase. The composition of the palm/palmkernel oil based hard fats varies depending on several factors and is very often proprietary to the suppliers, which are primarily based in Malaysia. Interesterification is usually used to produce these blends. Canola oil is used only as the liquid oil component of these no-*trans* isomer products. Becel, which has been on the market for many years in parts of Europe and in Canada, is the prime example of this type of product. Canola oil is often the preferred liquid oil, because it has the lowest saturated fatty acid content and supplies some linolenic acid, yet has good flavour stability. This oil is also used together with other liquid oils to make up the liquid oil component.

Soft margarine based on partially hydrogenated hard fat is also produced with canola oil as the sole liquid, non-hydrogenated component, or along with other liquid vegetable oils. In these margarines, canola oil can be used as the partially hydrogenated hard fat, as well. One, or a combination of several of the hydrogenated oils listed in Table 4.15 and in Table 4.16, can be used. However, because of the tendency of canola-based hydrogenated hard fat to form β-crystals over time, partially hydrogenated soybean oil or other palmitic acid containing oils, such as partially hydrogenated cottonseed oil, are preferred as the hard fat. This avoids the tendency of the margarine to have a coarse, sandy texture due to β-crystallization. Table 4.17 lists typical compositions of these three types of soft margarine using canola oil.

In the past, margarine oils made entirely from canola oil were produced, especially in Canada and Sweden. This is still of interest when the hard fat must be made from canola oil because of cost or oil availability. Using partially hydrogenated canola hard fat requires control of β-crystals, which must be suppressed. This can be done by a) adding about 0.3–0.5% of sorbitan tristearate

Table 4.17 Soft (tub) margarine using canola oil

Oil type	Composition (%)	Solid fat indices (at °C) 10.0	21.1	33.3
1. No *trans*				
a) palm/palmkernel hard fat	8 }			
b) canola oil, or other liquid vegetable oils, including blends to achieve specific fatty acid compositions	92 }	5–7	4–5	1–2
2. *Trans*-containing				
a) hydrogenated canola hard fat	47 }			
b) canola (or other liquid vegetable oils, see 1b)	53 }	8–10	6–8	1–2
3. *Trans*-containing				
a) hydrogenated soy hard fat	25 }			
b) canola, or other liquid vegetable oils, see 1b)	75 }	8–10	6–8	1–2

Adapted from T. Mag (unpublished data).

to the fat blend or b) by using several selectively hydrogenated canola hard fats of different hardness to introduce a greater variety of triacylglycerols into the fat blend. Sorbitan tristearate and the greater variety of triacylglycerols interfere with the conversion to the β-form of fat crystals and, therefore retard the formation of a sandy margarine texture. Changing fatty acid position in triacylglycerols by interesterification of some or all of the hydrogenated canola hard stock used in the oil formulation can reduce the β-crystallization tendency. It is used in Europe, but not in North America.

All the above mentioned measures to control β-crystallization are costly and, in the case of sorbitan tristearate, a label declaration as an additive is required, giving the product an undesirable chemical connotation. Hence, its use is limited. In today's practice, blending with another hard fat that is relatively high in palmitic acid to raise the concentration of this acid to at least 8% in the hard fat blend is preferred. To meet this requirement, the oils used are palm at about 15% and partially hydrogenated cottonseed at about 30%. Further, when it is not required to maximize canola oil in the fat blend, partially hydrogenated soybean oil is used to supply the high melting portion of the blend instead of partially hydrogenated canola oil. Soybean oil contains 11% of palmitic acid, enough to confer acceptable crystal stability in the β′-form.

4.4.1.4 Hard (stick) margarines

Liquid and lightly hydrogenated canola oils are used to produce stick margarine. They do not contribute significantly to the crystal matrix of the product, as pointed out earlier. The tendency of the more highly hydrogenated canola oils,

such as those listed in Table 4.16, to form β-crystals means that these are not used to any significant extent as contributors to crystalline fat. They would have to be used in relatively large amounts, 40–50% in the fat blend, which makes it more difficult and costly to control β-crystallization. The liquid or lightly hydrogenated oil is generally used at 50–60% of the oil composition, the remainder being relatively highly hydrogenated soybean or cottonseed oil, or hydrogenated palm oil.

In situations where the use of canola oil must be maximized (that is, the hard fat component as well as the more liquid component must be from canola oil), the same approach as outlined above for soft margarine must be used. As was already pointed out, demand for stick margarine is declining, and the demand for margarine made entirely from canola oil is no longer significant in most countries that are accustomed to the use of canola oil.

4.4.1.5 Shortenings, baking and pastry margarine

Similar to the use of canola oil in making table margarine, liquid canola oil is heavily used to produce shortening, and baking and pastry margarines. Lightly hydrogenated canola oil of about IV 90 is used when better oxidative stability is required than can be achieved with liquid oil. When it is desired to use canola oil, even as the hard fat component in these formulations, then the considerations related to crystallization already discussed for margarine apply. Generally, highly hydrogenated canola oil is not much used.

Liquid canola oil or lightly hydrogenated canola oil is blended with the hard fats such as tallow, palm, partially hydrogenated soybean, and cottonseed oils and fully hydrogenated versions of these oils (stearins), to meet preferred specifications. Detailed compositions are usually proprietary. For baking applications, shortening and baking margarine, having the fat component with the β′-crystalline form is especially important for good performance. For this reason baking shortenings based totally on canola oil are not in use.

4.4.1.6 Antioxidant usage in canola oil products

Present practice is to avoid the use of synthetic antioxidants in edible oil products as much as possible. This also applies to canola oil products. For many edible oil products, users now specify that chemical additives cannot be used as ingredients. This avoids having to declare on the product label that the product contains a synthetic chemical antioxidant as an additive. Instead, there is increasing emphasis on preserving natural antioxidants present in canola oil (the tocopherols) during processing. Tocopherol losses occur primarily during deodorization because of the high temperatures applied. Processors are limiting deodorizing temperatures as much as possible when high tocopherol concentrations are demanded, consistent with achieving good deodorization. It is possible to retain as much as 80% of the original tocopherol content in the deodorized oil.

The tocopherols are especially important as antioxidants in frying, because of their low rate of evaporation and of destruction at frying temperatures (Pongracz 1988). The tocopherol content of standard canola oil is given in Table 4.6, together with the tocopherol content of some speciality canola oils and other common vegetable oils. The main tocopherols present in canola oil are α- and γ- tocopherols.

It is interesting to note that canola oil is more than twice as high in α-tocopherol (about 270 mg/kg) than soybean oil (about 116 mg/kg). α-Tocopherol is now recognised as the tocopherol with highest vitamin E function in humans (National Academy of Sciences, US 2000). Canola oil is thus a very good source of vitamin E.

The synthetic antioxidants that are used, when there are no restrictions on using them, are butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG) and tertiary butylhydroquinone (TBHQ). Added amounts are usually 0.02% (single or combined). This is the maximum allowable amount in Canada and the US, for example. Regulations governing synthetic antioxidant usage differ from country to country.

Citric acid is used as a metal chelating agent, usually as monoacylglycerol citrate at 0.01% by itself or along with BHA and BHT. In some countries, the US for example, citric acid can be used as a chelating agent without having to declare it on product labels when it is added to the oil in an aqueous solution in the cooling stage of the deodorization process. Lower amounts of 0.005% are often used.

4.4.1.7 Canola oil use in selected areas of the world

It is interesting to review, briefly, the use of canola oil in edible oil products in various countries in the world.

The US imports large amounts of canola oil from Canada in addition to some domestic production. Currently, about 90% of the canola oil is consumed in liquid form as salad oil and in salad dressings. This is a direct result of the emphasis on consuming oils which are low in saturated fatty acids and canola oil is lowest in saturated fat among vegetable oils. Canola oil is also being used in blended salad oils to achieve certain fatty acid profiles, as mentioned earlier. The relatively high use of canola oil in the US is remarkable, since none was used before 1983.

About 10% of canola oil is used as hydrogenated oil and consumed in the form of shortening. This appears to be mostly as frying fats (also termed frying shortenings in North America) to take advantage of the low concentration of saturated fat and low polyunsaturation as discussed before. Interestingly, virtually no canola oil, liquid or hydrogenated, is used in margarine formulation at the time of writing.

Mexico uses significant amounts of canola oil, predominantly in salad dressings or as a salad or cooking oil. This is mostly from seed imported from Canada and the European Union.

Japan uses large amounts of canola oil. It has imported Canadian canola seeds since the introduction of canola in the early 1970s, and has for many years taken about half of the Canadian canola crop. The oil is predominantly used in liquid, non-hydrogenated form as cooking oil and as salad and salad dressing oils, both pure and in blends with other oils. In a new development, it is used as base oil to produce diet cooking and salad oils made up of about 80% diacylglycerols (DAG oil). DAG oil is more easily hydrolyzed in the digestive system and is used as an immediate energy source rather than stored as body fat. This DAG oil technology is being introduced in the US (Anonymous 2001b).

In China, canola type rapeseed oil products still contribute a very small proportion of total rapeseed oil products. Oil from both high-erucic acid rapeseed and canola rapeseed represent the largest use of edible oil at present. The oil from these two sources is almost entirely used as cooking oil. There is very little of this oil used for margarine or shortening formulations at present. Efforts are being made to widen the spectrum of edible oil products and convert from HEAR cultivation to canola cultivation.

India, like China, does not use significant amounts of canola rapeseed oil. Instead mustard seed oil, which is high in erucic acid, similar to HEAR oil, is the most important oil used almost entirely as liquid cooking oil. Among the lower income segment of the population, and even in the middle class, this oil is not deodorized and is favoured for its taste. Undeodorized canola rapeseed oil cannot compete with mustard seed oil in flavour. Blending of canola oil with mustard oil lowers the content of erucic acid in the mustard oil. Unless taste preferences change and there is greater attention to the health implications of the types of fat in the diet, canola oil will be used only to a limited extent in the foreseeable future.

The Middle East is beginning to use canola oil in competition with sunflower and corn oil as salad and salad dressing/mayonnaise oil. In many countries at present margarine and vanaspati are based on hydrogenated soybean oil and on palm oil. Interest in canola oil is based on its nutritional properties, mainly its low saturated fatty acid content. There is considerable potential for using canola oil not only as a salad oil, but also, in its lightly hydrogenated form, as a vanaspati-like pourable frying fat.

Western and Eastern Europe use large amounts of canola oil, with the exception of France. Large amounts of liquid canola oil are used in salad oils, salad dressings, mayonnaise, and table and baking margarine. Lightly hydrogenated canola oil is heavily used for frying of snacks. This is very similar to Canadian practice. Canola oil use is driven, in part, by recognition of the positive health effects of its high oleic acid content, along with its low saturated fat, and the fact that European-grown canola seeds are not genetically modified (non-GM) at present, as opposed to oil from imported soybeans. Also, canola salad oil is considered by some to have a better shelf life than the other more highly polyunsaturated vegetable oils.

Southern Europe and France use relatively little canola oil. Instead, olive, sunflower and peanut oils predominate. In the case of France, this is somewhat surprising, since this country is a large producer of canola seeds. France uses large amounts of canola oil for biodiesel methyl ester production.

Australia/New Zealand produce canola seed and use the oil in much the same fashion as North America and parts of Europe.

South America uses sunflower and soybean oil and increasingly also palm oil. Canola oil is not a factor in food uses.

4.4.1.8 Canola/rapeseed oils with modified fatty acid composition

Since introduction of standard canola there has been considerable efforts by plant breeders to produce canola oils with modified fatty acid compositions. These efforts were primarily to improve oxidative stability, or crystallization properties, or to furnish lauric acid-containing oils, and more recently, canola oil containing γ-linolenic acid. The following is a list of these developments:

- low-linolenic acid canola oil (2% vs. 9%)
- high-oleic acid canola oil (69–77% vs. 60%)
- high-palmitic acid canola oil (10% vs. 4%)
- high-stearic acid canola oil (30% vs. 2%)
- lauric acid canola oil (about 33% 12:0)
- γ-linolenic acid canola oil (37% vs. about 1%)

The complete fatty acid compositions of some of these oils, namely low-linolenic, high-oleic acid, lauric acid and γ-linolenic acid oils, are given in Table 4.2.

Low-linolenic acid canola oil was developed in Canada in the 1980s to improve the oxidative stability of the oil so that light hydrogenation would be unnecessary. The linolenic acid content of this oil is reduced to about 2% compared to about 9% in the standard canola oil. This resulted in an increase in linoleic acid from 20–27% and an increase in oleic acid from about 60–61%. In Canada and the US, this oil is available in limited quantities and is used entirely for deep-frying in place of the lightly hydrogenated standard canola oil (Table 4.15). Its main advantage is the much lower *trans* isomer contents of about 1–3%, formed during deodorization, while the lightly hydrogenated oil contains 20–25%. Widespread use is hampered by its price which tends to be too high due to the low seed yields of the available varieties. Research on its frying stability and the storage stability of french fries by Warner and Mounts (1993) showed that these properties were improved. Work done by Przybylski and Eskin (1998), Zambiazi (1997), and Normand (1998) showed slight improvement in the frying stability of this oil and the storage stability of fried foods. It was found that this unexpected result may be related to the lower content of tocopherols (see Table 4.6). There are also anecdotal reports from industry that the frying stability of the oil is not sufficiently improved to warrant its higher price.

High-oleic acid canola oil is another development pursued in Canada, the US, Sweden, Australia, and elsewhere. As with low-linolenic acid canola oil, the aim was to produce a stable frying oil, which will not need hydrogenation and thus avoid formation of *trans* isomers. The oleic acid content in oil from seed developed in Canada is at about 78%, while linoleic acid is lowered to about 8% and linolenic acid to below 3% (see Table 4.2). Saturated fatty acid content is unchanged from the standard canola oil. There is limited commercial seed production for export to Japan. Also, there is increasing acceptance of the oil in Canada and the US. The frying performance in tests was found to be similar to lightly-hydrogenated standard canola and mid-oleic sunflower oil. Taste tests of french fries produced with this oil showed similar consumer acceptance as with typical frying fats used for making these products (Przybylski, unpublished data). In Australia, a canola oil with 69% oleic acid (Monola) is being offered for frying. In potato frying tests with ten other oils it was rated higher in sensory and chemical tests than the other oils (Anonymous 2000).

High-palmitic acid canola oil was initially developed in Sweden. The purpose was to prevent the β-crystallization of hydrogenated canola oil to make it more freely useable for margarine and shortenings. The oil contains about 10–12% palmitic acid compared to only 4% in the standard oil. This development has not gained significant commercial use because of the increased use of canola oil in liquid form in a large variety of edible fat products, following concerns about saturated fatty acids, and because of the ready availability of palmitic acid-containing oils for blending to control crystallization problems.

High-stearic acid canola oil with 25–30% stearic acid was developed but commercial scale production for food uses has not been achieved.

High-lauric acid canola oil was developed in the US as a replacement for coconut and palmkernel oils for both food and non-food uses. The oil contains about 35% lauric acid but up until now it has not found significant commercial use. The main reason for the lack of acceptance is said to be the significantly different fatty acid composition compared to coconut oil and the consequent difference in performance in typical coconut oil applications. Some use was made of the oil in the US as a base stock for a *trans* isomer free margarine and in Europe as a machine oil additive (Anonymous 2001a), but there is no longer any significant seed production.

γ-Linoleic acid canola oil is of interest. It is an example of a development for the nutrition supplement market.

4.4.2 High-erucic acid rapeseed (HEAR) oil

In countries that grow canola, HEAR oil is used only in special food applications (and several non-food uses). Its primary use is as a fully hydrogenated oil added to peanut butter (Japiske 1969) in amounts of 1–2% to prevent oiling, mainly in Canada and the US. The HEAR oil used contains about 45–50% erucic

acid, the highest erucic acid rapeseed oil available commercially at present. Because hydrogenated erucic acid (behenic) has a very high melting point, the completely hydrogenated HEAR oil is very effective in holding high amounts of liquid oil in its crystal matrix. The patent literature also mentions the use of fully hydrogenated HEAR oil in interesterification with palm stearin fraction to formulate a zero *trans* isomer margarine hard fat, but there appears to be no significant use of this material. The patent literature of the 1960s and 1970s contains a number of examples of other uses of fully hydrogenated HEAR oil. These uses were designed to exploit the β′-crystallization properties, either as hard stock in small amounts for baking shortenings or as base stock for conversion to monoacylglycerols. A listing of these patents is given by Teasdale and Mag (1983). However, it appears that there has been little or no sustained commercial use of these proposed fats.

Plant breeding work to raise the erucic acid content is being done in Canada and elsewhere. Indications are that the erucic acid content of about 80% is possible. This is of interest not only for some of the specialty food uses mentioned above, but especially for industrial lubricants.

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5 Sunflower oil

Monoj K. Gupta

5.1 Introduction

Sunflower oil is one of the most popular vegetable oils and in some countries it is preferred to soybean, cottonseed and palm oils. Unfortunately the sunflower is grown only in limited geographic locations and it is therefore under competitive pressure from other regional crops. The sunflower (botanical name: *Helianthus*) is a plant native to the Americas, and it was domesticated long before the arrival of European explorers. It was of substantial importance to the indigenous population of the New World, who used the meal to make a bread-like food and the oil for medicinal purposes and for seasoning wood and utensils. Cultivated sunflower (*Helianthus annuus*) was introduced into Europe by the Spanish in the fourteenth century. Its cultivation soon spread into Russia, where it received wide acceptance. Systematic studies of plant breeding in Russia began in Kharkhov in 1910 and extended to Kruglik (1912) and Saratov (1913). These studies were focused on breeding for improved oil yield and for other agronomic traits, such as superior insect resistance. Various high oil-containing sunflower varieties were produced from these experiments, several of which were introduced into the US and Canada in 1960.

The Canadian Department of Agriculture started sunflower breeding in Saskatchewan in 1937. US interest followed in 1950 with both the US Department of Agriculture (USDA) and the Texas Department of Agricultural Experimentation initiating similar programs. A high-oleic acid sunflower variety was introduced in the US in the early 1980s and was commercialized in the latter part of the decade. In 1998, the first commercial supply of mid-oleic sunflower was produced in the US. Currently, principal research on sunflower oil in the US is conducted by the USDA at an official Experimentation Station located in Fargo, North Dakota. Besides this station, there are 15–20 private seed companies in the country engaged in developing mid-oleic cultivars with higher oil yield and with good agronomic traits.

In the early 1970s, the National Sunflower Association (NSA) was formed in the US. It soon became the central facilitating body for the promotion of the sunflower industry. Based in Bismarck, North Dakota, the NSA is a non-profit organization, dedicated to expanding the economic opportunities of its constituency. The membership of the NSA includes sunflower growers, various support industries, and selected individual members. The sunflower support industry is comprised of breeders, grain storage and handling operators, and

seed crusher-refiners. The NSA performs several important functions for the sunflower industry including:

- Market development and promotion—investigates new markets and products and conducts aggressive promotion activities directed at the food trade and consumers in the US and overseas.
- Production research—coordinates research programs with universities and USDA. Offers limited grants in priority areas.
- Education—provides production and marketing information to growers through *Sunflower Magazine*, newsletters, media release, and meetings, and holds an annual meeting to present papers and exchange information.
- Policy issues—participates in legislative and policy development issues that may affect the members. The issues can be domestic or international.

The International Sunflower Association is a worldwide organization based in Paris, France. Its main function is to promote technical communication on sunflower research worldwide. The association publishes an annual Year Book, which is a membership directory. It also organizes a technical forum every four years. In addition, dovetailing with the technical forum, the association hold symposia every other year.

Russia has an active program on sunflower research. Krasnodar's agricultural program is similar to that of Texas A&M University. Several Central European countries (formerly known as the Eastern Block) have significant knowledge to offer as well but lack adequate resources to provide any useful technical assistance to growers or processors in the region.

5.2 Worldwide sunflower production

The sunflower is the fourth largest oil source in the world, after soybean (Chapter 2), palm (Chapter 3), and canola (edible rapeseed, Chapter 4) (see also Chapter 1). Demand for sunflower oil increased sharply in the mid-eighties when high polyunsaturated fatty acid (PUFA) margarine became the desired table margarine for health reasons. The demand for this commodity has fallen since then, and today sunflower oil faces tough competition, due to declining oil prices and competition from the other regional crops. Soybean has taken away acreage from sunflower in the US. In Europe, there is a shift toward canola production for bio-diesel.

The major sunflower producing countries are the former Soviet Union (former USSR), European Union (EU-15), Argentina, Central Europe, Turkey, US, South Africa, India, China, Myanmar (Burma), Australia and Pakistan. Many other countries produce sunflower oil in small quantities. Table 5.1 lists the world

Table 5.1 World production and disappearance of sunflower oil (in 1000 tonnes for crop years 1996/97–2000/01)

Crop year*	2000/01	1999/00	1998/99	1997/98	1996/97
Opening Stock	1124	949	871	971	1155
Production	8867	9567	9281	8444	9111
Imports	2393	2696	2998	3048	3203
Exports	2370	2729	3033	2997	3280
Disappearance	9175	9360	9168	8594	9217
Ending Stock	838	1124	949	871	971

*Crop year is counted from October to September.

production and disappearance data on sunflower oil for the past five years (*Oil World Annual Report* 2001). There has been a significant drop in sunflower production since 1999/2000. The production of sunflowers has received some encouragement due to price increase in recent months, but no real increase in production is anticipated for the crop year 2001/2002.

5.3 Obtaining the best results in growing sunflower plants

Like most other crops, certain conditions must be met in order to obtain a good yield of sunflower plants, for example:

- knowledge of proper soil type and conditions for growing sunflower, such as soil acidity and salinity
- soil preparation through tilling
- crop management: planting, plant population, inter-cropping, crop rotation
- irrigation
- crop nutrition/fertilization
- weed control
- parasitic weed control
- disease prevention
- insect control
- vermin control

The sunflower can only be grown in limited geographic areas due to soil and climatic requirements. Although it is reasonably drought-tolerant, it cannot tolerate extremes of temperature. The sunflower has been grown in heavy clay soils (vertisols) with good soil structure. Like most crops, sunflower production requires crop rotation and supplementation of depleted nutrients. The sunflower plant exhibits good performance at a soil pH range of 5.7–8 in heavy clay soil (Balmey and Nathanson 1977), while poor results were obtained in sandy loam soil at pH 4.6. High concentrations of sodium, especially in the form of

sodium chloride, are highly undesirable in sunflower cultivation. Sunflower plant breeders and growers indicate that proper sowing time is critical for a successful crop. The best sowing time depends upon geographic location, weather conditions and plant maturation time which, in turn, depends on the cultivar being planted. Sunflower seeds are generally planted at a depth of 3–7 cm. Germination decreases as the depth of planting increases beyond the optimum. A temperature above 10°C is preferred for proper germination of sunflower seeds, but a temperature of 7–10°C is generally considered to be adequate (National Sunflower Association 2001a). Plant population can vary. Plant breeders generally recommend 40,000–50,000 plants per hectare on non-irrigated land and 50,000–60,000 on irrigated land (Majid and Schneiter 1987). Spacing between plants and the rows is taken into consideration. Other factors to be taken into account are seed variety, latitude of the location, and terrain. Inter-cropping sunflowers has been successful though generally with a crop having a different maturation time. Inter-cropping sunflowers with peanuts is reported to improve the yield for both crops, possibly by providing essential nitrogen as a result of nitrogen fixation by the peanuts (Rao and Reddy 1991, Samui and Roy 1990).

Crop rotation requirements for sunflower plants are no different from those of other crops. Plant breeders do not generally recommend short-sequence rotation for sunflower crops. Monoculture or a short-sequence rotation tends to increase the number of soil borne diseases that affect the plants. Appropriate crop rotation reduces insect damage, improves weed control, disease control, and improves yield (Balmey *et al.* 1997). However, crop rotation does not reduce infestation from migratory insects.

Sunflower plants have a deep root system. This allows the plant to draw more nutrients and water from well below the surface (Dalal and Mayer 1986). Therefore, soil tillage and preparation become very important, especially with heavy clay soils or in sub-humid or semi-arid areas. Primary tillage addresses the soil compaction issue. This incorporates the plant residue (primarily stubble) into the soil and also controls weeds (Sallaway *et al.* 1988). Additionally, this process also helps the incorporation of the fertilizer and herbicide applied to the surface of the soil. Secondary tillage is carried out to prepare the soil for seeds. However, efforts are also being made to minimize or eliminate tillage to retain the maximum amount of stubble and to minimize soil erosion (National Sunflower Association 2001b). Tilling is a complex operation requiring extensive knowledge and skill. The idea is to allow the optimum amount of moisture and air for germination, root establishment, and to preserve the moisture retention potential of the soil for the sunflower plant to absorb adequate nutrients during the course of its life.

The availability of proper nutrients in the soil is important for the sunflower plant. Besides carbon (C), hydrogen (H), and oxygen (O), there are at least a dozen other elements that are essential for proper nourishment of

the sunflower plant (Balmey *et al.* 1987). These can be defined as macro- and micronutrients:

- macronutrients: nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), sodium (Na)
- micronutrients: iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), molybdenum (Mo), nickel (Ni), aluminum (Al).

Virgin soil can be rich in nutrients but at levels that may not be optimal. The soil should therefore be tested for its nutrient content before planting seeds. Nutrients are depleted with repeated production of crops and hence it is important to monitor the concentration of nutrients in the soil and supplement them as required (Seiler 1986). In most third-world countries fertilizer application and irrigation are costly and, sometimes, impossible.

This is apparent in the lower yield per acre in these growing areas and is true for all types of crops. Table 5.2 shows the figures for the harvested area and Table 5.3 shows the yield per acre (*Oil World* 2001) at various countries

Table 5.2 Harvested area in million hectares

Country	2000/01	1999/00	1996–01
European Union	1.92	2.00	2.16
Central Europe	1.93	2.46	2.15
Former USSR	7.99	8.52	7.13
South Africa	0.52	0.40	0.55
Argentina	1.94	3.48	3.16
US	1.06	1.39	1.20
China	1.07	1.02	0.88
India	1.30	1.43	1.65
Turkey	0.52	0.60	0.57
Other countries	1.51	1.53	1.41

Table 5.3 Yield (tonnes/hectare)

Country	2000/01	1999/00	1996–01
European Union*	1.74	1.55	1.66
Central Europe	1.15	1.34	1.28
Former USSR**	0.99	0.87	0.89
South Africa	1.22	1.34	1.24
Argentina*	1.59	1.65	1.72
US*	1.53	1.41	1.54
China*	1.68	1.73	1.72
India**	0.62	0.61	0.58
Turkey	1.12	1.33	1.26
Other countries**	0.90	0.93	0.92

*Countries with high yield.
**Countries with low yield.

Table 5.4 Likely symptoms of nutrient deficiency in sunflower

Observed symptoms	Likely nutrient deficiency
Upper leaves: 1. The entire leaf is pale green or yellow 2. Yellow to brown between veins	Sulfur
Lower leaves: 1. Leaves are yellow to brown in color 2. Leaves are green with brown-gray lesions	Phosphorus
Yellow color: 1. The entire leaf is yellow in color 2. Yellow color between veins on leaf-edges	Nitrogen
Cupped leaves	Potassium
Tissue death: 1. Narrow and leathery leaves 2. Short and thick roots	Zinc
Other symptoms: 1. Leaves whitish in color 2. Roots swollen behind tips	Iron

during the crop years 1999/00 and 2000/01 and the average during the period, 1996–2001. Except for South Africa and China, the production area declined last year with the largest drop in Argentina followed by that in Central Europe and the former USSR.

The essential nutrients need to be maintained at an optimum level for each element. Any excess can cause damage to the plants due to toxic reactions which impair growth. Similarly, deficiency of any of these nutrients will adversely affect the growth of the plant and the crop yield. Therefore, adequate knowledge about plant nutrition for the crop is essential for achieving best results. Table 5.4 lists some of the likely symptoms related to nutrient deficiency in sunflower (National Sunflower Association 2001c).

Weed control is critical for growing sunflowers. Weeds impair growth by competing for water and nutrients and, depending upon the type of weed, the sunflower plant can be deprived of light and space. The first two to four weeks after the emergence of sunflower plants are critical. The weeds, if emerging at the same time as the sunflower, can seriously deter its growth. The yield loss can range from 10–20% due to weed infestation. In some extreme cases as much as 50% reduction of yield has been reported. Application of planting and pre-emergence herbicide can significantly reduce the lost production of the crop (Nalewaja *et al.* 1972). Other methods of weed control are:

- harrowing or use of rotary hoe to remove shallow-bed weeds
- cultivating between rows
- using post-emergence herbicide applications.

Table 5.5 Registered herbicides in the US

Herbicide	Weed controlled	When to apply
Glyphosate	Emerged grass and broadleaf weeds	Pre-plant or any time before crop emergence
Paraquat	Emerged annual grass and broadleaf weeds	Pre-plant or any time before crop emergence
Eptam (EPTC)	Grass and some broadleaf weeds	Pre-plant incorporated: Fall, PPI after October 5
Sonalan (Ethalfluralin)	Grass and some broadleaf weeds and foxtail suppression	Pre-plant incorporated: spring, fall from October 1 to December 31
Prowl Pendimax (Pendimethalin)	Grass and some broadleaf weeds	Pre-plant incorporated
Trifluralin	Grass and some broadleaf weeds	Pre-plant incorporated fall, PPI after September 1; or spring
Spartan (Sulfentrazone)	Annual small seeded broadleaf weeds, including kochia, pigweed, lambsquarters, night shade and biennial wormwood	Early pre-plant; PPI or pre-emergence
Assert (Imazamethbenz)	Wild mustard	Post-emergence. Sunflower: less than 8 leaves or 15 inches high Wild mustard: prior to bloom
Poast (Sethoxodim)	Annual grass and quackgrass	Post-emergence
Paraquat	Desiccant	Backside of sunflower heads are yellow and bracts turning brown: seed moisture content $< 35\%$
Drexel Defol (Sodium chlorate)	Same as for Paraquat	Same as for Paraquat. Recommended for confection variety

PPI = Pre-plant incorporated.

Timely application of herbicide is important for attaining proper yield (Table 5.5).

Research work in the US potentially offers herbicide-resistant sunflower varieties that have been developed by non-biotechnological techniques. 'Express', being developed by DuPont and Pioneer, shows resistance to sulfonylurea herbicide. Another variety, 'Clearfield', is resistant to imazamox. The key decision on these products depends on the decision under Section 18 of the Environmental Protection Agency. Should Section 18 label be approved, Micogen CO. already has enough 'Clearfield' seeds to plant 15000 acres next year. Other companies will have 'Clearfield' seeds ready in 2003. 'Express' is expected to be commercially available in a few years (*The Sunflower*, December, 2001).

The sunflower is grown in many countries under rain-fed conditions without irrigation. It shows improved yield under irrigation (Balmey *et al.* 1997) because

of the deep and extensive root system of the plant. When water supply is limited, early irrigation is recommended to facilitate germination, emergence and adequate leaf expansion for proper plant growth and anthesis.

There are many parasitic weeds that can infest sunflower plants. Some of them are widespread and can be found in almost every sunflower-producing country. Parasitic plants deprive the host plant of its essential nutrients, including carbon. Serious yield reduction for the sunflower has been reported with the infestation of parasitic weeds.

The sunflower crop can suffer from a number of diseases. The commonly known diseases are: downy mildew, rust, verticillium wilt, scelerotinia wilt, head rot and phomposis. Plant pathologists have identified a number of genes in wild sunflower varieties that can provide resistance to these diseases in the developed hybrids. However, no single gene can offer the resistance to all of these diseases. Researchers are continuously working to incorporate improved resistance traits in the hybrids.

Insects are known to damage the sunflower plants. The most common insects are: the sunflower moth, the banded sunflower moth, midge, beetle, red sunflower seed weevil, gray sunflower weevil, sunflower stem weevil, European sunflower moth, head or seed damaging insects, foliage feeding insects, and stem-infesting insects. It is difficult to incorporate insect resistance traits into a hybrid without using the transgenic method. This is a major challenge for the sunflower industry.

Table 5.6 lists the names and recommended applications for insecticides registered for sunflower in the US (National Sunflower Association 2001e).

Table 5.6 Insecticides approved in the US for sunflower

Insect	Insecticides
Banded sunflower moth	Asana XL, Baythroid, Furadan 4F, Lorsban 4E, Scout X-TRA, Warrior
Sunflower moth	Asana XL, Baythroid, Endosulfane 3DC, Furadan 4F, Lorsban 4E, Methyl or Ethyl Parathion 8 EC, 6-3 Parathoin-methyl parathion, Scout X-TRA, Warrior
Sunflower seed weevil	Asana XL, Baythroid, Furadan 4F, Lorsban 4E, Methyl Parathion 8 EC, 6-3 Parathoin-methyl parathion, Scout X-TRA, Warrior
Sunflower midge	None known to be effective
Sunflower stem weevil	Asana XL, Carbaryl (Sevin), Furadan 4F, Lorsban 4E, Scout X-TRA, Warrior
Sunflower beetle	Asana XL, Baythroid, Carbaryl (Sevin), Furadan 4F, Lorsban 4E, Scout X-TRA, Warrior
Cutworm	Asana XL, Lorsban 4E, Lorsban 15G, Carbaryl (Sevin) 20% Bait, Sevin XLR, Warrior
Grasshopper	Asana XL, Furadan 4F, Lorsban 4E, 6-3 Methyl Parathion, Carbaryl (Sevin), Scout X-TRA, Warrior
Wireworm	Lindane (seed treatment)

Source: *The Sunflower*, March/April 2001.

Other natural pests that can also significantly reduce the yield of sunflowers include small rodents, deer, birds and rabbits. Birds and deer can pose a special challenge in certain countries because of governmental regulations against their elimination. For example, black migratory birds are protected in the US by law and the farmers cannot kill them. Deer hunting is allowed only for a limited time of the year. Crop damage from deer is not very significant. Blackbirds are the main source of crop damage. Controlling blackbirds can be very involved and the results may not be completely satisfactory. The Wildlife Services of USDA's Animal and Plant Health Inspection Services (APHIS) offers a program to the growers to control cattail, to reduce the breeding ground for the blackbirds. The EPA approved herbicide (Rodeo) is used. The mode of application of the herbicides has to follow the strict guidelines to protect the environment while controlling the weeds.

Birdshield, a product obtained from grapes, is sprayed to disperse blackbirds, if they start to show activity. Besides this, propane boomers, gunfire, hazing aircraft, or other legal means are applied to chase blackbirds from the sunflower fields.

5.4 Types of sunflowers

Dorrell and Vick (1997) described sunflower as an achene, a specific type of indehiscent fruit with a pointed base and a rounded top. The fruit is approximately 10–15 mm long and has a cross-section that has four sides. The pericarp (hull) consists of elongated and pigmented cells. Under the pericarp there are several layers of sclerenchyma cells with pitted walls and fibers with pitted walls. The seedcoat or testa lies beneath this layer. Contents of the hull and the endosperm vary somewhat between seed varieties. Typically, the hull ranges in weight from 20–25% of the whole seed. Oil, protein, fiber and ash contents from open pollinated and hybrid sunflowers are listed in Table 5.7 based on a study conducted at the USDA Research Center, Fargo, North Dakota:

- oil ranged from approximately 44–51%.
- protein ranged from approximately 17–19%.
- hull was mostly around 20–22% with two exceptions which were much higher.
- fiber residue ranged from 15 to 20%.
- ash was around 0.4%.

Traditional sunflower oil has a high linoleic acid content. This varies, but the oil from most common varieties contain about 65–70% linoleic acid. In contrast to this are the high-oleic (> 80% oleic acid and only 5–9% linoleic acid) and mid-oleic varieties (55–75% oleic acid and 15–35% linoleic acid). Table 5.8 shows the typical fatty acid composition of these three types of sunflower

Table 5.7 Proximate analyses of sunflower seeds

Variety	Wt/1000 seeds (g)	Hull (%)	Oil (%)	Protein (%)	Fiber residue (%)	Ash (%)
Peredovic*	61.0	20.0	48.7	19.2	14.6	0.416
Hybrid 894	50.0	27.5	43.6	19.4	20.1	0.447
Cargill 187	54.0	24.2	45.5	17.5	20.6	0.427
Interstate 3137	51.5	25.3	50.5	16.8	15.0	0.453
Mycogen 658	52.0	21.8	50.9	17.3	15.6	0.440
Pioneer 6451	55.0	21.4	49.6	16.5	15.6	0.431

*Open-pollinated cultivar.
All data are expressed on dry basis.
Grown in Casselton, North Dakota, USDA Study, 1994.

Table 5.8 Typical fatty acid composition of three types of sunflower oil (%)

Fatty acid	Traditional	High-oleic	Mid-oleic
Total saturates	11–13	9–10	< 10
Oleic acid	20–30	80–90	55–75
Linoleic acid	60–70	5–9	15–35
Linolenic acid	< 1	< 1	< 1
AOM (h)	10–12	40–50	25–35
Approximate iodine value	128	79	108

oils. Owing to the higher oleic and lower linoleic acid contents of the high and mid-oleic sunflower oils, the oxidative stability, measured as active oxygen method (AOM) by the AOCS. Values for these two oils are higher than that of refined, bleached and deodorized traditional sunflower oil.

In addition to oil and protein, sunflower contains a number of micro constituents. These include tocopherols, sterols and sterol-esters, phospholipids, waxes, carotenoids, chlorophyll, and trace metals. Tocopherols are natural antioxidants. Sunflower oil is high in α-tocopherol which makes the oil resistant to photo-oxidation. γ-Tocopherol, which provides oxidative stability against autoxidation, is present in sunflower oil only at low levels. Traditional sunflower oil is not suitable for making shelf-stable fried foods since the oil undergoes extensive autoxidation in the frying process. Some Russian varieties are known to contain high levels of both γ- and α-tocopherol and these are under investigation in the US by the USDA laboratory in Fargo, North Dakota.

Sterols and sterol esters are also natural antioxidants but studies on these compounds have advanced more in the area of human nutrition than in the area of their antioxidant property in oil.

Phospholipids (also known as phosphatides) are naturally present in all oilseeds. Like tocopherols and sterol esters, these compounds are oil-soluble and are found in the oil after seed extraction. There are of four major types of phospholipids:

- phosphatidylcholines
- phosphatidylethanolamines
- phosphatidylinositols
- phosphatidic acids

The phospholipid content of fully refined sunflower oil must be low. The oil processing industry uses phosphorus (P) as a measure of phospholipids, because of the specific molecular relationship between phosphorus and phospholipids. It is not difficult to reduce the phospholipid content of sunflower oil by chemical or physical refining process, which will be discussed in Sections 5.10 and 5.11.

Waxes are present on the pericarp of the sunflower seeds. To minimize the wax content of crude sunflower oil, it is necessary to de-hull the seeds properly before crushing. The wax gives a cloudy appearance to the oil when it is refrigerated, and this is undesirable for salad oil. The wax content in the oil is reduced in subsequent processing, called dewaxing, outlined in Section 5.15. Carotenoids are oil-soluble and impart a reddish tinge to the oil, but the level is reduced in the bleaching and deodorization steps of the refining process. Chlorophyll is not a serious issue in sunflower cultivation, except when the crop is harvested before it is fully mature, or when there is a wet harvest. Chlorophyll imparts a noticeably green color to the oil, though this is reduced in the bleaching process. There are some trace metals that are inherently present in most vegetable oils, and the oil also picks up additional iron during crushing, due to the reaction between the free fatty acid and processing equipment made of black iron. All trace metals in the oil are reduced in the bleaching process.

Table 5.9 shows the data on tocopherols, sterols and carotenoids, published by Bordoulina and Popov (1974). Table 5.10 shows the individual phospholipids in crude sunflower oil from the same literature source. Crude sunflower oil from the expeller process contains less than 0.2% of phospholipids.

Table 5.9 Minor components in crude sunflower oil

Cultivar	Tocopherols (ppm)	Sterols (%)	Phospholipids (%)	Carotenoids (ppm)
Armavriski 3497	684	0.3	0.86	1.1
Peredovik	672	0.28	0.75	1.3
Salyut	628	0.26	0.72	1.5
VNIMK 8931	698	0.30	0.82	1.6

Table 5.10 Distribution of phospholipids in crude sunflower oil

Cultivar	Phosphatidyl-choline (%)	Phosphatidyl-ethanolamine (%)	Phosphatidyl-inositol (%)	Phosphatidic acid (%)
Armavriski 3497	58.8	19.6	20.6	1.1
Peredovik	64.2	19.5	15.2	1.2
Salyut	56.1	17.0	22.4	4.5
VNIMK 8931	55.4	18.2	24.0	2.2

Table 5.11 Tocopherols (ppm) in crude sunflower, soybean and corn oil

Oil	α	β	γ	δ
Sunflower	608	17	11	–
Soybean	116	34	737	275
Corn (maize)	134	18	412	39

Table 5.12 Typical distribution (%) of sterols and sterol esters in crude sunflower, soybean and corn oil

Oil	Sterols	Sterol esters
Sunflower	72	28
Soybean	97	3
Corn (maize)	35	65

Details of the tocopherol components are shown in Table 5.11 (Muller-Mulot 1976) and of the sterols and sterol esters in Table 5.12 (Popov *et al.* 1975). Values for other typical vegetable oils, such as soybean and corn, are included for comparison. Both soybean and corn oils have higher levels of γ- and δ-tocopherol than sunflower oil. There is some difference between the sterol contents of the three oils, but the sterol ester content of corn oil is much higher than in either sunflower or soybean oils.

The wax content in the hulls was reported to be 800 to 1600 ppm by Morrison (1983). Krasil'nilov and co-workers (1972) reported that the sunflower seeds contain roughly 10,000 ppm of wax of which 83% is located on the hulls, 17% in the testa, and essentially none in the endosperm. This indicates that wax in the crude sunflower oil can be quite low if the seeds are properly de-hulled before crushing. In the US, typical wax content of crude sunflower oil ranges from 300–600 ppm.

Wax is an ester between fatty acid and alcohol. The fatty acids in sunflower wax resemble those of the oil itself. However, some higher molecular weight fatty acids, such as arachidic (20:0), behenic (22:0), and lignoceric (24:0) acids

are found in the wax, but not in the sunflower oil. Sunflower oil contains about 25% hard wax and the remainder is liquid wax (Popov *et al.* 1970).

Although the sunflower is grown for its oil, the meal portion contains some valuable protein for animal feed. The amount of meal and the protein depends on the degree of de-hulling and cleaning of the seeds prior to crushing. Properly de-hulled sunflower seed yields up to 40% protein in the meal after solvent extraction. Expelled meal contains approximately 37% protein. The protein content in the meal can drop significantly if the seed de-hulling and cleaning is inadequate, and can be as low as 28% by either solvent extraction or mechanical expeller process (Dorrell and Vick 1997). The amount and composition of the protein in the meal varies considerably depending on the seed variety, the method of seed cleaning and de-hulling, and to some degree on conditions used in the extraction or expeller process. The meal contains around 8% of carbohydrate in de-hulled and de-fatted meal. The typical sugars present are the soluble sugars, glucose, sucrose, raffinose, and trehalose, along with small amounts of insoluble sugars, cellulose, and peptic polysaccharides (a complex polysaccharide containing an amino acid moiety).

5.5 Confection or non-oil sunflower

Confection or non-oil sunflower was the main sunflower crop in the US before 1960. It is grown for use as a snack (whole seed roasted and salted), as a food ingredient, bird-feed and pet-food ingredient. The seed is black with white stripes. The hull is much thicker than the oil-producing sunflower variety. Larger seeds up to 16 mm in length are used for making snacks. Smaller seeds are used as food ingredients and the smallest ones are sold as bird seed or for making pet-food. Sunflower seed is a valuable source of vitamin E, selenium, iron and zinc. Comparative data on the nutrients are shown in Table 5.13 (National Sunflower Association 2001f). The micronutrients in sunflower kernel far exceed those from the other seeds listed in Table 5.13.

Table 5.13 Nutrient comparison of sunflower kernels to other nuts and seeds (serving size: 28.35 g, equivalent to one ounce)

Nutrient	Folate (mcg)	Vitamin E (mcg)	Selenium (mcg)	Iron (mcg)	Zinc (mcg)
Sunflower kernels	64.46	14.25	16.67	1.92	1.43
Blueberries	1.81	0.28	0.17	0.05	0.03
Sesame seeds	27.41	0.64	1.62	4.12	2.20
Almonds	8.22	7.42	2.24	1.22	0.95
Walnuts	27.78	0.83	1.30	0.72	1.28
Pecans	6.24	1.04	1.70	0.72	1.28
Hazelnuts	32.04	4.31	1.13	1.33	0.70

5.6 Potential for sunflower products in the US

Sunflower oil is popular in Mexico, the Middle East and Japan, because of its clean taste and appearance. Sunflower oil has been a premium oil and for the US, the oil has been an export-dependent commodity with 60–90% sold overseas. Most of the importing countries enjoyed a subsidy from their governments but these have been curtailed from time to time. This led to a glut of sunflower oil in the US and oil was then sold to domestic users at a discounted price. This did not help the growers.

Traditional sunflower oil is excellent for cooking, making salad dressing, margarine, and so on, but it cannot be used for manufacturing shelf-stable fried foods because of its poor oxidative stability. The oil must be partially hydrogenated for industrial frying application.

High-oleic sunflower oil, introduced into the US in the 1980s, is a good all-purpose oil and can be used even for industrial frying without hydrogenation. It is much higher in oleic acid and slightly lower in saturated fatty acids than the traditional sunflower oil. However, in spite of its advantages, its growth has been limited because the oil is very costly and is targeted only at those users willing to pay a high price for the oil. These factors led the National Sunflower Association from 1995 onwards to promote a mid-oleic sunflower oil. The first mid-oleic sunflower variety was developed at the USDA Research Facility in Fargo, North Dakota. Later several seed companies became engaged in developing mid-oleic sunflower oil. Fatty acid comparison data on the three types of sunflower oil are shown on Table 5.8. The mid-oleic sunflower was named NuSun in 1998 and the standard of identity accepted by the National Sunflower Association is shown as:

Analysis	**Value**
Total saturated fat content	$< 10\%$
Oleic acid content	55–75%
Linoleic acid content	15–35%

Unlike high-oleic sunflower oil, NuSun oil is now being grown and sold as a commodity oil in the US. Production of NuSun has grown steadily over the past three years, as shown in Table 5.14 (National Sunflower Association 2001f). The 2001–2002 figure represents 32% of the total sunflower acreage in the US. The goal is to replace all traditional sunflower in the country with NuSun in two more years.

NuSun has performed exceptionally well in food services, margarine, and in industrial and restaurant frying. The Procter & Gamble Co. have been using NuSun in their premium potato chips (Pringles). The company tested the oil for: shelf life, oil oxidation in frying, oleic acid content, impact on process reliability, and product flavor and stability. NuSun met all of the above requirements while

Table 5.14 Production of NuSun

Crop year	Total sunflower harvest (million hectares)	Change in harvested area (%)	NuSun harvested (million hectares)	NuSun hectares (% Total)	Yield of seeds (tonnes/ hectare)	Average oil in seeds (%)	NuSun oil yield (thousand tonnes)
1998	1.17	–	0.03	2.59	1.74	41.5	22
1999	1.09	−6.97	0.08	7.42	1.46	40.5	48
2000	0.86	−21.50	0.17	20.32	1.54	41.5	111
2001	0.84	−1.37	0.27	32.10	1.54	41.0	171

offering a clean flavor (National Sunflower Association 2001f). NuSun has also made its first market entry as bottled salad oil in Mexico. It is being test marketed in Mexico City by Santa Lucia (a Division of Arhus Olie of Denmark). Standard Brands of Taiwan is marketing bottled NuSun oil. High-oleic sunflower oil never enjoyed this kind of opportunity because of its high price.

A recent report shows that sunflower seed/oil is being used in the extruded form to blend into cattle feed. This supplies the necessary oil and replaces the animal fat from the current feed. Some feel that this provides a safeguard against 'mad-cow disease'. Cottonseed is widely used in dairy cattle feed in North America, but sunflower feed has produced equivalent results in dairy cattle feed and this could open up a sizeable use of sunflowers in North America (*The Sunflower*, December 2001, Nutritional Study on NuSun).

D. K. Phillips (Virginia Polytechnic Institute & State University) completed a study of the nutritional value of sunflower kernels in March 2001. He reported that sunflower kernel is rich in micronutrients that help to reduce the risk of cardiovascular and other diseases. The kernel is also rich in antioxidants and other micronutrients that make it a functional food. Nicolosi and Wilson (University of Massachusetts, Lowell Massachusetts) conducted a feeding study on hamsters to compare NuSun with traditional sunflower oil and olive oil (National Sunflower Association 2001f). Their study produced the following results:

- NuSun significantly lowered non-HDL cholesterol compared to the traditional sunflower oil. HDL cholesterol was not reduced significantly
- both NuSun and the traditional sunflower oil had similar levels of α-tocopherol; however, LDL α-tocopherol level was 77% higher in animals fed NuSun relative to animals fed traditional sunflower oil
- both NuSun and olive oil demonstrated reduced oxidative stress, relative to the traditional sunflower oil.

Kris-Etherton (Pennsylvania State University) is currently carrying out a nutritional study on 32 human subjects to compare diets with NuSun, olive

Table 5.15 Experimental diets in nutritional study comparing NuSun with olive oil and the standard American diet

Diet	Calories from fat (%)	Calories from saturated fatty acid (%)	Cholesterol (mg)	Dietary fiber (g/day)	Type of carbohydrate
NuSun	30	10	< 300	25	Complex
Olive oil	30	10	< 300	25	Complex
Average American diet	35	15	–	15	Simple

oil, and the average American diet. The subjects are moderately hypercholesterolemic men and women, age group 24–67, who have LDL-cholesterol levels between 40–90 percentile range for their age and gender, (according to the NHANES III National Health Institute – NIH Study), triacylglycerol levels < 350 mg/dl, and who are otherwise healthy.

In a three period cross-over study the subjects are to be randomly allocated to one of the three groups of diet: 1) NuSun, 2) olive oil, and 3) standard American diet. The subjects will consume the experimental diet for four weeks with a two-week break before crossing over to the other diets. Two sequential blood samples will be taken at baseline and during the last week of each experimental period.

The experimental diets are shown in Table 5.15. Different caloric levels ranging from 1500–3000 calories per day are offered, depending on the body weight. One meal is consumed on site and the other two are to be carried out by the subjects. The results of this nutritional study is expected to be released next year.

5.7 Crushing of sunflower seeds

The sunflower seed crushing process is typical for oilseeds. A good crushing yield and production of high quality crude oil starts in the field. Moisture levels in the seeds are critical for harvest and storage. It is recommended that the seeds are dried to a moisture content of 10% and that this level is maintained during short storage. For longer periods of storage (running into warmer weather), the recommended moisture content in the seeds is 8%. Damaged seeds develop mold very easily and should be cleaned before storage and then dried to moisture levels 1–2% lower than those suggested above prior to seed storage (Hofman and Hellevang 1997). The seeds may be infested before harvest or may become so during storage. In order to prevent infestation of the seeds, the silos should be clean, have all cracks and crevices filled, and be sprayed about two weeks before storing seeds. Seeds damaged by insects or obtained during poor harvesting conditions produce poor quality crude oil. High moisture and high storage

temperature of the seeds activate the lipase, lipoxygenase and phospholipase enzymes in the seeds. These enzymes give rise to several problems:

- lipase increases free fatty acid content of the oil
- lipoxygenase promotes oxidation of unsaturated fatty acids thereby reducing shelf life of the oil even if it is properly refined
- phospholipase increases the concentration of non-hydratable phospholipids in the oil making it more difficult to refine.

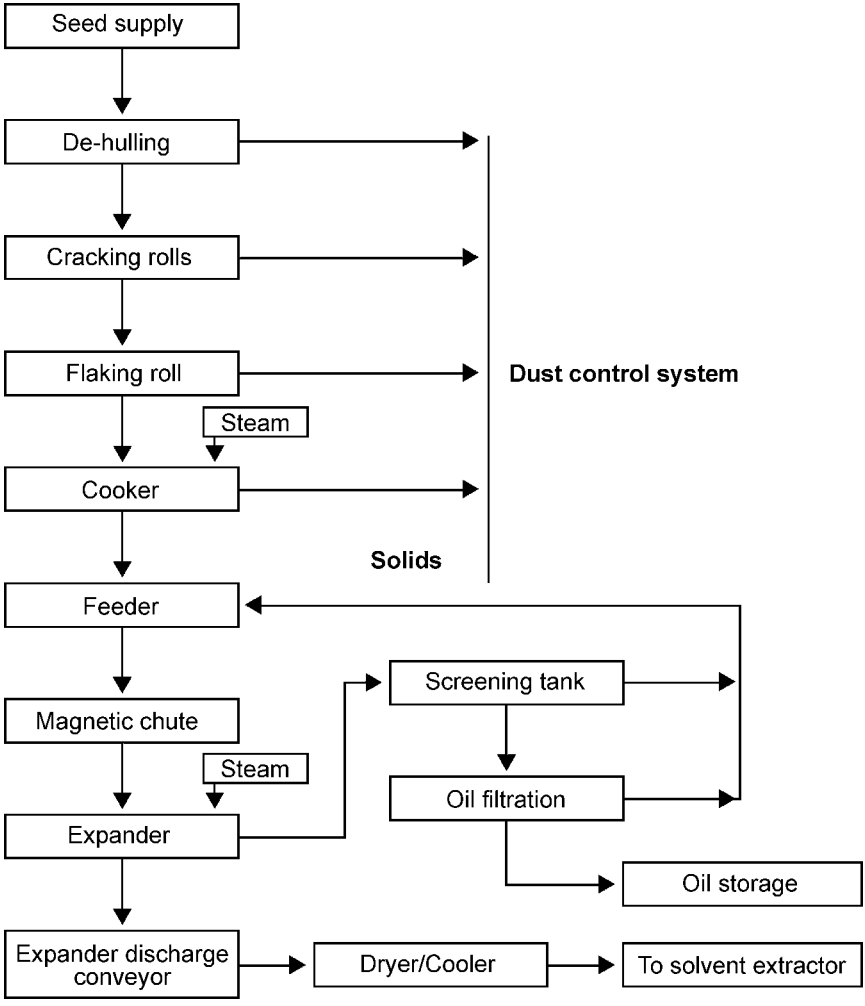

Figure 5.1 Typical sunflower crushing process diagram.

Therefore it is important to maintain proper moisture levels and temperature for the seeds in storage.

The crushing of sunflower seeds involves several steps. Figure 5.1 shows the typical schematic diagram for sunflower seed crushing. The seed supply comes from the storage silo. The seeds are cleaned, either before storage in the silos or before they are sent to the de-hulling to remove plant parts and other debris from the seeds. De-hulling opens up the seeds to separate the hulls from the kernel. This improves the protein content of the meal and also reduces the level of protein remaining in the crude oil.

After removing the hulls, the kernels are passed through cracking rolls to break them before flaking. The flakes are heated in cookers to make the flakes malleable which facilitates the expression of the oil. A feeder conveys the cooked flakes through a magnetic separator to remove tramp iron and into an expeller. In modern plants, an expander is used. This is a special extruder that expels the majority of the oil from the seeds and deactivates the enzymes present in the seeds even during the short time they are exposed to high temperature. The oil is filtered first through a coarse screen and then through a fine filter before storage. The extruded product (collets) is cooled in a dryer/cooler before proceeding to the solvent extractor. *n*-Hexane is used for oil extraction from seeds. Other solvents have been tried but hexane remains the solvent of choice in the industry. The solvent from the micella (oil-solvent mixture) is removed in a stripper. The crude oil, virtually solvent-free, is filtered, cooled and stored. Many extraction plants do not have the filter and cooler for the crude oil, and this can adversely affect the crude oil quality during storage.

The meal goes through a desolventizer/toaster and is cooled and stored. High heat in the de-solventizer/toaster is an important step for the complete removal of solvent and for the deactivation of tripsin inhibitor which is critical for feeding ruminants.

5.8 Sunflower oil degumming

There are two methods for degumming sunflower oil: water degumming and acid degumming. The following steps are used in the water degumming process:

- The oil is heated to approximately 65–70°C.
- The amount of phospholipid in the oil is determined.
- Deionized water is heated to the same temperature as the oil.
- Water, equal to the amount of phospholipid content in the oil, is mixed into the oil with a mechanical mixer. The mixing is not vigorous.
- The oil and water mixture has a residence time of 45–60 min in the tank with gentle agitation.

- The phospholipids precipitate out and are separated from the oil in a centrifuge.
- The wet gum has very little commercial value because of its low volume.
- Degummed oil can be taken straight to the chemical or physical refining process.

In the acid degumming process, the oil is treated with citric acid, though phosphoric acid has also been used by some oil processors to reduce the cost. Mixing the oil and citric acid is done in the same manner as in the water degumming process. The oil is sometimes heated to a slightly higher temperature and residence times of 60–90 min have been used by processors.

Acid degumming of sunflower oil is not generally required because of the low concentration of the phospholipids in the oil. Some processors degum poor quality sunflower oil with citric acid treatment. The results are satisfactory. However, this is not commonly followed in the sunflower processing industry. Some processors also pre-treat crude sunflower oil with phosphoric acid or citric acid before chemical refining. This is a common practice for refining most vegetable oils.

5.9 Sunflower oil refining

Crude sunflower oil is refined, bleached, winterized (dewaxed), and deodorized before being used for edible purposes. The crude oil contains several impurities that must be reduced in order to make the oil suitable for food application. There are two groups of impurities present in the crude sunflower oil:

- macro impurities which can be measured in percentage of the crude oil
- micro impurities that are present in small amounts, generally at ppm or even ppb levels

Although they are present in minute quantities, the presence or absence of some of the micro impurities can have very significant effect on the stability of the oil. The complete refining process involves a number of steps as outlined in Figure 5.2. Refining can be done in both batch and continuous processes. The batch process is used for small quantities of oil and has been virtually eliminated from the developed countries.

Crude oil is generally stored in large tanks with capacities up to a few thousand tonnes depending upon the size of the refinery. These tanks have optional heating coils but most of them do not have mechanical agitation. Agitation is beneficial because wax, phospholipids, and moisture tend to settle to the bottom of the tank and this may cause increased refining losses. Crude sunflower oil specifications

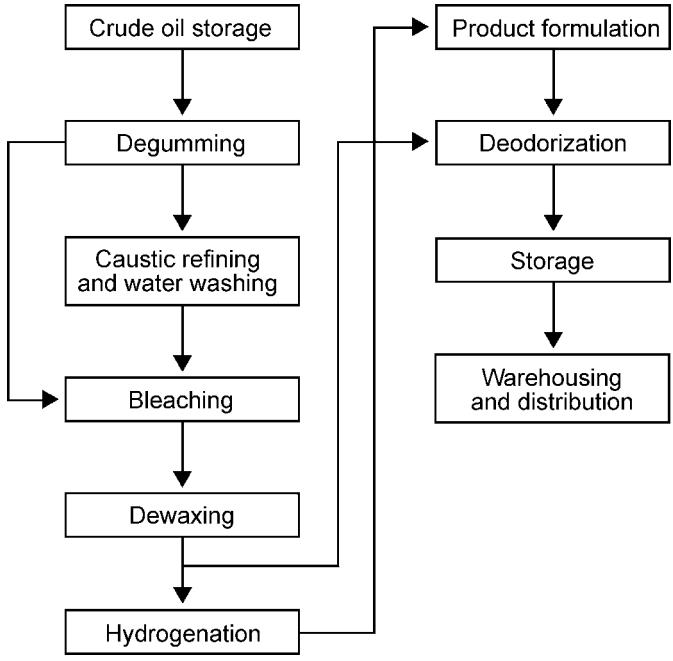

Figure 5.2 Schematic diagram for sunflower oil refining.

are shown below. This is set by Rule 14 of the American Fats and Oils, a trade organization in the US as shown below:

Item	Value
Flash point (°C)	121 minimum
Halpen test	negative
Saponification value	188–194
Unsaponifiables	1.3% maximum
Free fatty acids (as oleic acid)	2.0% maximum
Moisture and volatile	0.5% maximum
Insoluble impurities	0.3% maximum
Lovibond red color	2.5 maximum
Linolenic acid	1.0% maximum

The above specifications refer to macro components.

In addition to the above analysis, it is recommended that any refiner of sunflower oil should also check the following micro components because they indicate the true quality of the oil as salad oil or as other finished products such as margarine and shortening.

Analysis for important micro constituents is as follows:

Component	Typical concentration
Phosphorus (P)	200–400 ppm
Wax	300–600 ppm
Tocopherols	600–800 ppm
Carotenoids	1–1.5 ppm
Chlorophyll	200–500 ppb
Trace metals	
Calcium	25–50 ppm
Magnesium	20–40 ppm
Iron	< 5 ppm

In the refining process, removal of free fatty acid is quite rapid but it is not so for the removal of phospholipids especially if the seeds or the crude oil has been abused, so that there is an increase in the proportion of the non-hydratable phospholipids in the oil.

As mentioned earlier, the original batch refining process is now used in only a limited number of countries because of its limited capacity, high losses, and relatively poor quality of oil obtained.

There are two principal continuous refining processes: physical refining and chemical refining. Three other continuous refining techniques used in the sunflower oil industry are improved modifications of the above processes. These include the cold chemical refining process, the modified chemical refining process and the modified physical refining process.

5.10 Physical refining process

In physical refining, the crude oil is first degummed by treating it with citric acid. This converts most of the non-hydratable phospholipids to a hydratable type which are removed from the crude oil in a centrifuge. The oil is then treated with acid activated bleaching clay at 120–130°C under an absolute pressure (< 50 mm of mercury) using a vacuum ejector or a vacuum pump, and mechanically agitating the oil with bleaching clay for 30–45 min. The bleaching clay is separated from the oil in a plate and frame or a pressure leaf filter. The oil should be kept out of contact with air during filtration to prevent oxidation of the oil. The hot oil can be sent to a hydrogenation reactor or directly to product formulation when hydrogenation is not required. For dewaxing, the oil is cooled and taken through the dewaxing process which will be described later in Section 5.15. Finally the oil is refined through deodorization. In this process, the oil is steam-distilled under an absolute pressure of 3–6 mm of mercury

and at a temperature of 235–245°C in a batch, semi-continuous, or continuous deodorizer. The deodorized oil is rapidly cooled to < 150°C under vacuum and 50 ppm of citric acid is added to chelate any traces of metal. The oil is further cooled in external coolers to a temperature of 5°C above the melting point of the product if solid. If it is liquid, it should be cooled down to < 35°C. In all cases, the oil is saturated with nitrogen gas as it leaves the deodorizer and stored in nitrogen-blanketed tanks to protect the oil from oxidation. Physical refining can be effective only if the non-hydratable phospholipid level in the crude oil is low. This requires that neither the seeds nor the crude oil have been abused. Such oils tend to have a higher level of non-hydratable phospholipids which can cause some difficulty in dewaxing and hydrogenation, and may also make it difficult to reduce the free fatty acid level in the deodorized oil to less than 0.05%.

5.11 Chemical refining process

In the US, sunflower oil is refined by the Alfa Laval's long mix continuous oil refining process. Although it is better to degum the oil prior to refining, this procedure is not generally followed in the US, because the Alfa Laval long mix process removes the phospholipids from the oil quite effectively without prior degumming of the crude oil. In this process, the crude oil is mixed with a solution of sodium hydroxide through a high shear mixer at 27–30°C and then passed through a specially designed retention mixer to allow the sodium hydroxide to convert the non-hydratable phospholipids to a more hydratable form. This generally takes 3 min of residence time in a special retention mixer but a retention time up to 6 min does not hurt the oil. Typically, a 12–14 Degree Baume caustic solution is used for refining crude sunflower oil. A higher strength of caustic is not needed, unless the oil is high in non-hydratable phospholipids or very dark in color. The refined oil leaving the primary centrifuge contains 0.01–0.02% free fatty acid and 100–500 ppm of soap, and the latter must be removed. The refined oil is mixed with deionized water (10–15% of the oil flow), heated to 85° to 90°C, mixed, and then centrifuged to separate the water from the oil. The purpose of washing with water is to remove the soap from the refined oil. The water-washed oil contains 0.02–0.03% free fatty acid and 10–50 ppm of soap. The phosphorus content of the refined and water-washed oil is 5 ppm or less. Nearly 90% of the phospholipids of the original crude oil is removed in the refining and water-washing steps. In contrast to the physical refining process, this method is capable of refining crude sunflower oil containing a high level of non-hydratable phospholipids, and still producing a lower phosphorus content in the refined oil. The water-washed oil is bleached in the same manner as described under physical refining. It is recommended that a very low dosage of hydrated silica (Trysil or similar ingredients), a small amount of citric acid (50 ppm, oil

basis) and acid-activated bleaching clay is applied for a more complete removal of phosphorus, trace metals, and any products of oil oxidation that might remain from the crude oil stage. To obtain the best results the manufacturer of Trysil recommends removal of hydrated silica by filtration and further bleaching after addition of citric acid and bleaching clay. The bleached oil shows the following analyses:

Analysis	Value
Free fatty acid*	0.03–0.06%
Soap	0
Phosphorus	< 1 ppm
Iron	< 0.5 ppm
Calcium	< 0.2 ppm
Magnesium	< 0.2 ppm
Chlorophyll	< 30 ppb

There is usually less concern about the red color at this stage because removal of phosphorus, trace metals, and soap are of prime importance and the red color is reduced later in the deodorizer. The oil is deodorized under the same conditions as in physical refining except that in the latter the deodorizer is designed to handle a much larger volume of fatty acids and therefore has a few extra design features compared to the chemical refining process. The typical analysis for deodorized sunflower oil is shown below:

Analysis	Value
Free fatty acid*	0.01–0.03%
Soap	0
Phosphorus	< 1 ppm
Iron	< 0.5 ppm
Calcium	< 0.2 ppm
Magnesium	< 0.2 ppm
Chlorophyll	< 30 ppb
Lovibond Red color	< 1.5
Cold test, h at 0°C	5.5 minimum (general industry standard) > 24 for well dewaxed oil
Wax content in well dewaxed oil	< 15 ppm

*An increase in free fatty acid content is due to the hydrolysis of the soap in the water-washed oil by the acid activated bleaching clay. This number can be higher if the soap in the water-washed oil is higher.

5.12 Cold chemical refining process

This process is very similar in principle to the standard chemical refining process except:

- The crude oil is heated to 55°C and then slowly cooled down to 6–8°C.
- The oil is kept at this temperature for 24 h to allow complete separation of the wax from the oil.
- The tank is equipped with a special low-speed gentle agitator.
- The cold oil is treated with caustic in the same manner as in the standard Long-Mix chemical refining process.
- Soap and wax are separated from the oil in a primary centrifuge.
- The oil is then heated to 80–90°C for water washing as in the Long-Mix chemical refining process and centrifuged to remove excess soap and water.
- The oil is then heated for bleaching to the same temperature condition as described earlier under the physical refining process.

The remainder of the process is the same. This allows the separation of the wax and soap at the same time. The oil is also protected against the high temperature conditions used in the other methods for refining the oil.

In this process, cold degumming can be undertaken if desired. However, the separation centrifuge requires double the capacity of the standard degumming process because the viscosity of the oil is much higher at the lower temperature.

5.13 Modified chemical refining

The W. R. Grace Company of the US introduced this method to eliminate the water-washing step. The refined oil from the primary centrifuged is treated through the following steps:

- The oil is mixed with Trysil (hydrated silica) under atmospheric conditions for 15 min in the vacuum bleaching vessel.
- Vacuum is applied to the vacuum-bleaching vessel.
- Acid activated bleaching clay is added.
- The oil is heated to 120–130°C and the oil is treated for 30–45 min.
- The oil is filtered and handled as described in the earlier processes.

This process eliminates the use of water washing and produces good quality oil. The key is to have high quality crude oil with low phospholipids. Otherwise the cost of hydrated silica can be prohibitive.

5.14 Modified physical refining process

This process is based on the fact that a certain amount of soap is required for the hydrated silica to adsorb phospholipids from the oil. Since no caustic is used in physical refining process (Section 5.10), hydrated silica becomes ineffective in the physical process and does not remove any amount of phospholipids from the oil. In the modified physical refining process, the oil is analyzed for ppm of phosphorus. The required amount of caustic solution is added to the oil to produce soap. The concentration of soap produced (ppm) must match the ppm of phospholipids in the oil. The oil and caustic solution are mixed in a high shear mixer. Hydrated silica is added to the oil in a vacuum vessel. The remainder of the process is similar (bleaching, and so forth) to the physical refining process.

Modified physical refining process also eliminates effluent discharge but removes more phosphorus and trace metals than the physical refining process.

Both the modified chemical and modified physical refining processes were first introduced by the W. R. Grace Company, the inventor of the hydrated silica, Trysil. Other companies later introduced their versions of similar refining techniques.

5.15 Dewaxing

Dewaxing (also called winterization) of sunflower oil is essential when the oil is to be used as salad oil. The presence of wax makes the oil appear cloudy at room temperature. The oil normally becomes cloudy in 5–6 h but with proper dewaxing the oil remains clear after 24 h of storage at 0°C. The following steps are used to dewax sunflower oil:

- Crude oil is refined and bleached to low phosphorus (< 1 ppm) and low moisture content ($< 0.1\%$).
- The oil is heated to 55°C to make sure the oil is fully liquid.
- The oil is cooled slowly to 7–8°C.
- Cooled oil is held in a specially insulated tank with a special slow-speed mechanical agitator.
- Preferably, the oil is held for 12–24 h at this temperature.
- The oil is mixed with diatomaceous earth through an in-line mixing system and filtered through a pressure leaf filter pre-coated with diatomaceous earth.
- The filtered oil is collected, checked for cold test and filterable impurities, and then deodorized.
- The deodorized oil is checked again for cold test along with the other analyses listed earlier.

5.16 Hydrogenation

In this process the oil is reacted with hydrogen gas in the presence of a nickel catalyst. The majority of the oil is hydrogenated in batch reactors, commonly referred to as 'converters'. Continuous reactors are used in rare cases. The reaction is started by heating the catalyst and the oil with hydrogen gas bubbling through with mechanical agitation.

The hydrogenation reaction is exothermic and therefore the temperature in the reactor rises as the reaction starts. The reaction is conducted isothermally with the reactor temperature maintained within $\pm 1^{\circ}C$ using cooling water through the coils in the reactor. The reaction is continued until it reaches the desired end-point in terms of iodine value or solids content. The reaction may also be conducted adiabatically. The temperature of the reactor is allowed to rise until the reaction end-point is reached. Again the reaction end-point is determined by either iodine value or solids content of the oil. Normally, the reaction is monitored by checking the refractive index of the oil in the reactor because this figure has a strong correlation with the degree of unsaturation. Progress of the reaction may also be controlled automatically using other parameters such as temperature, gas flow control, net volume of gas used in the reaction, agitation, and so on. The following events occur during hydrogenation:

- Unsaturated fatty acid, especially linoleic acid, reacts with hydrogen gas to form oleic acid or other 18:1 isomers. Some *cis–trans* isomers of linoleic acid are also formed.
- The iodine value of the oil is reduced.
- The refractive index of the oil falls linearly with iodine value.
- The level of *trans* fatty acids in the oil rises. This reaches a peak and then declines as the 18:1acids react with more hydrogen to form stearic acid.
- The solid fat content continues to rise and eventually reaches a plateau.
- The melting point of the oil rises with hydrogenation and reaches a maximum.
- The reaction eventually stops when the unsaturated fatty acid level falls to a very low level.
- The oil consists mainly of glycerol esters of stearic acid (and some palmitic acid) at this point.

Table 5.16 shows the changes in fatty acid composition in traditional sunflower oil during hydrogenation. The oil is hydrogenated to various end-points depending on its application in specific products, such as table margarine, baking and shortening.

Traditional sunflower oil needs hydrogenation for industrial frying applications. The industry generally hydrogenates the oil to reduce the iodine value from 130 (nominal) to 108–110. The author's experience suggests that the iodine

Table 5.16 Changes in fatty acid composition of traditional sunflower oil during hydrogenation

Iodine value	Palmitic (%)	Stearic (%)	Oleic* (%)	Linoleic (%)
131.5	6.7	5.0	19.5	67.9
125.3	6.7	5.2	37.2	50.0
113.9	6.7	6.1	42.6	43.7
103.2	6.7	6.6	55.5	30.3
93.5	6.7	7.1	60.4	24.9
83.2	6.7	9.5	70.1	12.8
75.2	6.7	12.9	72.1	7.4
66.4	6.7	19.8	67.3	5.3

*Including positional and stereochemical isomers of 18:1.

value of the partially hydrogenated sunflower oil should be 100. At this level the oil has superior oxidative stability and also provides good fried food flavor. NuSun and high-oleic sunflower oil can be used in industrial frying application without hydrogenation. This is an advantage because the hydrogenated frying oil from traditional sunflower contains fatty acids with *trans* unsaturation.

5.17 Summary

Sunflower oil has some unique characteristics that are popular with consumers, who use the oil in cooking and salad dressings. The oil can be used to make any product for the domestic or industrial food market. The plant is grown in limited areas in the world and this restricts the growth potential for the oil. There is tough competition from other crops in the regions where the sunflower is grown. The depressed oil price has encouraged some growers in the US and Argentina to shift to other crops, primarily to soybean. Unfortunately, this did not help the overall oil market because of over-production of soybean.

Central European and the former USSR countries suffer from the lack of funding to establish proper agricultural conditions and proper infrastructure for the growth of sunflower. The oil produced in these regions suffers from poor yield, inferior quality and lack of reliability in terms of supply. With organized effort, whether in a private or government-assisted program, these regions could become a vital players for the growth of sunflower production. The latest research in the US offers the opportunity of having conventionally bred sunflower varieties that are resistant to certain herbicides. This may bring revolutionary changes in the sunflower industry. In the US, sunflower oil has been an export oil with a premium price. It has not been able to compete with soybean oil in price in the domestic market. The drive for high PUFA margarine no longer exists. The entire margarine formulation has taken a different turn. There is more need for soft table margarine for health reasons. This product, as well as stick margarine, can be made more economically by using part liquid

soybean oil in the formula. Like soybean oil, sunflower oil lacks oxidative stability in frying applications. Therefore, the large industrial users have not had any strong incentive to use traditional sunflower oil in the US. High-oleic sunflower oil offers higher oil stability but the marketing model chosen by the owners of this type of seeds has made the oil very costly for the industrial food processors. They cannot use this oil and deliver finished products to consumers at a reasonable price. The high-oleic variety also suffers from serious reduction in yield, making it very difficult to be competitive in price. The impetus behind the NuSun development was to make the oil more attractive in the US by making it a commodity applicable for restaurants, food services, and industrial frying, areas where traditional sunflower oil has not been successful.

The varieties, developed by USDA and seed companies, have already shown good yield and other agronomic traits. NuSun oil production was nearly 171,000 tonnes in the crop year of 2001. This volume was reached only four years after the first commercial crushing in 1998. The oil has all the appeal of traditional sunflower oil, while at the same time it is more stable, does not require hydrogenation for industrial frying application, and will be sold as commodity oil. A worldwide expansion of the NuSun variety could perhaps provide the boost that the sunflower oil industry needs today.

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6 The lauric (coconut and palmkernel) oils

T. P. Pantzaris and Yusof Basiron

6.1 Introduction

The lauric oils stand apart in the world of oils and fats. There are few of them, they move on their own higher price plateau and they do not mix comfortably with the common commodity oils and fats. There are only two lauric oils among the 17 major oils and fats in world commerce: coconut oil (CNO) and palmkernel oil (PKO) (*Oil World Annual* 2001). They are called 'laurics' because lauric acid (12:0) is the major fatty acid in these oils. The laurics are comprised of about 50% of lauric acid, while no other oil contains more than 1% (except butter fat, which contains about 3%).

Of course, there are other lauric oils in local production—for example, babassu, tukum, murumuru, ouricuri, cohume and cuphea—but they are available only in small quantities and do not enter international trade. This chapter deals with CNO and PKO and, in particular, with those aspects of their composition and properties which significantly influence their processing or utilisation in the food industry. Their food applications are very similar and so, to avoid repetition, are dealt with together under palmkernel oil.

6.2 Coconut oil

6.2.1 Composition

6.2.1.1 Coconuts

Coconut oil is derived from copra, which is the dried kernel or 'meat' of coconuts. The coconut palm is the species *Cocos nucifera*, which grows well in the humid regions a few degrees' latitude either side of the equator. The usual tall variety reaches a height of over 20 m. Typically, fresh coconut kernel contains (% wt) moisture (50), oil (34), ash (2.2), fibre, (3.0), protein (3.5), and carbohydrate (7.3) (Hui 1996).

6.2.1.2 Copra

Copra has the highest oil content of all oil-bearing crops, with an oil content of 65–68% and moisture at 4–7%. It is overwhelmingly a South East Asian crop. According to *Oil World Annual* (2001), world production in 2000/2001, was 5.5 million tonnes (MT), of which about 94% was produced in South East Asia, 3.5% in Latin America and 2.5% in Africa. The largest producing countries, by

far, are the Philippines and Indonesia. Yields vary from 0.3 T/ha in Africa to 0.9 in Latin America, with a world average of 0.51 (5-year period 1996–2000) (see also Chapter 1).

The oil is usually extracted from copra by pressing in screw presses (expellers), often followed by solvent, and the oil yields obtained are fairly uniform from one country to another and from year to year. In 2000/2001, the world average oil yield from copra crushing was 62.4%.

6.2.1.3 Coconut oil

World CNO production in 2000/2001, was 3.4 MT or 3% of total oils and fats, which came to 117 MT. The largest producing countries and their exports are shown in Figure 6.1. It is seen that the Philippines produce most oil while the Philippines and Indonesia together account for 66% of production and 88% of exports.

World CNO production seems to be stationary, or if anything falling. Regression analysis over the past 16 years (1985–2000), shows a negative trend of −20,300 T per annum ($r = 0.309$), which is not significantly different from zero ($p > 0.1$). Also CNO production is more variable than that of other oils. Over the same 16-year period, the mean annual output was 2.9 MT and the coefficient of variation 10.8%. Large variations in production are disadvantageous for an oil as they make supplies uncertain, lead to greater price fluctuations, and oblige industrial users to re-formulate their products around alternative oils.

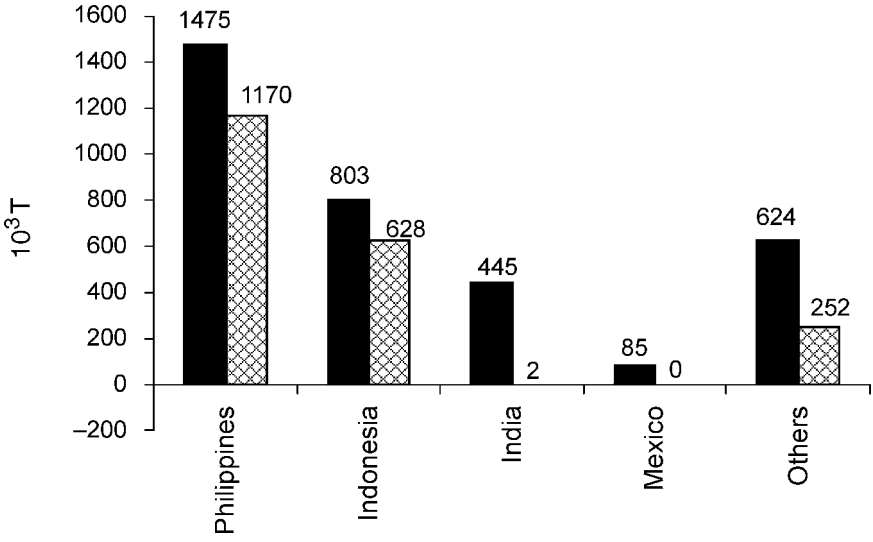

Figure 6.1 Coconut oil: major producing countries and their exports, 2000/2001 forecast. World production 3432 × 10^3 T, world exports 2052 × 10^3 T. Key: ■, production ▨, exports.

6.2.1.4 Composition

In addition to triacylglycerols and free fatty acids, crude CNO contains about 0.5% of unsaponifiable matter, though the Malaysian standard (MS239:1987) allows a maximum level of 0.8% and Codex (2001) up to 1.5%. This material consists mainly of sterols, tocols, squalene, colour compounds, carbohydrates and odour compounds (such as lactones). The pleasant odour and taste of CNO when the oil is extracted from fresh material is mainly due to γ- and δ-lactones, which are present in trace amounts (Young 1983).

6.2.1.5 Fatty acid composition

The lauric oils are characterised by their high level of the shorter and medium fatty acid chain lengths (C_6–C_{14}). These reach about 80% in CNO and about 70% in PKO while in the non-lauric vegetable oils they are below 2%. The major fatty acids are lauric (12:0) and myristic (14:0), at about 48% and 18% respectively, while no other fatty acid is present at more than about 8%. It is this heavy preponderance of lauric acid that gives CNO and PKO their sharp melting properties, meaning hardness at room temperature (20°C), combined with a low melting point (24–29°C). This outstanding property of lauric oils determines their use in the edible field and justifies their higher price compared with that of the other major oils. Because of their low unsaturation, the lauric oils are also very stable to oxidation. Coconut oil, with IV typically 8–9, is extremely stable. Stability values between 30 and 250 h (active oxygen method, AOM) have been reported for the crude oil (Young 1983, Swern 1979, p. 313) but 150 h is more typical. The stability of the refined oil is lower because of the loss of natural antioxidants during refining (around 33%) but much of the stability is restored after citric acid addition, which is a fairly standard practice in the deodorisation of oils. Very rarely, refined CNO develops a rubbery flavour within hours of deodorisation. The problem has been ascribed to the presence of sulfur compounds but it is very rare and has not been well studied.

The composition of CNO and other oils in respect of fatty acids, triacylglycerols, tocols, and sterols, was examined in a well-conducted series of surveys by the Leatherhead Food Research Association (LFRA), UK, commissioned partly by MAFF (Ministry of Agriculture, Fisheries and Food). In that study, LFRA (1989) tested a sample of 35 specimens from all the major origins between 1983 and 1988 and reported the mean, coefficient of variation, and range limits as well as all the individual results (Table 6.1).

Unfortunately, many researchers still report only the mean and range limits and do not cite the SD or even the sample size (number of specimens, *n*). Such information is of very limited value, since the range is only a crude and inefficient measure of variation and its expectation depends on *n*. With the mean, SD, and *n*, one can calculate statistical ranges, the probability of any particular deviation, and carry out many other powerful statistical assessments.

Table 6.1 Fatty acid composition (% mass) of CNO[a]

Fatty acid	Mean	CV[b] (%)	Range limits
6:0	0.4	32.7	tr–0.6
8:0	7.3	12.9	4.6–9.4
10:0	6.6	7.2	5.5–7.8
12:0	47.8	2.7	45.1–50.3
14:0	18.1	4.3	16.8–20.6
16:0	8.9	6.7	7.7–10.2
18:0	2.7	11.8	2.3–3.5
18:1	6.4	12.2	5.4–8.1
18:2	1.6	14.3	1.0–2.1
20:0	0.1	28.7	tr–0.2
Calc. iodine value	8.5	17.4	6.3–10.6
SMP[c] (°C)	24.1	2.5	23.0–25.0

[a]LFRA survey (1989) ($n = 35$).
[b]Coefficient of variation $= 100 \times$ SD/mean.
[c]Slip melting point, tr = trace.

Table 6.2 Fatty acid composition (% mass) of CNO (Codex 2001)

Fatty acid	Range limits
6:0	ND–0.7
8:0	4.6–10.0
10:0	5.0–8.0
12:0	45.1–53.2
14:0	16.8–21.0
16:0	7.5–10.2
18:0	2.0–4.0
18:1	5.0–10.0
18:2	1.0–2.5
18:3	ND–0.2
20:0	ND–0.2
20:1	ND–0.2
Others	ND
Iodine value	6.3–10.6

Source: Alinorm 01/17 Codex Alimentarius.
ND = not detectable (limit 0.05%).

Codex standards are becoming increasingly important in international trade and will continue to gain importance with time. The latest values from the 2001 Codex report (Codex 2001) are given in Table 6.2. Unfortunately, although there is some hope that Codex standards will be adopted as trading standards, in most cases the range limits they specify are the actual values to the exact decimal point reported on samples without any adjustment or rounding for the population parameters. Also, Codex standards do not take into account the fact that commercially traded oils can seldom be as pure as oils extracted in laboratories. Trading standards need wider limits and rounded values.

In respect of fatty acid composition (FAC), both CNO and PKO have about the same level of lauric acid (12:0). The main difference is that CNO has about twice as much caprylic (8:0) and capric acid (10:0) but half as much oleic acid (18:1). Before the advent of GLC it was difficult to test for adulteration or to distinguish between CNO and PKO in blends and use was made of the so-called Reichert and Polenske values, which are indicative of the short fatty acids present. These tests are highly empirical, laborious, and not very discriminating between CNO and PKO in blends with other oils. Though obsolete, they are still specified by Codex. The Reichert values for CNO and PKO are 6–8.5 and 4–7 respectively and 13–18 and 8–12 for the Polenske values. (Gunstone *et al.* 1994, pp. 61 and 85).

6.2.1.6 Triacylglycerol composition

The various triacylglycerols (TAG) of oils, may be separated and quantified by HPLC or by high-temperature programmed gas chromatography, according to their carbon numbers. The values obtained can then serve to distinguish them from other oils or to interpret their properties. Table 6.3 gives the TAG of CNO from the LFRA survey (1989, p. 37) of 34 specimens. It may be seen that in both CNO and PKO, the TAG range is C_{28} to C_{52} but CNO has more of the shorter chain lengths (C_{34} and below) and less of the longer chain lengths (C_{42} and above). The ratios of these two groups can be used to distinguish them from other lauric oils or from their own fractions.

In most cases, the triacylglycerol structure in terms of saturation is more useful in interpreting the physical properties of an oil and, for CNO, this was

Table 6.3 Triacylglycerol composition (carbon number, % mass) of CNO[a]

	Mean	CV[b] (%)	Range limits
C_{28}	0.8	16.7	0.5–10
C_{30}	3.5	15.5	2.6–5.0
C_{32}	13.4	10.5	10.8–17.5
C_{34}	17.1	6.9	15.6–20.1
C_{36}	19.1	3.3	18.3–20.6
C_{38}	16.5	3.8	15.1–18.0
C_{40}	10.2	6.4	8.4–11.9
C_{42}	7.3	9.0	5.5–8.8
C_{44}	4.1	11.7	2.8–4.7
C_{46}	2.5	16.8	1.6–3.0
C_{48}	2.1	20.1	1.2–2.6
C_{50}	1.5	28.1	0.7–2.0
C_{52}	1.2	45.1	ND–2.0
C_{54}	0.8	70.0	ND–1.7

[a]LFRA survey 1989 ($n = 34$); specimens collected in 1983 and 1988.
[b]Coefficient of variation = 100 SD/mean.
ND = not detected.

examined by fractional crystallisation methods in the later 1920s and middle 1940s (Hilditch and Meara 1945). It was concluded that the oil contained trisaturated (S_3) 84%, disaturated (S_2U) 12%, and monosaturated (SU_2) 4% triacylglycerols where S = saturated and U = unsaturated.

In the late 1960s, gas chromatography and its extensions enabled the complete characterisation of the triacylglycerols. It appears that CNO consists of 79 individual triacylglycerols with carbon numbers 28–52 and the major ones are approximately as follows (Bezard *et al.* 1971):

Trilaurin	L_3	> 10%
Caprodilaurin	CL_2	20%
Caprolauromyristin	CLM	12%
Dilauromyristin	L_2M	11%
Lauromyristopalmitin	LMP	< 3%
Caprolauroolein	CLO	4–5%

Symbols such as CLM include all the triacylglycerol isomers with these three acyl groups.

6.2.1.7 Tocols

The tocols (tocopherols and tocotrienols) are the most important class of antioxidants naturally present in vegetable oils and fats. Animal fats only contain trace amounts and this is reflected in their much lower oxidative stability compared with vegetable oils of equivalent degree of unsaturation. Bailey (1951, pp. 61–62) noted many years ago that at high levels tocols can act as prooxidants and that vegetable oils seem to contain near optimum levels for the their fatty acid composition.

Coconut oil has the lowest IV of all the 17 major oils and fats and contains only trace amounts of tocols. In a survey of 20 specimens, LFRA (1989) found a mean value of only 9.7 mg/kg and a range from 0 to 44 mg/kg, but the distribution was very skewed and 8 of the 20 specimens contained none at all. The main isomers present were α-tocopherol and α-tocotrienol (Table 6.4). The large variation in tocol levels found in different specimens of CNO and in oils in general is probably mostly due to the loss or destruction of tocols during handling and storage, since during autoxidation they are sacrificed first. The Codex (2001, p. 35) standard gives exactly the same range limits for the various tocols as the LFRA survey, except for the total tocol range which has been rounded to 0–50.

The various tocol isomers are forms of vitamin E, the most active of which is α-tocopherol. Relative to that, the activities of the other isomers vary from 0 to 50% (Sheppard and Pennington 1993).

As mentioned earlier, the oxidative stability of refined CNO, as measured by the AOM test, is greatly enhanced by addition of citric acid after deodorisation, which is virtually standard practice in industry. In the absence of natural antioxidants, the chelating action of citric acid on the pro-oxidant trace metals has a

Table 6.4 Tocol content of CNO[a]

	Mean[b]	Median[b]	SD[b]	Range limits[b,c]
Tocopherols (mg/kg)				
α-Tocopherol	3.2	ND	5.8	ND–17
β-Tocopherol	0.95	ND	2.5	ND–11
γ-Tocopherol	1.25	ND	3.4	ND–14
δ-Tocopherol	ND	ND		ND
Sub-total	5.5	1	8.0	0–31
Tocotrienols (mg/kg)				
α-Tocotrienol	4.2	ND	10.6	ND–44
β-Tocotrienol	ND	ND		ND
γ-Tocotrienol	ND	ND		ND–1
δ-Tocotrienol	ND	ND		ND
Sub-total	4.2	ND	10.5	ND–44
Total tocols	9.7	5	12.1	ND–44

ND=not detected.
[a]After LFRA Survey (1989) ($n = 20$).
[b]Calculated by the writer from the individual results in the LFRA report.
[c]The Codex draft standard in Alinorm 01/17, Table 4, gives the same range limits, except for total tocols, which are given as ND–50.

particularly strong effect. Similarly, it is known from practical experience that both CNO and PKO respond strongly to the addition of synthetic antioxidants such as BHA and BHT.

6.2.1.8 Sterols

Sterols are crystalline alcohols present in oils, either in the free form or esterified with fatty acids. In CNO they amount to about 1000 mg/kg (ppm) and make up about 20% of the unsaponifiable fraction. Those present in the major oils do not seem to have any strong effect on their behaviour, but they do have important nutritional effects. Cholesterol, for example, which occurs overwhelmingly in animal fats, elevates serum cholesterol, and recently it has been found that phytosterols reduce it. This has led to the appearance of phytosterol-enriched margarines on the market.

Leatherhead Food RA (1989, p. 41) reported the sterol level (mean and range) of 23 specimens of CNO from all major producing countries and Codex (2001) has adopted the same range limits (Table 6.5). The mean values were 836 mg/kg for desmethyl sterols, 39 mg/kg for monomethyl sterols and 146 mg/kg for dimethyl sterols.

The main sterols present are β-sitosterol and Δ^5-avenasterol.The presence or absence of individual sterols and their ratios can give important indications of

Table 6.5 Sterol composition of CNO sterol fraction (%) and total level (mg/kg oil)[a]

	Mean	SD[b]	Range limits	Codex range limits
Desmethylsterols				
LFRA ($n = 23$)				
Cholesterol	1.8	3.03	0.6–3.0	ND–3.0
Brassicasterol	0.4	0.26	ND–0.9	ND–0.3
Campesterol	8.8	1.10	7.5–11.2	6.0–11.2
Stigmasterol	12.7	2.19	11.4–15.6	11.4–15.6
β-Sitosterol	46.1	4.08	32.6–50.7	32.6–50.7
Δ^5-Avenasterol	27.4	4.69	20.0–40.7	20.0–40.7
Δ^7-Stigmasterol	0.3	0.94	ND–3.0	ND–3.0
Δ^7-Avenasterol	1.6	0.95	ND–3.0	ND–3.6
Unknown	0.9	1.00	ND–3.6	
Total (mg/kg oil)	836.4	163.40	470–1139	400–1200
Monomethyl sterols (*n*=4)	39.0	8.1	32–46	
Dimethyl sterols (*n*=3)	146	46	95–84	

[a]After LFRA Survey (1989) and Draft Codex (2001).
[b]Calculated by the writer from the individual results given in the LFRA report.
ND = not detected defined as $\leq 0.05\%$.

the authenticity of various oils and the composition of blends. Compared with PKO, CNO contains less sitosterol and more avenasterol.

6.2.1.9 Hydrocarbons

Hydrocarbons are the least polar of natural compounds but they form an important class of substances found in oils. The paraffinic hydrocarbons (alkanes) are the most important group.

The occurrence of normal alkanes in living matter was reviewed by Lester (1979). In most cases the major alkanes contain an odd number of carbon atoms and in higher plants, the typical range is *n*-C_{15} to *n*-C_{35}. In oils and fats, the alkane concentration and composition is to some extent dependent on the condition of the raw material from which the oil was extracted. It was shown, for example, that their concentration in crude PKO from fresh whole kernels, was 3.7 mg/kg, while that from low quality kernels was 15.4 mg/kg (Tan and Kuntom 1994). Also, processing of the oil has been shown to reduce the total hydrocarbon concentration by more than one third (Kuksis 1964).

Probably the most important concern about hydrocarbon levels in the oils and fats industry is in detection of contamination with petroleum products, which occasionally takes place during shipment or other handling of oils.

An extensive study of the *n*-alkane levels in various fats and some mineral oils has been published by the CSL Food Science Laboratory, Torry, UK (Moffat *et al.* 1995), and a summary of their findings is given in Table 6.6. The mean values ranged from 2.3 mg/kg in PKO and 7.7 mg/kg in CNO to 139.6 mg/kg in

Table 6.6 Sum of individual *n*-alkanes from C_{15} to C_{33} in crude oils (mg/kg or ppm)

Oil	Mean	SD	N
Coconut	7.7	6.6	4
Palmkernel	2.3	0.6	4
Corn	59.1	5.8	4
Groundnut	18.0	9.2	4
Palm	5.7	3.9	14
Sunflower	139.6	24.4	15
Soyabean	17.1	6.2	15
Rapeseed	83.9	7.0	15
Vegetable	4.2[a]	–	2
Lard	18.0[b]	23.5	6
Tallow	38.7	18.1	6
Fish	9.4	3.8	3
Crude petroleum	72,200	–	1
Diesel oil	148,562	–	1

Source: Moffat *et al*. 1995.
SD = standard deviation, N=sample size.
[a]Retail specimens.
[b]3 deodorised and 3 retail specimens.

sunflower oil. The levels in mineral oils were of a different order of magnitude (i.e. 72,000 to 149,000 mg/kg).

6.2.1.10 Chemical and physical characteristics

The major characteristics usually included in national and international standards and trading specifications and used for quality control in laboratories are as follows.

Those for crude oils include the free fatty acids (FFA), iodine value (IV), saponification value (SV), refractive index (RI), specific gravity (SG), unsaponifiable matter (US), and moisture plus impurities (M&I). These are intended to give a quick impression of the authenticity of the oil and the likely losses in refining. For refined oils, the values also usually include the colour, peroxide value (PV), slip melting point (SMP) and solid fat content (SFC), if appropriate. These are indications of quality and behaviour in use. As the SFC test relies on nuclear magnetic resonance, these values are also known as NMR or N values. The Malaysian standard for crude and refined CNO (MS1987) is shown in Table 6.7 and the Codex (2001) draft standard in Table 6.8.

6.2.1.11 Iodine value

The iodine value (IV) is primarily a measure of unsaturation, but in the case of unhydrogenated solid fats, it is also a very good measure of consistency. There is a strong correlation between the IV, the SMP, and SFC of unhydrogenated fats of the same species. The correlation applies also to hydrogenated oils,

Table 6.7 Malaysian standard MS 239 (1987): requirements for coconut oil

Characteristics	Crude		Refined
	Grade 1	Grade 2	
FFA (as lauric) (%) max	1.0	3.5	0.1
Moisture and Insol, impurities (%) max	0.50	*	0.10
Iodine value (Wijs)	7.5–10.5	*	*
Colour ($5\frac{1}{4}''$) Lovibond cell, max	3R	4R	1.5R
Refractive index at 40°C	1.4480–1.4490	*	*
Spec. gravity at 30/30°C	0.915–0.920	*	*
Saponification value (mgKOH/g)	248–264	*	*
Unsaponifiable matter (%) max	0.8	*	0.5

*As for grade 1.

Table 6.8 Codex (2001) draft standard for CNO

Chemical and physical characteristics			
Relative density 40/20°C			0.908–0.921
Refractive index (N_D40°C)			1.448–1.450
Saponification values (mgKOH/g)			248–265
Iodine value			6.3–10.6
Unsaponifiable matter (g/kg)			≤ 15
Quality characteristics (apply to both CNO and PKO)			
Matter volatile at 105°C			0.2% m/m
Insoluble impurities			0.05% m/m
Soap content			0.005% m/m
Iron (Fe)			
virgin oil			0.5 mg/kg
refined oil			5.0 mg/kg
Copper (Cu)			
virgin oil			0.1 mg/kg
refined oil			0.4 mg/kg
Acid value			
virgin oil			4.0 mg KOH/g oil
refined oil			0.6 mg KOH/g oil
Peroxide value			
virgin oil			up to 15 me/kg
refined oil			up to 10 me/kg
	CNO	PKO	
Reichert value	6–8.5	4–7	
Polenske value	13–18	8–12	

provided they have been processed under the same selectivity conditions. This is because *cis* and *trans* isomers have the same IV but very different consistency. Use is made of this relationship in controlling the hydrogenation reaction, which requires quick tests. The IV test, when accelerated by the use of mercuric acetate,

can be performed in about five minutes which is much faster than the mp and also has a smaller experimental error. In our experience the IV test is the best method of control for the hydrogenation of lauric and many other oils.

The Codex draft standard (Table 6.8) specifies the IV range of CNO as 6.3–10.6, while both the Malaysian Standard (Table 6.7) and the MEOMA trading specification give 7.5–10.5, a considerably narrower range. Oil of lower IV comes from kernel meat which has had the testa (the thin brown layer between kernel and shell) pared off, as in the production of desiccated coconut. This 'parings oil' has an IV of about 48–50 (Hui 1996, p. 100).

6.2.1.12 Melting point

Melting point (mp) is undoubtedly the most widely used measure of the consistency of oils and fats. It is always specified for refined fats in commercial transactions and it is also the one giving rise to most problems in the quality control laboratories of end-users. The test is highly empirical, it has a large experimental error, and there are many versions of it—a good indication that none of them is entirely satisfactory. The underlying reason for this is that fats, being mixtures of triacylglycerols, do not melt sharply at a single temperature like pure organic compounds, but do so progressively over a temperature range. For lauric oils, which melt relatively sharply, this is much less of a problem.

Widely used methods in the past were the Wiley mp in the US and the complete fusion in Europe but more recently, the AOCS method Cc 3-25 for the slip melting point (SMP), has been rapidly gaining acceptance, especially in international transactions. Unfortunately, although there is a broad correlation between the results of the various methods, there is no exact conversion equation valid for all oils, because each method measures a different point on the melting curve and the curves have different slopes.

One might expect that there would be reasonable relationship between the mp and the SFC at that temperature. According to our assessment of a large number of data, the SMP usually corresponds to a SFC of about 5% but this figure is not constant and varies somewhat from one fat to another. Some SFC values we found were 3.1% for CNO ($n = 38$), 2.3% for HCNO ($n = 32$), 6.5% for PKO ($n = 118$) and 4.7% for HPKO IV1 ($n = 141$) but some individual specimens gave large deviations. Neither Codex, the Malaysian Standard or MEOMA specify a mp for CNO but the LFRA survey found a mean value of 24.1°C (Table 6.1), while a collection of specimens from industry in the UK showed 24.7°C (Table 6.9). The agreement is quite good in view of the fact that these were different samples, tested by different laboratories, over different periods of time.

6.2.1.13 Solid fat content

The melting point gives only limited information of the consistency of a fat, as it only measures one point near the end of the melting curve and fats of the

Table 6.9 Melting characteristics of RBD CNO[a]

	Mean	Median	SD	Range limits
Iodine value	8.45	8.40	0.530	7.5–10.5
Slip melting point	24.7	24.7	0.18	24.2–25.0
N20[b]	35.6	35.9	1.58	32.0–39.5
N25	1.0	0.9	0.85	0–3.5

[a]Specimens from UK industry ($n = 38$).
[b]N20 etc = NMR value (or SFC) at 20°C.

same melting point can have widely different consistency at room temperature. The most satisfactory measure of consistency is the SFC, which can give the complete melting profile of a fat. The SFC method is based on NMR effects, and should not be confused with the older solid fat index (SFI) method, also known as solid content index (SCI), which was based on dilatometry. Nevertheless, there is a fairly good correlation between the results of the two methods, but the conversion equations depend on the type of fat and the temperature and so they are rather clumsy. For lauric oils and similar confectionery fats, the conversion tables, used by a multinational company in the EU, were consistent with the following equations:

$$\begin{aligned} \text{SFC} &= \text{D20}/18.62 - 4.5, \\ &= \text{D25}/20.19 - 3.4, \\ &= \text{D30}/23.98 - 1.1, \\ &= \text{D35}/27.08 - 1.0, \\ &= \text{D40}/29.33 - 0.9 \\ \text{D} &= \text{dilation value } \mu\text{l}/\ 25\ \text{g fat} = 25 \times \text{SFI} \end{aligned}$$

Solid fat content values are usually only specified for refined oils since that is the grade of relevance to end users. Those for refined CNO are shown in Table 6.9. In most cases, they can also be assumed to be the same for the crude oil, unless its FFA is very high. Fatty acids and especially partial glycerol esters have different SFC from triacylglycerols. Lauric oils form strong eutectics with non-lauric oils, affecting the SFC at certain temperatures. Figure 6.2, for blends of CNO and PO, shows a strong eutectic at 20°C for the 50/50 blend but none at 30°C. This property has been utilised to produce soft blends of high oxidative stability, for example, for spraying oils for savoury biscuits.

6.2.1.14 Other physical characteristics

Other physical characteristics of CNO (Table 6.10) such as viscosity, density, heat capacity (specific heat) and heat of fusion, are important, not only for theoretical considerations but also for plant design and engineering purposes in general. Viscosity is an important property, which determines, for example, the diameter of pipes and the power needed when oils are pumped or stirred.

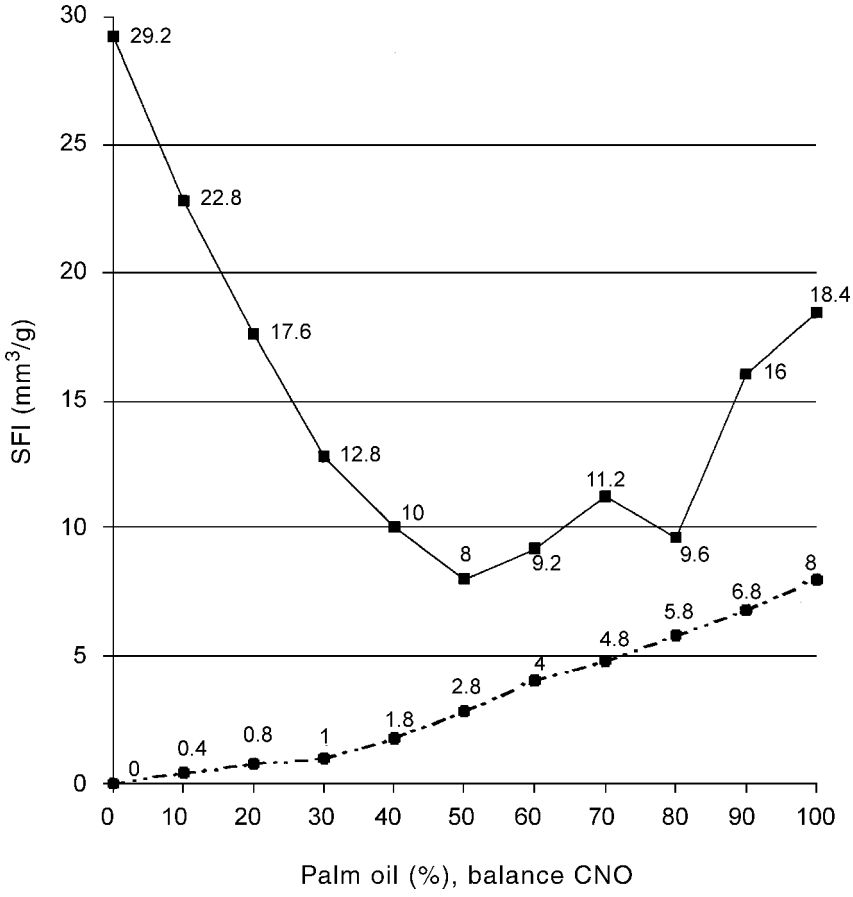

Figure 6.2 Eutectic formation coconut oil/palm oil blends, from author's data. Key: -●-, 30°C; —■—, 20°C.

Viscosity is also important for mouth feel. When consumers say they prefer a 'light' oil for example, they really mean one of low viscosity. Viscosity also affects the rate of oil draining from fried foods and consequently, the oil content and taste sensation obtained. In a homologous series of compounds, viscosity increases directly with the molecular weight and inversely with unsaturation. The laurics are among the least viscous of oils but differences among most food oils are small. Hydroxyl groups in the molecule as in castor oil, and polymerisation as occurs in frying, greatly increase viscosity.

A word is needed on specific heat. When liquid oils are heated, only the specific heat is involved but oils in storage tanks often solidify and solid fats need both the specific heat and the latent heat of fusion, which is much larger.

Table 6.10 Miscellaneous physical properties of coconut oil

Parameter	Value	Reference
Boiling point (°C) at 760 mmHg	298.9[a]	Swern 1979, p. 178
Boiling point (°C) at 1 mmHg	130.2[a]	Swern 1979, p. 178
Dielectric constant, approx	3.1	Swern 1979, p. 226
Heat of combustion (cal/g)	9020	Swern 1979, p. 196
Heat of fusion (cal/g) 46.3°C	46.2[b]	Swern 1979, p. 199
Heat of vaporisation (cal/g)	69[a]	Swern 1979, p. 209
Heat of vaporisation (cal/g)	51[b]	Swern 1979, p. 209
Kin. viscosity (C. Stokes) (37.8°C)	29.79	Swern 1979, p. 178
Kin. viscosity (C. Stokes) (98.9°C)	6.06	Swern 1979, p. 178
Refractive index (n_D 40°C)	1.448–1.450	Codex 2001
Rel. density (40°/20°C)	0.908–0.921	Codex 2001
Setting point (°C)	21.8–23.0	Swern 1979, p. 317
Slip melting point (°C)	23.0–25.0	LFRA 1989, p. 25
Specific gravity (20°/4°C)	0.9226	Swern 1979, p. 178
Specific gravity change/°C	7.13×10^{-4}	Cocks and Van Rede 1966, p. 84
Specific heat (cal/g) 66°C	0.510[b]	Swern 1979, p. 198
Specific heat (cal/g) 97°C	0.530[b]	Swern 1979, p. 198
Thermal conductivity (BTU/h.ft^2 °F.ft)[c]		
72.5°C	0.111[a]	Swern 1979, p. 211
148°C	0.0803[a]	Swern 1979, p. 211
Titre (°C)	20–24	Swern 1979, p. 317
Vapour pressure (mmHg) 188°C	0.001[b]	Swern 1979, p. 205
Vapour pressure (mmHg) 244°C	0.05[b]	Swern 1979, p. 205

[a]Lauric acid.
[b]Trilaurin.
[c]=1 BTU/h.ft^2 °F. ft=1.731 W/hm°C.

However, in general, fats are far from completely solid at ambient temperatures and the SFC must be taken into account in the calculations.

6.2.1.15 Trade specifications

The specifications and test values of oils given in various surveys and in the national and international standards (such as Codex), provide a useful insight into their properties and can be used as guides for good quality. However, they are intended to be advisory only and are not implied in any contract, unless they are specifically included. Commercial contracts are normally based on trade specifications which give rounded values for a few basic characteristics. The specifications of the Malaysian Edible Oil Manufacturers' Association (MEOMA 2001) for crude and refined CNO are shown in Table 6.11 and those of a major EU refiner for both refined and hydrogenated CNO are shown in Table 6.12.

Trade specifications show what is possible on the industrial scale. A very common mistake made by end-users is to ask for some small change or a narrower range in a particular property of commodity oils. This is nearly always

Table 6.11 MEOMA specifications for crude and refined CNO: for export market (MEOMA 2001)

	Parameter	Value
Crude coconut oil, Grade 1	FFA (as lauric acid)	1.0% max
	Moisture and Insol.	0.5% max
	Iodine value (Wijs)	7.5–10.5
Crude coconut oil, Grade 2	FFA (as lauric acid)	3.5% max
	Moisture and Insol.	0.5% max
	Iodine value (Wijs)	7.5–10.5
RBD coconut oil	FFA (as lauric acid)	0.1% max
	Moisture and Insol.	0.1% max
	Iodine value (Wijs)	7.5–10.5
	Colour ($5\frac{1}{4}''$ Lovibond cell)	Red 1.5 max

Source: Handbook of Malaysian Edible Oil Manufacturers Association, 2000–2001, Kuala Lumpur, Malaysia.

Table 6.12 Selling specification[a] for RBD CNO and HCNO[b]

Characteristics	RBD CNO	RBD HCNO
Colour ($5\frac{1}{4}''$) Lovibond cell, max	1.2R–4.5Y	1.2R–4.5Y
FFA (lauric) (%) max	0.1	0.1
PV (me/kg) max	1.0	1.0
Iodine value (Wijs)	7–10	0–2
Sap. value (mgKOH/g)	255–260	255–260
Setting point (°C)	–	27–28
Slip point (°C)	24–26	32–34
N 20[c]	34–41	53–61
N 30	max 0.6	3.5–6.0
N 40	–	max 0.6

[a]After data from major EU manufacturer.
[b]Hydrogenated CNO.
[c]N 20 etc = NMR value (SFC) at 20°C.

impossible. Firstly, oils and fats are natural products and most of their properties are fixed by nature. Secondly, even for those properties which can be controlled by the refiner by selection or special processing, the changes would be disproportionately expensive to implement in large-scale continuous plants, except where very large orders are involved.

6.2.2 Processing and applications

6.2.2.1 Hydrogenation

Coconut oil with IV of only about 8 is not changed much by hydrogenation. Even with full saturation its SMP only rises from around 24° to about 34°C. For this

Table 6.13 Melting characteristics of HCNO[a]

Parameter	Mean	Median	SD	Range limits
Iodine value	0.80	0.75	0.481	0.0–2.0
Slip melting point	34.4	34.7	1.46	30.75–36.75
N20[b]	53.9	53.9	1.86	51.0–59.0
N25	15.0	15.0	2.03	11.0–20.0
N30	4.5	4.5	1.15	2.5–6.5
N35	2.0	2.0	0.77	0.5–3.5

[a]Specimens from UK industry ($n = 32$).
[b]N20 etc=NMR value or SFC (%) at 20°C.

reason it is usually fully hydrogenated to IV about 1 and intermediate products, if required, are made by blending with soft (unhydrogenated) oil. In industry and commerce unhydrogenated oils are called 'soft' and hydrogenated ones 'hard' or 'hardened'. At such low IV, the *trans* fatty acid content is negligible and catalyst selectivity or hydrogenation conditions are of little consequence. For this reason, in lauric oils, the mp, SFC and IV are highly correlated and their inter-relationships can be used to detect admixtures or to assess the quality of fractionated fats and so on.

Some important characteristics of HCNO, based on our assessment of data on 32 specimens from the UK industry, are shown in Table 6.13 and may be compared with those of unhydrogenated CNO in Table 6.9. A point worth noting is that, for HCNO, mp values of well above 40°C sometimes seen in the literature must be wrong even if they refer to complete fusion.

6.2.2.2 Interesterification

The interesterification process has not found any significant application to CNO itself. The most important property of CNO and HCNO is their short plastic range and interesterification does not improve this very significantly. Nevertheless, some interesting products can be made by interesterfication of blends of CNO or PKO with palm oil and palm stearin to produce margarine fats, and these are described under PKO.

6.2.2.3 Fractionation

Although fractionation of CNO is not carried out on any large scale, coconut stearin is produced on a small scale in the EU, US, and probably elsewhere. It is an exceptionally sharp-melting product. The yield of stearin from CNO fractionation is much less than is obtained from PKO and so the product tends to be relatively expensive. The major characteristic values of CNO stearin produced by a major EU manufacturer are shown in Table 6.14.

6.2.2.4 Food applications of CNO

Coconut oil is very extensively used for food products and has a high quality image but its oleochemical use is probably almost as large. As only its food

Table 6.14 Typical characteristics of RBD coconut stearin[a]

Parameter	
PV (me/kg) max	1.0
Iodine value (Wijs)	4–7
Slip melting point (°C)	28
N20[b]	47
N25	26
N30	4
N35	0

[a]Data from a major EU manufacturer.
[b]N20 etc = NMR value or SFC (%) at 20°C.

applications are of concern to us here and since these overlap to a very large extent with those of PKO, they are discussed together in Section 6.3.

6.3 Palmkernel oil

6.3.1 Composition

6.3.1.1 Origin

Palmkernel oil (PKO) is the smaller of the two lauric oils among the 17 major oils and fats in world production, coconut oil (CNO) being bigger by about 20% (*Oil World* 2001). The two oils have very similar fatty acid composition and both are derived from the fruit of palm trees, but they belong to different species. The coconut palm is *Cocos nucifera* while the oil palm, which gives both palm oil (PO) and PKO is *Elaeis guineensis* (Hartley 1988). This tree is generally believed to have originated in the humid jungle forests of East Africa and there is some evidence that palm oil derived from the flesh of the fruit may have been consumed in Egypt at the time of the Pharaohs, some 5000 years ago (Raymond 1961).

The variety cultivated in nearly all the world's plantations is the hybrid *Tenera*, which is the cross between the varieties *Dura* and *Pisifera* and gives the highest yield of oil per hectare of any crop. The economic efficiency of the oil palm is easily seen from the following simple calculation. Soyabean cultivation in the US, for example, gives a yield of about 2.5 T of beans per hectare (1 hectare is 2.47 acres), which then gives about 0.5 T of oil and 2 T of meal. Taking the value of the meal as about half that of the oil, the total income to the farmer is equivalent to 1.5 T of oil. In South East Asia, the oil palms yield about 4 T of palm oil, plus 0.5 T of PKO, plus 0.5 T of palmkernel meal (PKM), with income equivalent to 4.5 T of oil.

6.3.1.2 The palm fruit

The palm fruit is oval shaped, about 3 cm long and looks like a small red plum. The outer fleshy mesocarp gives the PO while the kernel, which is inside a hard

shell, gives the PKO. The two oils from the same fruit are entirely different in fatty acid composition. Unfortunately, these oils have often been confused and this has led to some grossly erroneous statements.

The palm fruit is formed in large clusters of 15–25 kg each, called fresh fruit bunches (FFB), which grow and mature on the tree progressively, so that harvesting is done throughout the year, every 10–14 days. The average yield from an FFB, is about 19% PO and 5.5% kernels (PK) (Malaysia 2000 average) and are called the oil extraction ratio (OER) and kernel extraction ratio (KER) respectively. They are very important parameters in plantation economics.

In commercial crushings, the ratio of PO/PKO obtained from the fruit is about 8:1—a useful fact for oil traders to remember when they try to estimate production from incomplete data.

6.3.1.3 Palmkernels

After harvesting, the FFBs are quickly transported to the PO mill where they are sterilised with steam and the fruit stripped off. The fruit is then pressed to obtain PO from the fleshy mesocarp. The nuts are hard and survive the pressure unbroken. They are separated from the fibres, cracked to remove the shell, and dried to a moisture content below 8% to prevent mould growth.

The PK which contain about 50% of oil (on dry basis) are then crushed in screw presses (expellers) to yield PKO and PKM. The PKM from the presses can be solvent extracted to recover more oil but this process is no longer economically viable and is becoming obsolete. The average commercial yield from PK crushings is 45% PKO and 53% PKM, the balance being process loss (Malaysia, 2000 average).

In 2000, world PK production reached 6.5 MT, of which 84% was produced in South East Asia, 11% in Africa and 5% in Latin America. The largest producing countries are Malaysia and Indonesia, which together, account for nearly 80% of the world total.

6.3.1.4 Palmkernel oil

In 2000/2001, world PKO production came to 2.9 MT or 2.5% of total oils and fats. The largest producing countries and their exports are shown in Figure 6.3. It is seen that, as in the case of palmkernels, the major countries involved are Malaysia and Indonesia which together account for 78% of production and 90% of exports.

World palmkernel oil production has been growing faster than the total oils and fats, the respective annual growth rates over the past 10 years being 6.2% and 3.6%, while CNO production has not shown any growth. For the two lauric oils combined, the annual growth rate has been 3.5%, about the same as for the total oils and fats.

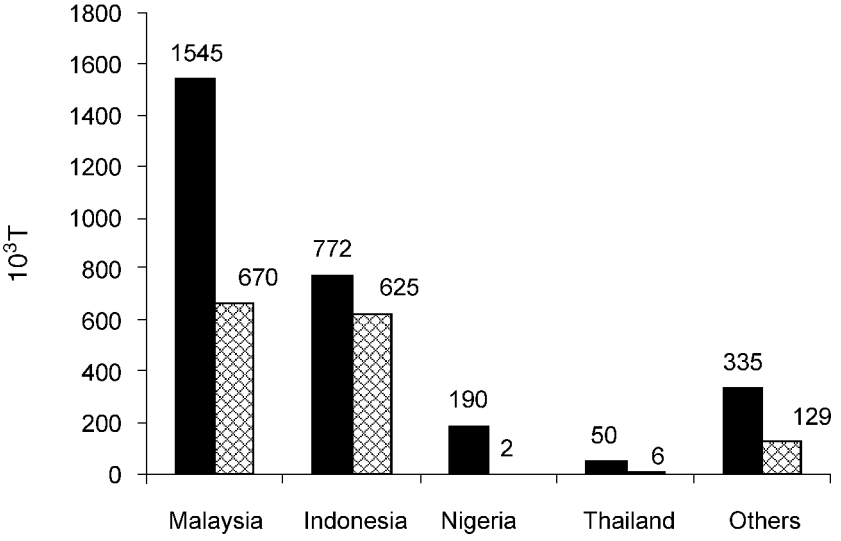

Figure 6.3 Palmkernel oil: major producing countries and their exports 2000/2001 forecast. World production 2892 × 10^3 T, world exports 1432 × 10^3 T. Key: ■, production; ▨, exports.

6.3.1.5 General composition

The fatty acid composition and properties of PKO are very similar to those of CNO. The main difference is that PKO has a little less of the shorter chain fatty acids, C_8 and lower, and higher unsaturation, with typical IV 18.5 against 8.5 for CNO. In the past, before the introduction of GLC, the Reichert and Polenske tests were used to distinguish PKO from CNO (see Section 6.2.1.5). These tests were used to measure the levels of the short-chain fatty acids. The introduction of GLC has now made them obsolete but they are still specified by Codex.

The major fatty acids in PKO are C_{12} (lauric acid) at about 48%, C_{14} (myristic acid) at about 16% and 18:1 (oleic acid) at about 15% (Codex 2001). No other fatty acid is present at more than 10%. The heavy preponderance of a single saturated fatty acid, combined with low levels of unsaturation, gives the oil its steep melting profile.

Besides triacylglycerols and FFA, crude PKO contains about 0.8% unsaponifiable matter such as sterols, tocols, triterpene alcohols, hydrocarbons and lactones.

Even after full hydrogenation, the melting point of PKO does not rise much above mouth temperature and fractionation gives a stearin (PKOs) with even sharper melting. Fats melting sharply just below mouth temperature leave a clean, cool, non-greasy sensation on the palate, impossible for any of the common non-lauric oils to match. Cocoa butter is the only other natural fat with

similar properties but it is very much an expensive speciality fat and is not included among the 17 major oils and fats in world trade.

The best method of assessing the sharpness of melting of a fat is organoleptically by a trained panel or, even better, by an outstanding individual. But the information so obtained cannot be communicated or stored in quantitative terms and so use is made of the solid fat content (SFC) at various temperatures. Even this method, however, lacks the simplicity and clear message of a single number.

6.3.1.6 Fatty acid composition

In 2001, about 50% of world PKO production and exports were of Malaysian origin. A well-conducted large survey of oil from that source was undertaken by PORIM* (now MPOB) in 1981, based on 118 specimens of commercially produced oil from 16 mills. This was followed by a smaller survey with 68 specimens in 1984. Both were reported by Siew and Berger (1986). The results of the two surveys were quite similar and so for the sake of simplicity, they have been combined in Table 6.15.

Another well conducted survey of PKO, with 71 specimens from 18 origins, was reported by LFRA (1989), with the oil extracted from the kernels in the laboratory to ensure purity (Table 6.16). This is the same report mentioned earlier under CNO. The only weakness of this study was that the number of specimens from each origin was not weighted in proportion to the level of production

Table 6.15 Fatty acid composition (% mass) of Malaysian PKO[a]

Fatty acid	Mean	SD	Range limits ($n = 186$)
6:0	0.3	0.07	0.1–0.5
8:0	4.4	0.47	3.4–5.9
10:0	3.7	0.24	3.3–4.4
12:0	48.4	0.94	46.3–51.1
14:0	15.6	0.33	14.3–16.8
16:0	7.7	0.36	6.5–8.9
18:0	1.9	0.19	1.6–2.6
18:1	15.0	0.74	13.2–16.4
18:2	2.7	0.22	2.2–3.4
Others	0.2	0.09	tr–0.9
Iodine value (Wijs)	17.8	0.57	16.2–19.6
SMP (°C)	27.3	0.33	25.9–28.0
Sap. value	245	1.4	243–249
Unsap. (%)	0.3	0.16	0.1–0.8

tr = trace; SMP = slip melting point; Sap. values = saponification value; Unsap. = unsaponifiable matter.

[a]Combined PORIM surveys of 1981 ($n = 118$) and 1984 ($n = 68$) (Siew and Berger 1986).

Table 6.16 Fatty acid composition (% mass) of PKO[a]

Fatty acid	Mean	CV[b] (%)	Range limits
6:0	0.2	60.9	ND–0.8
8:0	3.3	13.4	2.1–4.7
10:0	3.5	9.0	2.6–4.5
12:0	47.8	3.7	43.6–53.2
14:0	16.3	2.6	15.3–17.2
16:0	8.5	7.3	7.1–10.0
18:0	2.4	15.1	1.3–3.0
18:1	15.4	9.2	11.9–19.3
18:2	2.4	16.2	1.4–3.3
Calc IV[c]	17.55	7.9	14.1–21.0
SMP[d]	26.4	3.5	24.0–28.3

[a]Leatherhead Food RA Survey (1989) ($n = 71$).
[b]Coefficient of variation CV = 100 × SD/mean.
[c]Iodine value calculated from the fatty acid composition.
[d]Slip melting point.

Table 6.17 Fatty acid composition (% mass) of PKO[a]

Fatty acid	Range limits	Mid point[b]
6:0	ND–0.8	0.4
8:0	2.4–6.2	4.3
10:0	2.6–5.0	3.8
12:0	45.0–55.0	50.0
14:0	14.0–18.0	16.0
16:0	6.5–10.0	8.25
16.1	ND–0.2	0.1
18:0	1.0–3.0	2.0
18:1	12.0–19.0	15.5
18:2	1.0–3.5	2.25
Iodine value	14.1–21.0	17.55

[a]Codex (2001) draft standard.
[b]Calculated by the writer.
ND = not detectable.

of the country. However, in practice, this is of small consequence, since the composition of all origins is very similar. Nevertheless, it may be noted that in most tests the SDs of the results of the LFRA survey are larger than those of the PORIM survey. With rapidly increasing international trade in commodities, the Codex Alimentarius standards (Table 6.17) are gaining in importance. Even though they are meant to be only advisory and expressly not for enforcement by governments, customs authorities at some ports do, nevertheless, enforce them and trade arbitrators rely on them for their decisions. Their strong points are that they have an official status, are recognised by most countries, and are easily available.

6.3.1.7 Triacylglycerol composition

The properties of oils depend more on their triacylglycerols than on their fatty acids. The problem is that their determination in terms of component fatty acids and position on the glycerol moiety is more difficult, and the number of individual triacylglycerols is far greater than the number of fatty acids, which make comparisons difficult. For example, 6 different fatty acids can give 216 (6^3) chemically different triacylglycerols. Usually therefore, the triacylglycerols are determined in groups based on their carbon numbers, which reduces their number considerably but makes the interpretation of oil properties more difficult. Carbon numbers for saturated and unsaturated fatty acids are the same and the same triacylglycerol carbon number can be made up of different fatty acids.

The triacylglycerol composition of PKO in terms of carbon number, as found in the LFRA survey (LFRA 1989), is shown in Table 6.18. It may be seen that both PKO and CNO have the same range of carbon numbers C_{28}–C_{52} but PKO has less of C_{34} and below and more of C_{42} and above. The triglyceride composition of Malaysian PKO, as found in the PORIM surveys, is quite close to that in the LFRA, which confirms that, as expected, regional variations are small—the same (*Tenera*) hybrids growing in countries with similar climates. The Codex standards do not include the triacylglycerol composition of oils.

6.3.1.8 Tocols

The tocols (tocopherols and tocotrienols) are the most important class of natural antioxidants present in the unsaponifiable fraction of oils. Refining of the crude oil reduces the tocol level by about one third depending on process conditions

Table 6.18 Triacylglycerol composition carbon numbers (% mass) of PKO[a]

Carbon number	Mean	CV[b] (%)	Range limits
28	0.6	45.8	0.3–2.2
30	1.4	18.2	0.9–2.6
32	6.5	10.7	4.8–8.0
34	8.5	8.9	6.2–10.0
36	21.6	5.8	16.6–24.1
38	16.4	3.9	13.2–17.6
40	9.8	3.7	8.3–10.5
42	9.1	4.1	8.2–9.8
44	6.6	6.2	5.5–7.4
46	5.4	8.4	4.1–6.5
48	6.1	10.4	4.7–7.6
50	2.6	22.1	1.6–5.8
52	2.7	30.9	1.5–7.8
54	2.7	31.2	1.7–7.9

[a]LFRA survey 1989 ($n = 66$).

[b]Coefficient of variation $= 100 \times$ SD/mean.

Table 6.19 Tocol content of PKO[a]

	Mean[b]	Median[c]	SD[b]	Range[c]
Tocopherols (mg/kg)				
α-Tocopherol	2.2	0	7.8	ND–44
β-Tocopherol	21.0	6	47.5	ND–248
γ-Tocopherol	8.7	0	44.6	ND–257
Sub-total	31.9	10	63.6	ND–257
Tocotrienols (mg/kg)				
γ-Tocotrienol	2.3	0	10.5	ND–60
Total tocols	34.2	10	63.8	ND–257

[a]After LFRA Survey (1989) ($n = 33$).
[b]The values in this table have been calculated by the writer from the individual results in the LFRA report.
[c]The Codex draft standard in Alinorm 01/17, Table 4, gives the same range limits, except for the total tocols which are given as ND–260.
ND = Not detected.

(especially deodorisation temperature) but much is also lost through aeration or ageing of the oil.

The tocol composition of PKO has been reported in the LFRA survey (LFRA 1989) on 33 specimens. As the report only gives the values of the individual specimens, we have calculated the mean, SD and range limits (Table 6.19). It may be seen that the isomers present are α, β, γ-tocopherol and γ-tocotrienol but the latter was only present in four of the 33 specimens. The presence and level of tocotrienols in PKO can therefore be used as a test for (though not proof of) adulteration with palm olein, the most likely adulterant.

Codex (2001) have adopted the same range limits, except for the total tocol maximum, which has been rounded to 260 mg/kg from 257 mg/kg in the LFRA survey.

6.3.1.9 Sterols

Sterols are crystalline alcohols which in PKO, as in CNO, account for about 20% of the unsaponifiable fraction. Their role in the properties of oils is not fully understood but, as mentioned earlier, they do have nutritional effects.

The LFRA (1989) survey has reported the sterol content in a sample of 24 PKO specimens and its range limits were subsequently incorporated in the Codex draft standard (Codex 2001) (see Table 6.20). Total sterols amount to about 1000 mg/kg of oil and the major ones present are β-sitosterol (about 70% of the total), stigmasterol (about 15%), and campesterol (about 10%). Compared with CNO, PKO contains more sitosterol and less avenasterol. The ratio β-sitosterol/δ-5-avenasterol is below 2 in CNO and above 10 in PKO. For comprehensive data on the composition of oils, see Gunstone and co-workers (1994).

Table 6.20 Sterol composition of PKO sterol fraction (%) and total level (mg/kg oil)[a]

	Mean (%)	SD[b]	Range limits	Codex range limits
Desmethyl sterols				
LFRA ($n = 24$)				
Cholesterol	1.6	0.58	0.6–3.7	0.6–3.7
Brassicasterol	0.1	0.10	ND–0.8	ND–0.8
Campesterol	10.0	1.07	8.4–12.7	8.4–12.7
Stigmasterol	13.8	1.25	12.0–16.6	12.0–16.6
β-Sitosterol	67.6	2.8	62.6–73.1	62.6–73.1
δ-5-Avenasterol	5.8	1.90	1.4–9.0	1.4–9.0
δ-7-Stigmasterol	0.5	0.56	ND–2.1	ND–2.1
δ-7-Avenasterol	0.1	0.29	ND–1.4	ND–1.4
Others	0.6	0.55	ND–2.7	ND–2.7
Total (mg/kg oil)	1056	–	792–1406	700–1400
Monomethyl sterols ($n = 5$)	18.4	10.8	9–34	
Dimethyl sterols ($n = 3$)	142.3	23.7	116–162	

[a]After LFRA Survey (1989) and Draft Codex (2001).
[b]SD = standard deviation, calculated by the writer from the individual results in the report.
ND = not detectable.

6.3.2 Properties

6.3.2.1 Chemical and physical characteristics

Under this heading are included the characteristics usually specified in national and international standards and trading specifications. These are the values most often used in the quality control laboratories of oil processors and users. For a general discussion of IV, mp and SFC, see also under CNO (Sections 6.2.2.2 to 6.2.2.4).

The Malaysian standard for crude PKO (CPKO), MS80:1987 (Table 6.21) is based on the results of the 1981 survey carried out by PORIM (now MPOB), which tested 118 specimens from various locations throughout the country. It gives not only the mean and range values but also the standard deviation (SD) and sample size, which makes it more useful than most of the standards for other oils, which only give ranges (the crudest measure of variation). The Codex (2001) draft standard for these characteristics is shown in Table 6.22. This is less comprehensive than the Malaysian standard. For example, it does not include the very important characteristics of SMP and SFC and it has much wider ranges. Narrow ranges ensure a purer product.

Characteristics such as viscosity, specific heat and boiling point are not usually specified, but are nevertheless important for theoretical and engineering as well as food manufacturing purposes. Mostly they are functions of the molecular weight and degree of unsaturation of the oil and Table 6.23 gives a number of them.

Table 6.21 Malaysian standard MS80:1987. Guideline identity characteristics* for crude palmkernel oil ($n = 118$)

Identity characteristics	Observed range	Mean	SD
Refractive index at 40°C	1.4500–1.4518	1.4509	0.005
Saponification value (mgKOH/g)	243–249	245	1.4
Unsaponifiable matter (% by mass)	0.1–0.8	0.3	0.16
Iodine value (Wijs)	16.2–19.2	17.8	0.6
Slip melting point (°C)	25.9–28.0	27.3	0.33
Fatty acid composition (wt % as methyl esters by GLC)			
6:0	0.1–0.5	0.3	0.07
8:0	3.4–5.9	4.4	0.47
10:0	3.3–4.4	3.7	0.24
12:0	46.3–51.1	48.3	0.94
14:0	14.3–16.8	15.6	0.33
16:0	6.5–8.9	7.8	0.36
18:0	1.6–2.6	2.0	0.19
18:1	13.2–16.4	15.1	0.74
18:2	2.2–3.4	2.7	0.22
Others	tr–0.9	0.2	0.09
Solid fat content (% by continuous wave NMR) at			
5°C	68.0–76.8	72.8	1.77
10°C	61.6–71.2	67.6	2.12
15°C	50.7–60.0	55.7	2.31
20°C	34.2–45.5	40.1	2.54
25°C	10.2–21.5	17.1	2.18
30°C	nil	–	–
Total carotenoids (as carotene) (mg.kg)	4.3–11.8	7.6	1.5

*Based on the results of an analysis of 118 samples from mills and bulking installations throughout Malaysia over 2 months in 1981. The characteristics of processed palmkernel oil differ in no significant ways from the above figures with the exception of carotenoids, which are removed during refining.

Table 6.22 Chemical and physical characteristics of PKO; Codex (2001) draft standard

Relative density 40/20°C	0.899–0.94
Refractive index (n_D 40°C)	1.448–1.452
Saponification values (mgKOH/g oil)	230–234
Iodine value	14.1–21.0
Unsaponifiable matter (g/kg)	≤ 10
Quality characteristics Apply to both CNO and PKO (see Table 6.8)	

Table 6.23 Miscellaneous physical properties of PKO

Parameter	Value	Reference
Boiling point (°C) at 760 mmHg	298.9C[a]	Swern 1979, p. 178
Boiling point (°C) at 1 mmHg	130.2°C[a]	Swern 1979, p. 178
Dielectric constant, approx	3.1	Swern 1979, p. 226
Heat of combustion (cal/g)	9150	Swern 1979, p. 196
Heat of fusion (cal/g) 46.3°C	46.2[b]	Swern 1979, p. 199
Heat of vaporisation (cal/g)	69[a]	Swern 1979, p. 209
Heat of vaporisation (cal/g)	51[b]	Swern 1979, p. 209
Kin. viscosity (C. Stokes) (37.8°C)	30.92	Swern 1979, p. 178
Kin. viscosity (C. Stokes) (98.9°C)	6.50	Swern 1979, p. 178
Refractive index (n_D 40°C)	1.448–1.452	Codex 2001
Rel. density (40°/20°C)	0.899–0.914	Codex 2001
Setting point (°C)	20–26	Swern 1979, p. 319
Slip melting point (°C)	26.4	LFRA 1989, p. 25
Specific gravity (20°/4°C)	0.9190	Swern 1979, p. 178
Specific gravity change/°C	7.05×10^{-4}	Cocks and Van Rede 1966, p. 84
Specific heat (cal/g) 66°C	0.510[b]	Swern 1979, p. 198
Specific heat (cal/g) 97°C	0.530[b]	Swern 1979, p. 198
Thermal conductivity (BTU/h.ft^2 °F.ft)[c]		
72.5°C	0.111[a]	Swern 1979, p. 211
148°C	0.0803[a]	Swern 1979, p. 211
Titre (°C)	20–25	Akzo Chemi tech.lit
Vapour pressure (mmHg) 188°C	0.001[b]	Swern 1979, p. 205
Vapour pressure (mmHg) 244°C	0.05[b]	Swern 1979, p. 205

[a]Lauric acid.
[b]Trilaurin.
[c]1 BTU/h.ft^2 °F ft = 1.731 W/hm°C.

Viscosity is a very important property for chemical engineering calculations and also in frying operations. Some valuable tests for assessing the condition of frying oils during use depend on viscosity measurements. Oils have relatively high viscosity compared with most other organic compounds because of their long chain lengths. One should distinguish between the absolute or dynamic viscosity (poises) and the kinematic viscosity (stokes) which is measured by instruments using time of efflux, falling ball, rising bubble, and so on. The kinematic viscosity is equal to the dynamic viscosity divided by the fluid density at the temperature of the test. Some widely used instruments measure the kinematic viscosity by determining the time of efflux of a fixed volume of the fluid through an orifice and often the time itself is used to indicate the viscosity, for example, 100 seconds Redwood No.1 or 150 seconds Saybolt. Much data in engineering company literature, product specifications and reference tables are still of this type.

Many equations have been proposed to describe the change in viscosity of oils with temperature, or to derive the viscosity from other characteristics,

but the latter are all too complicated for practical use. For most practical purposes, use can be made of the fact that an approximately linear relationship exists between the logarithm of the dynamic viscosity and the reciprocal of the absolute temperature (Swern 1979, p. 179), over the temperature range used in the processing and handling of oils in the food industry. In our experience this relationship is not particularly good for triacylglycerols, and in most cases a better linear relationship exists between the logarithm of viscosity and the logarithm of the temperature (°C), which is much more convenient.

Under most circumstances, except for conditions of very high pressure, oils and fats behave like Newtonian fluids and show less change in viscosity with temperature than do mineral oils. The viscosity of oils and fats increases with their molecular weight and decreases with unsaturation but the effect of the latter is small. The lauric oils, because of their shorter chain lengths, have lower viscosity than the other major oils, despite the lower unsaturation of the former. Hydroxyl groups in the molecule, as in castor oil, polymerisation, as in blown linseed oil, or extensive frying greatly increase viscosity.

Density is extremely important in commercial transactions. Apart from retail, oils are bought and sold by weight and the huge quantities transported in ships, or stored in bulking installations and oil refineries, depend on volume and density measurements to estimate their weight. The density of oils and fats increases with unsaturation but decreases with increasing molecular weight and almost linearly with increasing temperature. The average temperature co-efficient for CNO and PKO between 20° and 60°C is 7.1×10^{-4}/°C (Cocks and Van Rede 1966). Examples for some simple triacylglycerols, quoted by Swern (1979, p. 189) in g/ml at 80°C, are as follows:

Fatty acid	TAG
12:0	0.8801
14:0	0.8722
16:0	0.8662
18:0	0.8632
18:1	0.8693*

In frying applications—especially in the domestic and catering sectors—the smoke point of oils is often used to assess their discard point. This value depends primarily on the free fatty acid (FFA) content and on the boiling point of the fatty acids. At 760 mm Hg, lauric acid has a boiling point of 298.9°C compared with 351.5°C for palmitic acid and 376.1°C for stearic acid (Swern 1979, p. 205). Unsaturation reduces the boiling point to a very small extent.

*Author's estimate based on a value of 0.9078 at 25°C.

Table 6.24 MEOMA specifications for PKO products for export market (MEOMA 2001)

	Parameter	Value
Crude palmkernel oil	FFA (as lauric acid)	5.0% max
	Moisture and insol.	0.5% max
	Iodine value (Wijs)	19 max at time of shipment
Crude palmkernel olein	FFA (as lauric acid)	5.0% max
	Moisture and insol.	0.5% max
	Iodine value (Wijs)	21 min
Crude palmkernel stearin	FFA (as lauric acid)	5.0% max
	Moisture and insol.	0.5% max
	Iodine value (Wijs)	8 max
RBD palmkernel oil	FFA (as lauric acid)	0.1% max
	Moisture and insol.	0.1% max
	Iodine value (Wijs)	19 max at time of shipment
	Colour ($5\frac{1}{4}''$ Lovibond cell)	Red 1.5 max
RBD palmkernel olein	FFA (as lauric acid)	0.1% max
	Moisture and insol.	0.1% max
	Iodine Value (wijs)	21 min at time of shipment
	Colour ($5\frac{1}{4}''$ Lovibond cell)	Red 1.5 max
RBD palmkernel stearin	FFA (as lauric acid)	0.1% max
	Moisture and insol.	0.1% max
	Iodine value (Wijs)	8 max
	Colour ($5\frac{1}{4}''$ Lovibond cell)	Red 1.5 max

6.3.2.2 Trade specifications

Surveys of oils and fats by research laboratories and national standards published by government bodies are the best sources of information on the properties they cover. However, they are only advisory and commerce is conducted on the basis of trade specifications issued by manufacturers or their associations. Malaysian origin is the major PKO grade and, when bought from origin, it is normally traded according to the specification issued by the Malaysian Edible Oils Manufacturers' Association (MEOMA 2001). Its importance is also increased by the fact that Indonesian origin (second in world trade) is also traded according to the same specification. The MEOMA specifications cover crude and refined PKO as well as PK stearin (PKOs), PK olein (PKOo) and PKM. (See Table 6.24).

6.3.3 Processing

6.3.3.1 Hydrogenation

Palmkernel oil has an IV of about 18 and can be hydrogenated to produce a range of products of different SMP/IV combinations. Usually, these are available in SMP steps of 2–3°C and Table 6.25 shows the characteristics of a typical range of HPKO products from a major EU manufacturer.

The oxidative stability of PKO, although good, is not as good as might be expected from its degree of unsaturation. This is most probably due to its low

Table 6.25 Selling specification of HPKO products[a]

	PKO	HPKO 32[b]	HPKO 34	HPKO 37	HPKO 40
Colour ($5\frac{1}{4}''$ Lovibond cell)	1R 10Y	1R 10Y	1R 10Y	1R 10Y	1R 10Y
FFA (as lauric), (%) max	0.1	0.1	0.1	0.1	0.1
PV (me/kg) max	1.0	1.0	1.0	1.0	1.0
Iodine value (Wijs)	14–19	7–10	5–8	2.5–5	Max 2
Sap. value (mgKOH/g)	242–246	242–246	242–246	242–246	242–246
Setting point (°C)	–	28.5–29.5	29.5–31.5	31.5–32.5	33.5–34.5
Slip point (°C)	27–29	32–35	34–37	37–39	40–42.5
N 20[c]	42.5–47.5	64–70	66–72	76–82	78–84
N 30	Max 1.7	6–11	10–15	20–25	28–34
N 35	–	0–2	2–4	7–12	11–15
N 40	–	Max 0.5	Max 1.5	2.5–4.5	4–8
Shelf life, bulk	2–3 d	2w	2w	2w	2w
Shelf life, packed	1m	3m	3m	3m	3m

[a]Data from a major EU manufacturer.
[b]HPKO 32 = Hydrogenated palmkernel oil, SMP 32°C.
[c]N20 etc = NMR value (or SFC) at 20°C.

content of tocols and, as in the case of CNO, it responds strongly to even a very small addition of synthetic antioxidants (BHA, BHT) and chelating agents such as citric acid. Its stability is also greatly increased by a small degree of hydrogenation. As seen from the table, the recommended maximum storage time by the manufacturer is six times longer for the hydrogenated grades than for the unhydrogenated oil.

The various HPKO grades are usually offered in the market under brand names and in many cases their description does not exclude presence of PKOo which is lower priced. The effect of this practice is to increase the IV and to lower the C_{12} content and the SFC values at a given mp; but unless large amounts are present, the effect is small and careful comparisons are needed to detect it.

6.3.3.2 Interesterification

Interesterification of straight lauric oils has only been used to a small extent in industry and it seems to have been confined almost entirely to PKO products.

There are two types of interesterification: random, which is carried out in the fully molten state, and directed, which is carried out with the fat partially solidified. The two types produce different results but the former is far more common and 'interesterification' may be assumed to refer to the random type (randomisation), unless otherwise stated. The usual catalyst employed is sodium methoxide at about 0.1%.

This reaction rearranges the fatty acid radicals on the glycerol backbone, according to the laws of probability and so it can often be used to harden soft oils or change the melting profile of blends. All this is achieved without producing any *trans* or positional isomers, and without any change in the degree of unsaturation.

Formulae for calculating the triacylglycerol composition of interesterified fats are derived from probability considerations and a good exposition of the subject is given by Bailey (1951). Since every possible triacylglycerol has a chance of being formed, the number calculated from even a few fatty acids will be quite large and interpretation of oil properties difficult.

In most cases in industry, we simply want to know the triacylglycerol composition of an interesterified oil in terms of degree of saturation. If s and u are the mole fractions of saturated (S) and unsaturated (U) fatty acids, for example 70% and 30% respectively, then the mole fractions of the various triacylglycerol types will be as follows:

$$
\begin{aligned}
S_3 = s^3 = 0.7^3 &= 34.3\% \\
S_2U = 3 \times s^2 \times u = 3 \times 0.7^2 \times 0.3 &= 44.1\% \\
SU_2 = 3 \times s \times u^2 = 3 \times 0.7 \times 0.3^2 &= 18.9\% \\
U_3 = u^3 = 0.3^3 &= 2.7\% \\
\text{Total} &\quad 100\%
\end{aligned}
$$

The following simple rules are self-evident:

- the mp of a fat is determined principally by the amount of S_3
- fats with high levels of both S_3 and U_3 will be plastic (flat SFC curve)
- fats consisting mostly of a single type of glycerol ester, e.g. S_2U, will be sharp melting.

Lauric oils contain mostly S_3 while cocoa butter contains mainly S_2U and both melt sharply, although over different temperature ranges. The usual reason for the use of interesterification on vegetable oils is to reduce the tail of the SFC/temperature curve and so improve mouth feel. Accordingly, it has been applied to HPKO and HPKOo to make them more similar to PKOs. The problem is that the cost of interesterification comes on top of that of hydrogenation and PKOs still has a much better SFC profile as a CBS.

Interesterification of PKO and PKOo with palm stearin and liquid oil has possibilities in *trans*-free margarine blends, especially during periods when the price of lauric oils is in line with that of other oils. Palm stearin is normally the lowest cost vegetable hard fat. The following results from our experiments show the effect of interesterification on HPKOo (Table 6.26). It should be noted that the SFC 20°C remains virtually the same, while the SMP is reduced by over 6°C.

Table 6.27 shows the effect of interesterification on HPKO and the characteristics of confectionery fats, using interesterified HPKO (Sreenivasan 1978). Unfortunately, the all-important SFI values at 30°C have not been included.

The overall conclusion is that interesterification of lauric oils reduces the SFC at 35°C and 40°C, which is good but, unfortunately, it also reduces the values at

Table 6.26 Effect of interesterification on HPKOo

			SFC			
HPKOo	IV	SMP (°C)	20°C	30°C	35°C	40°C
Before	0.9	41.3	58.9	29.0	16.7	8.3
After	0.9	34.9	58.0	24.9	4.0	0

Table 6.27 Confectionery fats from HPKO and interesterified HPKO

		Solid fax index (SFI)			
	mp (°C)	10°C	20°C	35°C	38°C
100/0 HPKO/IeHPKO[a]	46.8	74.2	67.0	15.4	11.7
80/20 HPKO/IeHPKO	46.0	72.4	62.6	12.4	8.5
65/35 HPKO/IeHPKO	44.2	71.0	59.7	10.2	6.7
50/50 HPKO/IeHPKO	41.7	70.0	57.4	8.7	5.2
0/100 HPKO/IeHPKO	35.0	65.0	49.9	1.4	1.2

[a]HPKO = Hydrogenated palmkernel oil, Ie = Interesterified.
Source: Sreenivasan 1978.

30°C and in most cases, also at 20°C, which is undesirable. The improvement in SFC profile obtained by interesterification is inferior to that from fractionation.

6.3.3.3 Fractionation

For good mouth feel, coatings (the usual name for substitute chocolate and similar products) must have a SMP below 35–36°C. Some pharmaceutical products, such as suppositories, also have this requirement. At this SMP, the SFC profile of HPKO is not entirely satisfactory. Its SFCs at 20°C, and especially at 30°C, are not high enough and 'chocolate' products based on it lack good snap and tend to become too soft during the warmer months in temperate countries. Another deficiency of HPKO, not previously highlighted in the literature as far as we know, is that its mouth feel seems to become waxier over time. It is possible that it gradually recrystallises into higher melting crystals because trilaurin is β-stable.

A much better SFC profile is only obtained from PKOs or cocoa butter. However, cocoa butter is in a higher price bracket and also presents its own special handling problems, such as the need for tempering and its incompatibility with other fats.

The fractionation processes used on lauric oils are either detergent based (e.g. Lanza, Alpha Laval)—often called 'wet fractionation'—or pressure filtration, often called 'dry fractionation'. Both are competitive: the former has higher capital costs but gives higher yield, while the latter has lower capital costs but gives lower yield. The quality obtainable is very similar. Solvent fractionation gives the highest yield but it is prohibitively expensive for lauric oils.

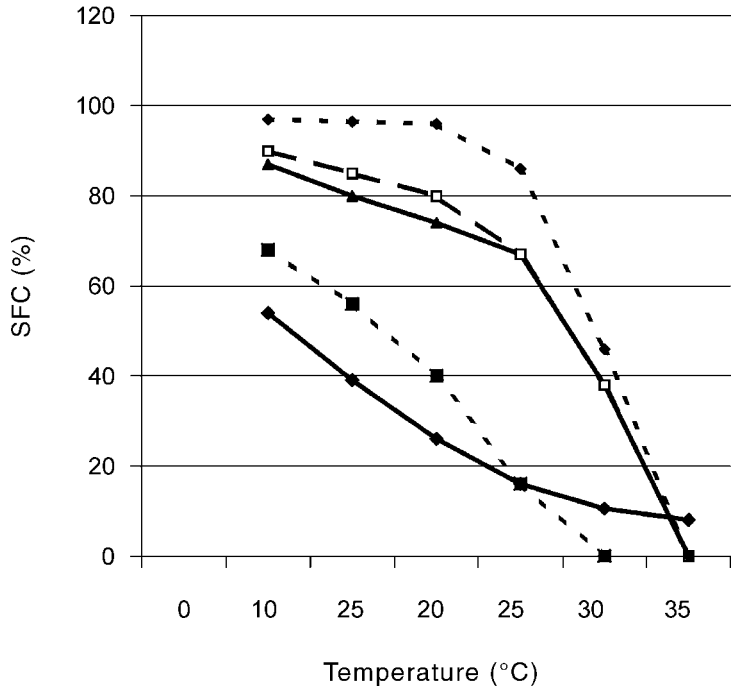

Figure 6.4 SFC of cocoa butter, PKO product and palm oil. Average values from Malaysian manufacturers' literature. Key: —◆—, PO; ···■--, PKO; —▲—, CB; — □ —, PKOs; ···◆--, HPKOs35.

Figure 6.4 shows the melting behaviour in terms of SFC values of PKO, PKOs and HPKOs35, together with those for cocoa butter and PO for comparison. The data used for the graphs are average values calculated by the writer from Malaysian manufacturers' specifications.

Although only three basic products are normally made from PKO (PKO itself, PKOo and PKOs), there are also hydrogenated and blended versions, which complicate the picture considerably. The simplest way to distinguish between them is from their iodine value/slip melting point relationships, and a more certain characterisation can be made by examining their SFC profile and fatty acid composition.

The characteristics of PKOo and PKOs are covered by Malaysian Standard MS 1436;1998 and MS 1437:1998, shown in Table 6.28 and Table 6.29 respectively. These were based on surveys conducted by PORIM (now MPOB).

From Tables 6.21, 6.28 and 6.29 it may be noted that the C_{12} content is highest in the stearin and lowest in the olein. The level of this fatty acid is therefore an important index of fractionation efficiency and of the quality of the product. The differences in the melting profiles are obvious. In practice, two qualities of PKOs are made: one with IV 6–8 and SMP about 31–33°C and the other

Table 6.28 Malaysian standard for palmkernel olein[a]

Identity characteristics	Observed min to max
Apparent density (g/ml) at 40°C	0.9039–0.9056
Refractive index (n_D 40°C)	1.4514–1.4522
Saponification value (mg KOH/g oil)	231–244
Unsaponfiable matter (% by wt)	0.26–0.72
Fatty acid composition (wt % as methyl ester)	
6:0	0.2–0.4
8:0	3.6–5.0
10:0	3.2–4.5
12:0	42.0–46.5
14:0	12.3–15.5
16:0	7.4–10.6
18:0	1.8–3.0
18:1	14.6–21.3
18:2	2.6–3.8
20:0	0–0.3
Iodine value (Wijs)	20.6–26.0
Slip melting point (°C)	21.8–26.0
Solid fat content (%) (by NMR)	
Temperature (°C)	
5	55.4–71.2
10	43.0–67.0
15	25.1–51.7
20	8.5–32.7
25	0–12.0
30	0

[a]MS 1436:1998 ($n = 52$).

hydrogenated to IV below 2 and SMP about 34–36°C. Proprietary brands may be based on blends of the two, and may also contain emulsifiers for enhanced performance in particular applications, such as bloom resistance or viscosity reduction in coatings.

Hydrogenated PKOo can be made to resemble the SFC of PKO and HPKO but the C_{12} content will be a little lower, the SFC curve will not be quite as steep, and the mouth feel will be a little inferior. However in practice, only keen tasters can tell the difference. It is worth noting that with PKO—contrary to the case with PO—the most valuable product is the stearin and the least valuable is the olein. By blending the basic PKO products (oil, olein and stearin) in different proportions, hydrogenating to different melting points and/or interesterifying, a large number of graduated speciality products can be made for the same end uses, but offering different performance/cost combinations. These are the differences which distinguish the branded products of different manufacturers.

The MEOMA trading specification for PKOs and PKOo are shown together those of PKO in Table 6.24.

Table 6.29 Malaysian standard for palmkernel stearin[a]

Identity characteristics	Observed min to max
Apparent density (g/ml) at 40°C	0.9040–0.9059
Refractive index (n_D40°C)	1.4499–1.4501
Saponification value (mg KOH/g oil)	245–255
Unsaponfiable matter (% by wt)	0.22–0.60
Fatty acid composition (wt % as methyl ester)	
6:0	0–0.1
8:0	1.5–2.6
10:0	2.5–3.0
12:0	54.8–58.2
14:0	21.1–24.1
16:0	7.2–9.0
18:0	1.3–2.4
18:1	4.6–7.2
18:2	0.6–1.3
20:0	0–0.3
Iodine value (Wijs)	5.8–8.0
Slip melting point (°C)	31.3–33.1
Solid fat content (%) (by NMR)	
Temperature (°C)	
5	88.1–94.6
10	87.5–93.2
15	83.6–92.2
20	77.0–86.0
25	55.0–76.0
30	22.0–44.0
35	0

[a]MS 1437:1998 ($n = 49$).

6.3.4 Food uses

6.3.4.1 Edible uses of lauric oils—coconut and palmkernel

Because of their similarity in composition and properties, PKO and CNO have similar uses in both the edible and the non-edible fields, but there are some differences which are worth noting.

Palmkernel oil is more unsaturated and so can be hydrogenated to a wider range of products for the food industry, while CNO has a greater content of the more valuable shorter-chain fatty acids, which make it a little more attractive to the oleochemical industry. Some of the main food applications are given below.

6.3.4.2 Margarine

Margarine is a major food product, especially in western countries, with world production in 2000 of 10 MT and the trend is still rising about 1.5% annually (*Oil World* 2001). It was invented by Hippolyte Mège Mouries of France, who won a State prize for it, and is used as a substitute for butter. It was granted a

patent in 1869. From then on until relatively recently margarine manufacturers used butter as their model and lauric oils formed major components (up to 50%) in some old formulae (Andersen 1954).

After World War II, with the universal adoption of home refrigerators, it was found that butter was not easy to spread at low temperatures and soft margarines were introduced to overcome this shortcoming. This type of margarine has now become by far the major one for household use.

In the EU, margarine is required by law to contain a minimum of 80% fat but a large demand has also developed for products containing less fat and these are called 'spreads'. These may contain any fat level the manufacturers wish and most of the comments on margarine below apply to the spreads as well.

Margarines currently on the market fall into four major types and three basic formulations:

- soft table margarine, tub-filled—all vegetable, rich in polyunsaturates and low in *trans* fatty acids (often below 1%)
- medium hardness, table/kitchen margarine, wrapped blocks, vegetable/animal/marine blends
- bakery or industrial margarine, for cakes and general bakery goods; same formulation as for medium hard margarine but packed in large cartons (about 12 kg)
- puff pastry margarine for use in bakeries for laminated doughs; firm, tough and malleable to withstand rolling into very thin layers; vegetable/animal/marine blends and packed in large cartons (about 12 kg).

There are also some other minor specialised types such as those designed for cake creams but their volume is small. Also in many countries now, the trend is towards all-vegetable formulations, even for bakery use.

The steep SFC profile and high degree of saturation of lauric fats severely restrict their level of inclusion in modern soft, spreadable, polyunsaturated margarines, and their price also tends to inhibit their use in trade margarines. Nevertheless, lauric fats do have their use in special cake cream margarines, and to a small extent, in household margarines. According to published data for the UK, in 1999, the average lauric inclusion in margarines was 3.3% (*Oil World* 2000) and in the EU, inclusion levels are probably double that. Cake cream margarines typically contain about 20% lauric fat.

Lauric oils in margarines contribute short-chain fatty acids, which make the fatty acid composition of the blend more like that of butter and give a cooler mouth feel. Their steep-melting properties and eutectic formation also help to counterbalance the high melting point of vegetable stearins such as POs and the flat melting profile of PO, which now feature prominently in most margarine formulations. Interesterification of such blends allows greater inclusion of hard fats. Table 6.30 gives examples of some low-*trans* margarine formulae containing lauric oils, developed by MPOB.

Table 6.30 Margarine formulations using lauric fats[a]

	SMP (°C)	N10[b]	N20	N30	N35	N40
Table, soft, tub						
Ie[40:20:40 POs:PKOo:RSO][c]	–	26.3	8.6	1.4	–	–
55:45In[60:20:20 POs:PKOo:SFO]:SFO	34.0	16.0	1.0	5.9	–	–
Table/kitchen wrapped[d]						
Ie[60:20:20 POs:PKOo:SFO]	38.5	33.7	18.9	7.1	–	–
Ie[80:20 Poo:PKO]	–	40.4	20.1	5.9	1.8	–
Ie[50:20:30 POs:PKO:RSO]	–	42.0	24.0	9.3	5.2	–
Industrial						
10:60:30 Pos:PO:PKO	–	55.4	27.9	13.7	9.1	8.4
Puff pastry						
80:20 POs:PKO	–	57.8	31.1	16.8	12.2	10.1

[a]Data from PORIM (Palm Oil Research Institute of Malaysia) (now MPOB); Suria *et al.* 1995.
[b]N20 etc. = NMR value (SFC) at 20°C.
[c]Ie = Interesterified, POs = palm stearin, PO = palm oil, PKO = palmkernel oil, PKOo = palmkernel olein, SFO = sunflower oil, RSO = Rapeseed oil.
[d]Also suitable for bakery/industrial margarine.

6.3.4.3 Frying oils

There have been some erroneous statements that the lauric oils are not suitable for frying, because of their tendency to foam when oil from the food being fried leaks into the lauric oil, and also because of their lower smoke point, compared with the non-lauric oils.

However, these deficiencies only matter when deep frying and lauric oils are highly suitable for shallow frying. In this operation, the fat in the pan is only a few millimetres deep and foaming is not a problem. Neither is smoking a concern because the oil is only used once and its FFA is about 0.1%.

In the EU, some very successful branded fats for shallow frying are based on straight CNO. Apparently the pure white hard fat and its 'lightness' on the palate (low viscosity) have a high consumer appeal. Pure CNO is also used in some brands of popping corn containing a tablet of fat in the same packet, designed for popping at home. Palmkernel oil can be used equally well for the same purposes but CNO has been the traditional fat of choice.

6.3.4.4 Speciality fats—cocoa butter substitutes

Speciality fats are used extensively in the food industry for applications where specific physical or chemical properties are essential. Most confectionery products, for example, have a high fat content and as a result, the fat consistency and melting behaviour in the mouth are critical.

The cocoa butter substitutes (CBS) are among the most important classes of speciality fats. The standard of comparison for these substitutes is cocoa

butter. These fats can be divided into lauric and non-lauric types. They must have a very steep SFC curve and melt in the appropriate temperature range. For this profile, the lauric types rely on high content of lauric acid, while the non-lauric types rely on high content of *trans* fatty acids. The lauric type has better mouth feel and better contraction on cooling, but very limited compatibility with cocoa butter (maximum 6% CB in the fat phase), while the high *trans* type has longer shelf life (before bloom) and some compatibility with cocoa butter. In CBS applications shelf life is normally limited by bloom formation (a surface defect), not by rancidity. From this classification, we exclude the cocoa butter equivalents (CBE), which form another class with somewhat different uses.

The physical properties of PKOs resemble particularly closely those of cocoa butter, and it is generally acknowledged that the best types of CBS are made from this fat. Substantial quantities of PKO are therefore fractionated in Western Europe, the US and Malaysia for this purpose. Coconut stearin, on the other hand, while having exceptionally sharp melting properties and mouth feel, has a melting point which is too low for substitute chocolate and most coatings. It is also obtained in lower yield and so is more costly to produce. Its uses, therefore, are restricted to the finest biscuit creams and a small number of luxury products.

Hydrogenated palmkernel stearin (HPKOs) of SMP about 35°C has even higher SFC at 20°C than cocoa butter. In substitute chocolate formulations, often called 'coatings', it tolerates the softening effect of full cream milk powder and gives the highest contractions on cooling. These properties make it especially suitable for hollow moulded substitute chocolate confectionery such as Easter eggs, moulded bars and high quality biscuit creams.

Hydrogenated PKO products of SMP from 32° to 38°C (according to climate) are used for lower cost, but their SFC profile is flatter and they are of lower quality than PKOs. Nevertheless, most substitute chocolate for biscuit fillings, coatings, cakes, ice cream, and so on, are made from these fats. The SFC profiles of some confectionery fats are shown in Figure 6.4. Hydrogenated PKO tastes waxier than one might expect from its SFC profile, especially after some storage, and this is quite noticeable in 'chocolate' bars. Interesterification overcomes this defect, but increases the cost and since the SFC profile is still clearly not as good as PKOs, interesterified products have not gained wide use. Examples of substitute chocolate formulation used in Europe, are shown in Table 6.31.

Sometimes substitute chocolate products develop soapy rancidity. This is usually blamed on the lauric fat, but in nearly every case this can be traced to defects in the other ingredients, such as the use of cocoa powder of high bacterial count or high moisture left in the product—this should be below 1.0%.

6.3.4.5 Filling creams

Filling creams for biscuit sandwiches, wafers and cakes are usually called simply 'creams', and are used in large quantities in biscuit factories and bakeries. These products are among the most popular lines. The creams are composed essentially of sugar, fat and milk solids. The fat content is about 22–46% with an average

Table 6.31 Substitute chocolate coatings, using PKO-based CBS[a]

	Light coatings					Dark coatings				
	1	2	3	4	5	Choc drops	1	2	3	4
CP(22/24)[b]	–	4.0	–	–	–	–	–	–	–	–
CP(10/12)	6.0	2.0	6.0	4.5	3.7	8.0	16.0	18.0	20.0	22.0
FCMP(25)[c]	16.0	12.0	–	–	–	–	–	–	–	–
SMP[d]	–	6.0	12.0	16.0	22.0	22.4	4.0	–	–	–
CBS	31.5	31.8	35.5	35.5	34.2	25.6	34.0	36.0	34.0	32.0
Sugar	46.5	44.2	46.5	44.0	40.1	44.0	46.0	46.0	46.0	46.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Fat content	36.1	35.9	36.1	35.9	34.6	26.4	35.6	37.8	36.0	34.2

	Vermicelli	White chocolate
CP(10/12)	8.0	–
SMP	22.0	28.0
Flour	–	–
Gum arabic	0.25	–
CBS	16.0	33.0
Sugar	53.75	39.0
Total	100.0	100.0
Fat content	16.8	33.0

[a]After Loders and Nucoline Limited, UK.
[b]CP 22/24 etc = cocoa powder 22/24% fat.
[c]FCMP = full cream milk powder, assumed 25% fat.
[d]SMP = skimmed milk powder.
All recipes to contain: lecithin 0.5%, vanillin 0.06% and salt 0.5%.

of 33% (Manley 1998), and it is desirable that the hardness of the cream be proportional to the hardness of the dough layers. Thus biscuit creams are harder than cake creams.

The eating quality of the cream is determined primarily by the physical properties of the fat and the fat/sugar ratio. The finest creams for biscuits and wafers are made from CNO or PKO stearins, but these are only used in luxury brands. In the vast majority of cases, they are made from blends of CNO, PKO or PKOo and their hydrogenated versions. Important considerations are adhesion to the biscuit shells and their rate of setting. Lauric fats, because of their shorter chain length, adhere better to the shells and set faster than non-laurics, so that the freshly-made biscuits in a factory can be transported on conveyors, cooled quickly, handled, and packed without coming apart or sliding off centre. Lower cost creams are sometimes made from non-lauric hydrogenated fats, or even from all-purpose shortenings, but they never have the sharp-melting properties of lauric-based products and they tend to taste either waxy or greasy with a tendency to squeeze out. Examples of biscuit cream formulations are given in Table 6.32.

Table 6.32 Filling creams for biscuit sandwiches[a]

	1 Custard	2 Mint	3 Bourbon	4 Lemon puff
Fat	22	41	31	30
Sugar	57	52	41	53.5
Dextrose	–	–	17	12.5
FCMP[b]	–	7	–	–
SMP[c]	–	–	–	4
Whey powder	16	–	–	–
Chocolate	–	–	11	–
Recycled biscuits	5	–	–	–
Total	100	100	100	100
Lecithin	0.4	0.5	–	–
Flavour, colour etc	As required			
Fat content	22.5	43.5	34	30

[a]After Manley 1998.
[b]Full cream milk powder.
[c]Skim milk product.
Recipes 1 and 2 represent extreme values of fat content and in this respect, recipe 4 is more typical. Recipe 3 uses real chocolate. Lower cost types can be made using substitute chocolate or cocoa powder and extra fat.
Flavour includes lecithin and salt.

Table 6.33 Filling creams for sandwiched wafers[a]

	1 Chocolate	2 Vanilla	3 Orange
Fat	28	30	32
Sugar	42	45	47
Skimmed milk powder	3.5	–	–
Cocoa	3.5	–	–
Recycled trimmings	23	25	21
Total	100	100	100
Flavour, colour etc	As required		
Fat content	33.4	33.7	36.1

[a]After Manley 1998.

Wafer cream formulae are the same, except that they always include much re-work from trimmings and they are applied warmer so that they can be spread thinly on the fragile wafer sheets (Table 6.33). The cream in wafer sandwiches is 70–75% of the product weight, and because the amount is so high and the wafer shells have a light delicate texture the SFC profile of lauric fats is essential. Coconut stearin is probably the ideal fat for this product.

6.3.4.6 Toffees and caramels

These two products are very similar to each other and the terms are used interchangeably. They consist of boiled sugar (sucrose), glucose, and milk solids, but usually incorporate some fat to adjust their texture, hardness, chewiness and richness of taste. Fat also 'shortens' the product and reduces stickiness on wrapping materials by inhibiting moisture absorption, and so delaying sugar inversion. Hardness depends primarily on the temperature of boiling but also the fat content. Some of these products are fairly hard and sold as wrapped pieces, while others are much softer and spreadable when warm (around 45°C). The fats used are usually based on hydrogenated lauric fats because of their sharp melting and setting properties and long shelf life. Premium products often incorporate some PKOs for enhanced eating quality. Typical recipes are shown in Tables 6.34 and 6.35.

6.3.4.7 Ice cream

Ice cream is the most popular dessert in the Western world and it is also an important food product in the nutrition of children. In most countries therefore

Table 6.34 Soft caramel/toffee for fillings and toppings[a]

	1	2
Skimmed sweetened condensed milk	50	50
Glucose syrup (42DE)	20	12
Glucose syrup (63DE)	–	24
Invert sugar	19	6
HCNO/HPKO	21	21
Flavour	As required	

[a]After Manley 1998.

Table 6.35 Toffee for wrapping[a]

Recipe No.	1	2	3
Toffee type	Low boil	Medium boil	High boil
Boiling temp.	118°C	124°C	135°C
White sugar	25	20	20
Brown sugar	–	5	5
Glucose	25	25	25
Full cream sweetened condensed milk	29.5	27	27
Lauric fat	15[b]	15[c]	15[d]
Dairy butter	5	–	–
Salt	0.5	0.5	0.5
Flavour	As required		

[a]After Loders & Nucoline Ltd, UK.
[b]PKOs.
[c]25/75 PKOs/HPKO 34/36.
[d]CNO or PKO.

its composition and hygiene are specified by law. In the EU in 1998, its market was worth £9.4 billion (US $13.7 billion) and most of it was eaten at home. 'Soft-mix' outsells the 'scooping' type by a factor of 3:1 (Birds Eye Walls 1999).

Coconut oil and PKO are the best fats for non-dairy ice cream because of their combination of high SFC at about 0°C, low melting point, and perfectly bland taste. Coconut oil is the fat used in the classic Italian ice cream recipes and PKO is the obvious alternative. However, because of price considerations, most mass market ice cream in Europe is probably made from palm oil/hydrogenated palm oil blends. Proprietary ice cream fats are often based on hydrogenated blends of PKO (or PKOo) and palm olein.

Similarly, CNO and PKOo are used to make the 'chocolate' for dipping ice cream. This is made by diluting standard chocolate with extra fat. The product must have low viscosity, low melting point and yet set quickly, so that the ice cream does not melt and drip into it. Also the coating must not be too brittle and flake off at the time of eating. The requirements are quite finely balanced. A typical formula for soft ice cream is shown in Table 6.36 but the range of composition is approximately as follows: fat (5–12%), milk solids—not fat (10–16%), added sugar (11–17%), emulsifiers (0.4–0.7%), stabiliser (0.1–0.3%), inorganic salts (1.0%), and water (to 100%).

6.3.4.8 Non-dairy whipping creams

This product, like ice cream, is an emulsion of fat globules in water, but the higher fat content of whipping creams (about 28%) makes the melting behaviour of the fat very important. This product is also very critical in its fat requirements, because it must whip quickly to a high, but not too high, volume and hold that volume for many hours with as little shrinkage and leakage as possible. Pure HPKO (mp 34–36 or 36–38°C), sometimes with addition of PKOs, is

Table 6.36 Soft-serve ice cream[a]

	Kg
Fat	6
Sugar	12
Skimmed milk powder	9
Wheat flour	3
Water	66
GMS	0.5
Sodium alginate	0.3
Flavour	As required
Colour	As required
	96.8

[a]After Loders & Nicoline Limited, UK.

Table 6.37 Non-dairy whipping cream[a]

	%
HPKO	29.00
Sugar	4.00
Skimmed milk powder	1.94
Methyl ethyl cellulose	0.73
Myverol 1840	0.19
Monoacylglycerol (high mono)	0.10
Sodium alginate	0.07
Sodium citrate	0.16
β-Carotene	0.001
Flavour	0.002
Water	63.81
	100.00

[a]Major EU manufacturer.

the standard fat used. A high SFC at 20°C and low SMP are essential for this product. A high melting point gives a 'cotton wool' mouth feel. Performance also depends on particular fat/emulsifier combinations and the manufacturers of whipping creams appear to be particularly keen to keep their formulae secret. A typical formula is shown in Table 6.37.

6.3.4.9 Non-dairy creamers (coffee whiteners)

Full cream milk powder has a very short shelf life, does not disperse well in hot liquids, and has only modest whitening power. Coffee whiteners are designed to improve on these qualities. As they have a very large surface area in relation to their weight, only fats of very high oxidative stability can be used. Fully hydrogenated CNO or PKO are the most suitable fats because when reduced to IV below 2 they have extremely high stability and yet reasonably low melting points. Where lower stability is acceptable, hydrogenated PO 42–44 is often used but most of the leading international brands are made with HCNO or HPKO. In a survey of nine commercial powdered products, MPOB found a mean fat content of 31.3%, SD 1.8% and range 28.7–33.3%. Formulae of powdered and liquid coffee whitener are shown in Table 6.38.

6.3.4.10 Filled milk

This is a large sales volume product in which the milk fat has been replaced by vegetable fat and sold either as 'evaporated' or as dry powder. It is widely used in countries where fresh milk is not readily and cheaply available. Starting with skimmed milk or butter milk, the specified fat is added and homogenised together in the presence of some monoacylglycerols to help the homogenisation and ensure a stable emulsion. The final product usually contains about 3.5% fat and 0.25% monoacylglycerols. In many respects the requirements from the fat

Table 6.38 Formulae for non-dairy creamers (%)

	Powdered[a]	Liquid[b]
HPKO (IV 2 max)	32.3	10.0
Sodium caseinate	12.0	0.8
Maltodextrin (28 DE)	54.0	10.0
Monoacylglycerol	1.0	0.6
Gum carrageenan	0.06	0.05
Dipotassium phosphate (K_2HPO_4)	0.6	0.2
Colour, flavour	As required	As required
Water	–	78.35
	99.96	100.00

[a]After a major EU manufacturer.
[b]MPOB.

are the same as for non-dairy creamers. Coconut oil has been the traditional fat used because of its high oxidative stability, low melting point, and bland taste—milk is particularly sensitive to the slightest unusual taste. Palmkernel oil is also used but it is not quite as stable as CNO.

For the highest oxidative stability, especially in the powdered product, with its very high specific surface area, HNCO, HPKO or HPKOo (fully hydrogenated), are extremely stable, and are highly suitable. For the evaporated product, which is usually canned, there is no need to hydrogenate and CNO or PKO are used, often with addition of sunflower or corn oil to provide essential fatty acids, especially in countries where the evaporated product may be (wrongly) used for baby feeding. Where lower costs are required, PO or hydrogenated PO are used. Hydrogenated seed oils, especially those containing significant linolenic acid levels, are not very suitable because even when hydrogenated sufficiently to show high accelerated stability values (AOM, Rancimat, for example), they tend to revert to a 'hydrogenated' flavour, which is particularly noticeable in 'milk' products.

6.3.4.11 Medium-chain triglycerides (MCT)

Coconut and palmkernel oils are the basic sources of MCT oils. These oils are based on triacylglycerols of caprylic (8:0) and capric (10:0) fatty acids, and they differ from ordinary oils in respect of their digestion and metabolism. Because of their low molecular weight, MCT oils are easily absorbed in the digestive tract and are used immediately as energy sources in the body and thus avoid being stored in the adipose tissue. These properties make them useful ingredients in sports foods, infant foods, and in clinical nutrition (enteral/parenteral food). In addition to these applications, MCT oils have found useful applications in various dietetic and health food products, and some manufacturers have also started to incorporate them into products such as margarine and chocolate spreads which consumers perceive as fattening.

Table 6.39 'Chocolate' spreads, using MCT oils[a]

	Chocolate spread, sugar-based (%)	Chocolate spread, sugar-free, probiotic (%)
Cocoa, defatted	7	7
Skimmed milk powder	12.5	12.5
Inulin	–	47
MCT oil	30	31
Emulsifier (E471, monoacylglycerol)	2	2
Sugar	48	–
Sweetener (sodium cyclamate)	–	0.25
Lecithin	0.5	0.5
Flavour (hazelnut, vanilla)	As required	As required
	100.00	100.00

[a]Roche 1998.

Because of their short chain lengths and full saturation, MCT oils are much less viscous and much more resistant to oxidation than ordinary oils—properties which make them useful (and harmless) lubricants for special purposes.

MCT oils are usually made by esterification of distilled C_8 and C_{10} fatty acids, derived from the acid–oil byproducts of lauric oil refining or from high pressure splitting of lauric oils. Another route is the direct molecular distillation of lauric oils. The C_8 to C_{10}-depleted oils are then even richer sources of lauric and myristic acids for the oleochemical and soap industries. Examples of MCT oils used in dietetic chocolate spread are shown in Table 6.39.

6.3.4.12 Health aspects

A note on health aspects is appropriate because the lauric oils are more than 80% saturated. This is much more than the major liquid oils such as soyabean, sunflower and rapeseed, which are respectively only 16%, 12% and 7% saturated. Nutritionally this may be thought of as a great disadvantage but such simple comparisons can be misleading. Lauric oils are only used in foods where a sharp melting hard fat is needed. When liquid oils are hydrogenated to a similar consistency, they contain not only more saturates but also *trans* fatty acids, which some recent studies have shown to be even more objectionable with regard to serum cholesterol profiles than the saturated ones (Byers 1997, Pietinen *et al*. 1998).

Another consideration is that fatty acids below C_{12} are metabolised by a different pathway and are not deposited in adipose tissue. This is beneficial with respect to those factors which promote coronary heart disease. In countries such as the Philippines, where CNO is virtually the only oil in the diet, the population does not show unusually high rates of heart disease.

In Western countries, lauric oils, because of their higher price and special properties, are only used where they are clearly necessary on technical grounds, and so only reach a very low level in the diet. In the EU, for example, in 2000/2001, the annual *per capita* disappearance (use for all purposes including soap, oleochemicals, and waste) of the two lauric oils combined, was only 3.5 kg against 48 kg for total oils and fats. The amount used for edible purposes is probably below 2.5 kg. In the US, the figures are even lower with values of 2.2 kg and 51 kg (*Oil World Annual* 2001). About half of that lauric volume is used for non-edible purposes and so the amount used for food is probably only about 1.1 kg/ca.

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7 Cottonseed oil

Richard D. O'Brien

7.1 Introduction

Cottonseed is a byproduct of cotton production and, as such, is dependent upon the supply of and demand for the cotton fiber surrounding the oilseed. Cotton is one of the oldest culture crops. There were cotton fields in India 4000 years ago. When Columbus discovered America, he found the cotton plant already there. The use of oil from cottonseed dates from more recent times but it was one of the earliest seeds used to produce oil. Prior to World War II, cottonseed dominated the world edible oil market because it was in ample supply, it was generally at a lower price than competing oils, and it was preferred by many food processors. It was the dominant vegetable oil in the US as well as in England and the European edible oil industry in general, even though these latter countries also utilized a variety of oilseeds and tree fruits available in their home countries and from their colonies. Through research and experimentation, chemists developed a clear, odorless, bland-flavored cottonseed oil that set the standard for edible fats and oils globally. Scientific and technical advances, developed to process cottonseed oil, became the corner stones of the edible fats and oil industry as it is known today. Cottonseed oil lost its dominant position due to cottonseed shortages and to an increased demand for edible oil. Nevertheless, because of its flavor, stability and structure, cottonseed oil continues to be in demand by food processors.

7.2 Cottonseed oil properties

Crude cottonseed oil, derived mainly from the seeds of *Gossypium hirsutum* (American) or *Gossypium barbadense* (Egyptian) varieties of cotton, has a strong, characteristic flavor and a dark, reddish-brown color from the presence of highly colored material extracted from the seed. It is a member of a particularly useful group of vegetable oils, whose fatty acids consist substantially of C_{16} and C_{18} fatty acids containing no more than two double bonds. Cottonseed is stable in the β' crystal form which is desirable in most 'solid' products because it promotes a smooth workable consistency, usually referred to as plasticity. The reverted flavor of deodorized cottonseed is usually described as nutty or nut-like, which is more acceptable at higher degrees of oxidation than other vegetable oils. Its characteristics make it a highly desirable food oil for use

in salad and cooking oils, shortenings, margarines, and specialty fats and oils products.

The characteristics of a particular cottonseed oil sample are dependent upon the variety of cotton grown and on growing conditions such as temperature, soil conditions, fertilizers and rainfall, as well as the handling and storage conditions after harvesting. Factors that contribute to variations in the properties of cottonseed oil before it is crushed or extracted from the seed are geographic regions, climate, fertilizers, seed handling, and storage conditions. (Tharp 1948; Stansbury *et al.* 1953; Cherry 1983; Jones and King 1990, 1996).

7.2.1 Cottonseed oil triacylglycerol composition

Both the chemical and physical properties of fats and oils are largely determined by the fatty acids that they contain and their position within the triacylglycerol molecule. Chemically, all fats and oils are esters of glycerol and fatty acids. Nevertheless, the physical properties of natural fats and oils vary widely. This is because (i) the proportion of the fatty acids vary over wide ranges, and (ii) the triacylglycerol structures vary for each individual oil and fat. Fats and oils are commonly referred to as triacylglycerols (triglycerides) because the glycerol molecule has three hydroxyl groups where a fatty acid can be attached. All triacylglycerols have the same glycerol unit, so it is the fatty acids which contribute the different properties. The fatty acid components are distinguished in three ways: (i) chain length, (ii) the number and position of the double bonds, and (iii) the position of the fatty acids within the glycerol molecule. Variations in these characteristics are responsible for the chemical and physical differences experienced with edible fats and oils. The fatty acid profile of cottonseed oil is typical of the oleic–linoleic group of vegetable oils, since these two unsaturated fatty acids make up almost 75% of the total fatty acids. Oleic makes up about 22%, linoleic about 52% and linolenic acid is usually less than 1%. Palmitic acid, a saturated fatty acid usually associated with β' crystals, makes up around 24% of the total. Only minor amounts of other saturated fatty acids, stearic and myristic, are detected in typical cottonseed oils.

Cottonseed oil contains up to 0.5% of a pair of unique fatty acids: malvalic (18:1) and sterculic (19:1). These acids are characterized by the presence of a cyclopropene group at or near the center of the fatty acid chain. Under appropriate conditions these give colored compounds and the development of a red color in the Halphen test (reaction with sulfur in carbon disulfide in the presence of amyl alcohol) is due to the cyclopropene acids and therefore characteristic of cottonseed oil (and other minor oils containing cyclopropene acids). This test for cottonseed oil was developed over a century ago in 1897. Inclusion of cyclopropenoid acids in animal diets causes undesirable physiological effects such as reduced egg production, poor hatching, and pink egg whites in chickens, and in rats, decreased growth and sexual development and

carcinogenic properties. Conventional processing, specifically hydrogenation and deodorization, largely inactivate these acids. For example their level is reduced from 0.53 to 0.04% by deodorization (Jones and King 1996).

The triacylglycerol structure of an edible fat or oil is affected by the fatty acids present and the point of attachment of each acyl chain to the glycerol. Triacylglycerols with three identical fatty acids are called monoacid triacylglycerols. Triacylglycerols containing more than one type of fatty acid are called mixed triacylglycerols. A mixed triacylglycerol containing three different fatty acids has three regioisomeric forms and six stereoisomeric forms, depending on which fatty acid is in the middle, *sn*-2, or β-position of the glycerol portion of the molecule and which fatty acids are in the α or outer positions (*sn*-1 and *sn*-3). The distribution of the fatty acids in cottonseed oil is considered to be nonrandom, with the saturated fatty acids positioned predominately in the *sn*-1 and/or *sn*-3 positions and the unsaturated fatty acids in the β or *sn*-2 position. Since linoleic, oleic and palmitic fatty acids account for over 90% of cottonseed oil's fatty acid composition, most of the triacylglycerols contain some combination of these fatty acids. Analysis of cottonseed oil by semiquantitative thin-layer chromatography indicated that the distribution of saturated (S) and unsaturated fatty acids (U) in the 1, 2, and 3 acyl positions were: 11.8% SUS, 4.4% SSU, 12.3% USU, and 42% UUS. Almost 30% of the triacylglycerols contain only unsaturated fatty acids but no molecules are completely saturated (Jones and King 1996).

Genetic engineering has been applied to a number of oilseed plants, including cotton, to alter the fatty acid profile. Generally, it has been found that fatty acid composition can be changed to improve functionality or for nutritional reasons. To improve oxidative and frying stability, the primary thrust of research has been to increase the level of oleic acid at the expense of the polyunsaturated acids particularly responsible for oxidation and polymerization. To enhance functionality and plasticity, emphasis has been on increasing the level of saturated acids such as palmitic and/or stearic. Such oils then do not need to undergo partial hydrogenation, which produces the *trans* isomers now believed to be nutritionally undesirable. Oils with reduced content of saturated acids have also been developed. This permits a 'lower-saturated' claim to be put on the label. Seeds have also been modified to produce oils with useful levels of C_{12} and C_{14} acids as alternatives to the commodity lauric oils (coconut and palmkernel, see Chapter 6).

Generally, it appears that genetic engineering may enable the farmer to grow functional oils superior to those obtained by traditional blending and processing techniques. However there are limiting factors to this improved technology, particularly identity preservation (IP) and economics. IP requires segregated fields, storage, handling, transportation of seed and of oil, and seed extraction. Existing systems are designed mainly to handle very large quantities of commodity oilseeds. IP is only one of the factors contributing to the final cost of the premium product—a cost which end-users have proved reluctant to

accept. Success has come where the modified product has displaced the earlier form and itself become the commodity product as with rapeseed/canola oil.

Despite the difficulties, Australian scientists have developed improved cottonseed oils with enhanced levels of oleic (20% raised to 77% mainly at the expense of linoleic acid) and of stearic acid (2% raised to 38% at the expense of both oleic and linoleic acid) (Anon 2001).

7.2.2 Cottonseed oil nonglyceride components

The primary constituents in crude vegetable oils (the triacylglycerols) are accompanied by varying amounts of nonglyceride materials. Cottonseed oil is unusual for the amount and variety of such substances present in the crude oil. The content of nonglyceride substances, exclusive of free fatty acids, commonly amounts to 2% or more in the crude oil. These minor components, also referred to as the unsaponifiable fraction, consist of phospholipids, tocopherols, sterols, resins, carbohydrates, pesticides, and gossypol and other pigments. Some, but not all, of the nonglyceride materials are undesirable. Therefore, the objective in all edible oil processing is to remove the objectionable impurities with minimum loss of the desirable constituents.

7.2.2.1 Gossypol

Cottonseed oil is unique among the commercially important fats and oils in the presence of a relatively complex system of pigments. Most of the pigments are of the gossypol type. These are biologically active terpenoid substances present in discrete glands in many parts of the cotton plant, including the seed. During seed processing, the glands are ruptured allowing the gossypol and other similar substances to mix with the protein and oil. Fortunately for the oil processor, most of the gossypol binds to the protein. However, since gossypol and its chemically-related compounds are strong pigments, it is a major objective during caustic refining and bleaching to remove as much of the color pigments as possible. Gossypol compounds give crude cottonseed oil a red color so dark that it usually appears to be black. The characteristic yellow–amber color of refined, bleached and deodorized cottonseed oil is primarily due to the remaining gossypol after processing. Analyses have indicated that alkali-refining and bleaching reduce the gossypol content of cottonseed oil to less than 1 ppm from 0.05–0.42% in solvent-extracted oil and from 0.25–0.47% in screw-pressed oil (Jones and King 1996).

7.2.2.2 Phospholipids

These components, known to oil processors as phosphatides, together with small quantities of carbohydrates and resins, are frequently referred to as ‘gums’, which have adverse effects on product quality and refined oil yield. Phospholipids are emulsifiers and so hinder the separation of oil and water phases

in the caustic-refining process. The phospholipids are broadly separated into hydratable and non-hydratable types. The former can be removed by treatment with water but the non-hydratable compounds, which are salts or coordination compounds of calcium and magnesium, primarily with phosphatidic acid, can only be rendered insoluble in the oil by the use chemical reagents, the most commonly used being phosphoric acid.

Phospholipid content is normally calculated from the determination of total phosphorus and the use of a factor relating the molecular weight of phosphorus to the mean molecular weight of the phospholipids in the oil. Typically, the amount of phospholipids in cottonseed crude oil varies from about 0.7–0.9%. The phospholipids can also be beneficial in that they act as synergists for the tocopherols which inhibit autoxidation of vegetable oils. This synergistic effect is partly responsible for the oxidative stability of crude cottonseed oil (Jones and King 1996).

7.2.2.3 Tocopherols

As well as constituting the family of E vitamins, the tocopherols are natural antioxidants when present at levels below 2000 ppm. At higher levels they act as pro-oxidants. These natural fat-soluble antioxidants exist in at least seven forms with α-, β-, γ-, and δ-tocopherol predominating in most vegetable oils. α-Tocopherol contributes vitamin E activity and some oxidative resistance but the γ and δ forms are the more effective antioxidants. Crude cottonseed oil contains about 1000 ppm of tocopherols but up to a third can be lost during processing. The tocopherol content decreases during each stage of processing with the highest reductions occurring during chemical refining and deodorization. Caustic refining can remove as much as 10–20% of the tocopherols, and 30–60% of the remainder can be lost during deodorization.

7.2.2.4 Sterols

Sterols are crystalline, neutral, unsaponifiable, high-melting alcohols with multiple-ring structures. Though minor components of all natural fats and oils, the sterols are major constituents of the unsaponifiable matter remaining in processed vegetable oils. The remainder consists mainly of saturated and unsaturated hydrocarbons. The sterols are colorless, heat-stable and relatively inert. They do not contribute any important physical or chemical property to a fat or oil but they may exert a nutritional influence. Chemical refining removes a portion of the sterols, but more effective separation requires fractional crystallization, molecular distillation, or high-temperature steam distillation. Vegetable oil soapstock from caustic refining and deodorizer residues are both rich sources for sterol reclamation. An evaluation, comparing caustic-refined cottonseed oil with deodorized cottonseed salad oil, showed a reduction of total sterols from 0.574 to 0.397 mg/100 g of oil (Norcia and Rosenthal 1966). The phytosterols, recovered

from processing byproducts, are the starting materials for the synthesis of sex hormones and the preparation of synthetic vitamin D.

7.2.2.5 Pesticides

Pesticides are used to increase agriculture production throughout the world. The majority of the pesticides applied eventually reach the soil surface where they gradually spread, translocate to other environments, and eventually degrade. Translocation to oil-bearing plant seeds has also been demonstrated. Processing studies have shown that neither solvent extraction nor bleaching affect pesticide levels in the vegetable oils. However, it was found that pesticides were removed by volatilization during hydrogenation and deodorization (Smith *et al.* 1968; Mounts *et al.* 1969; Chaudry *et al.* 1976). US government agencies, recognizing that the insecticides are distilled from edible oils during deodorization, have forbidden the use of deodorization distillates in animal feeds.

7.2.2.6 Trace metals

Vegetable oils contain varying levels of trace metals depending upon exposure during the growing season and subsequently during extraction and processing. These metals reduce the efficiency of the subsequent processing and are harmful to product quality and human health. Trace quantities of copper, iron, manganese, and nickel substantially reduce the oxidative stability of oils while calcium, sodium, and magnesium reduce the efficiency of refining, bleaching, and hydrogenation systems. The effects of the metals can be diminished by the use of chelating agents at various process points to sequester the trace metals (Flider and Orthoefer 1981). The most widely used are citric and phosphoric acids.

7.2.3 Cottonseed oil physical characteristics

The physical properties of all fats and oils, including cottonseed oil, are determined by their chemical composition. Physical characteristics are of practical importance because most applications depend on the melting behavior, solubility, flavor, density, appearance and on other physical properties to provide functionality in finished products. Appropriate analytical and physical evaluation methods are used to measure these attributes for identification, trading, and control purposes.

7.2.3.1 Melting point

The usual definition for a melting point is the temperature at which a material changes from solid to liquid. Determination of the melting point for fats and oils is difficult because these compounds do not have true melting points, as the different components melt at different temperatures. Fats and oils are complex mixtures of triacylglycerols that pass through a gradual softening before becoming completely liquid. Melting point measurement is further complicated

by the fact that fat crystals can exist in several polymorphic modifications, depending on the specific triacylglycerol involved and on the temperature–time pretreatment or tempering of the sample. For a melting point one figure within the melting range must be selected. Several methods to determine the melting point have been standardized by AOCS and other organizations, each providing slightly different values: capillary melting point, softening point, slip melting point (SMP), Wiley melting point, Mettler dropping point, and others. The temperature range at which cottonseed oil changes from a solid to a liquid is 50–60°F (10–16°C).

7.2.3.2 Solid fat index

This parameter has become the single most important criterion for the melting behavior and crystalline structure of fats and oils products. It determines the proportion of solid and liquid materials at a given temperature. The solid fat index analysis is an empirical measure of the solid fat content. It is calculated from the specific volume at various temperatures using a dilatometric scale graduated in units of ml $\times 1000$. Values for the solid content are usually determined at 50, 70, 80, 92 and 104°F (10, 21.1, 26.7, 33.3 and 40°C). Except in the US, this parameter is now measured by broad band pulse ^{1}H NMR. Unlike the tropical oils, cottonseed and other oleic/linoleic oils do not contain any significant quantity of triacylglycerols with two or three saturated fatty acids; therefore, the solid fat index at the lowest temperature usually measured would have very low values. Natural cottonseed oil can have a solid fat index content at 50°F (10°C) but not at the higher temperature measurements.

7.2.3.3 Cold test

The ability of an oil to remain liquid during refrigerator storage is determined by the cold test analysis; crystallization resistance is measured as the time in hours before the oil appears cloudy at 32°F (0°C). Standardized AOCS Method Cc 11-53 requires that dry filtered oil be placed in a sealed 4-ounce bottle and submerged in an ice bath. A 'go-no-go' examination for clarity after $5\frac{1}{2}$ hours is stipulated by the Official AOCS Method: however, most laboratories practice the alternative procedure which continues the clarity examination until a cloud appears. The cold test procedure was developed to evaluate cottonseed oil for the production of mayonnaise and salad dressings. Oil that solidifies at refrigerator temperatures will cause an emulsion-break with a resultant separation of the oil and water phases. Currently, the cold test is also utilized to ensure that bottled oils for retail sale will not develop an unattractive appearance on the grocery shelf.

7.2.3.4 Cloud point

An empirical cloud point analysis is performed by stirring a sample of fat while it is being cooled until the oil has clouded enough to block a light beam of known intensity. Both cloud point and congeal point values are more closely related to

consistency than melting point. A definite relationship exists between the cloud point results and the solid fat index values at 92°F (33.3°C). Cottonseed oil that has not been winterized or hydrogenated will have a cloud point of 30–38°F (−1.1–3.3°C). Winterized cottonseed salad oil, with the hard fraction removed, will have a cloud point of approximately 22–26°F (5.6–3.3°C).

7.2.3.5 Titer

The titer test, AOCS Method Cc 12-59, measures the solidification point of the fatty acids. Titer analyses are used predominately in the soap and fatty acid industries. For edible oils, titer values are commonly specified for oils that have been hydrogenated to almost complete saturation. Cottonseed oil hydrogenated to an iodine value of 5 or less should have a titer value of about 60°C.

7.2.3.6 Pour point

The pour point, another 'melting point' determination, of an oil is the temperature at which it just remains pourable. For crude cottonseed oil, the pour point is between 25 and 32°F. The pour point temperature rises as the oil is saturated: for hydrogenated cottonseed the pour point will be higher than for the unhardened oil and can be as high as 140°F (60°C) depending upon the degree of saturation.

7.2.3.7 Refractive index

The refractive index of fats and oils is an important characteristic because of the ease and speed with which it can be determined precisely, the small amount of sample required, and its relationship to structure. It is useful for source oil identification, for observing progress of reactions rapidly, and for establishing purity. With minor exceptions the general relationships between refractive index and the composition of an oil product are as follows: refractive indices increase as chain length increases, increase as the number of double bonds increase, are higher for triacylglycerols than for fatty acids, and are higher for monoacylglycerols than for corresponding triacylglycerols. The indices of mixed triacylglycerols are close to corresponding simple triacylglycerols. Refractive index values decrease as the temperature is increased. By reference to a predetermined curve relating the refractive index at temperature measured to iodine value, a rapid estimation of the iodine value may be made. One source of error in this method is that *trans* acids formed during hydrogenation affect refractive index values but not iodine value.

7.2.3.8 Viscosity

The physical property of a fluid or semi-fluid that enables it to develop and maintain a certain amount of shearing stress dependent upon the velocity of flow and then to offer continued resistance to flow is defined as viscosity. The viscosity of an oil is temperature dependent; rate of flow increases as the temperature increases. For edible fats and oils, viscosity decreases as saturation

decreases and with shorter chain lengths. Most vegetable oils in the linoleic category have similar viscosities; however, cottonseed oil should be slightly less viscous due a higher saturation level than the other oils in this category.

7.2.3.9 Specific gravity

The density of cottonseed oil is affected both by temperature and fatty acid composition. Density decreases about 0.000638 units for each °C or 0.000355 for each °F increase when heated in the 150–500°F range. At lower temperatures the change is greater or about 0.00069 units per °C for cottonseed oil between 0 and 40°C. The specific gravity of vegetable oils has an inverse relationship with molecular weight and a direct relationship with the degree of unsaturation. Lund (1948) developed an equation based on saponification and iodine values to predict the specific gravity of liquid vegetable oils at 15°/15°C:

$$\begin{aligned}\text{Specific gravity} = {} & 0.8475 + 0.0003\ (\text{saponification value}) \\ & + 0.00014\ (\text{iodine value})\end{aligned}$$

A liter of cottonseed oil with a specific gravity of 0.917 will weigh 917 g or 917 kg/m^3. A US gallon of cottonseed oil with this specific gravity would weigh 7.66 pounds.

7.2.3.10 Smoke point

The smoke, fire and flash points of cottonseed oil, like other fats and oils, are almost entirely dependent upon the free fatty acid content. The smoke point of fats and oils decreases when the triacylglycerols are split to form free fatty acids and glycerol. That is, a partially hydrolyzed oil smokes at a lower temperature. The glycerol portion decomposes to form acrolein and this is the major source of the smoke evolved from heated fats and oils. Cottonseed oil with a 0.01% free fatty acid, like other long chain fatty acid oils, will have a smoke point of approximately 450°F (230°C).

7.2.3.11 Flash point

Flash point is the temperature at which the volatile products are evolved at such a rate that they are capable of being ignited but not supporting combustion. A crude cottonseed oil with a free fatty acid content of 1.8% was found to have a flash point of 560°F (293°C). Solvent-extracted oils can have a lower flash point due to a solvent residue. A flash point test identifies this crude oil deficiency and so prevents accidental fire or explosion in an atmosphere that is not explosion-proof. Crude vegetable oil shipments received with a flash point below 250°F can be rejected under most trading rules.

7.2.3.12 Color

The Wesson method is the principal method for color measurement in the US edible oil industry. This has been utilized for many years primarily because of

its simplicity. AOCS Method Cc 13b-45 determines the color of a melted fat or oil product by comparison with red and yellow Lovibond glasses of known characteristics. Crude cottonseed oil has a dark reddish-brown color from the presence of highly colored material extracted from the seed. After processing, the oil typically has a rich golden yellow color which is lighter than peanut and corn oils but darker than soybean, sunflower, canola and safflower oils. Some of the color found in cottonseed oil comes from carotene but most of the color is due a low residual level of gossypol and its derivatives. While the carotene color pigments are rendered colorless by heat bleaching and some of the pigments may be removed by adsorption bleaching, gossypol can only be removed by alkali-refining. Color removal is dependent upon the cottonseed handling and on storage conditions prior to crushing. Cottonseed oil darkens when exposed to high temperature. The color is trapped and cannot removed even with caustic refining. Vegetable oil trading rules recognize the color removable problems with cottonseed oil with premium grades specifying bleach color as well as refining loss. The trading rules have established price adjustments for higher colors and refining losses. The best crude cottonseed oil grade is 'prime crude cottonseed oil' which requires that the oil be capable of refining to not less than 7.6 red on the Lovibond scale. Maximum colors for 'basis prime crude', 'off crude', and 'reddish off crude' oils are 12, 20, and 30 red. No maximum red color is specified for 'low grade cottonseed oil'.

7.2.3.13 Flavor

One of the most important palatability parameters for edible fats and oils users is flavor. Generally, the flavor of an edible oil product should be completely bland, so that it can enhance the food product's flavor rather than contribute one. Cottonseed oil is well known for its initial bland flavor and the nutty flavor it develops with oxidation. It has been used as the standard for comparison with other oils for both flavor and odor. The nutty flavor developed with oxidation is more pleasant than the oxidized flavor of some of the other oils in the oleic linoleic classifications. For example, soybean oil reverts to a 'painty', green, watermelon-type flavor with oxidation. Another major cause of off-flavors in food oils is hydrolysis. The free fatty acids liberated with hydrolysis have distinct flavors and odors. These are more disagreeable when the fatty acid chain length is shorter than 14 carbons. Cottonseed oil which contains mostly C_{16} and C_{18} fatty acids does not become unpalatable until the FFA exceeds 1.0%.

7.2.3.14 Consistency

Fats and oils are polymorphic, which means that with cooling a series of increasingly organized crystal changes occur until a final crystal form is achieved. Each fat and oil has an inherent crystallization tendency, either β or β'. The tiny, uniform, tightly-knit, needle-like β' crystals produce smooth textured shortening, margarine and speciality solidified oil products with good plasticity,

heat resistance and good creaming properties. The larger, high melting, self-occluding, coarse, stable β crystals produce grainy, sandy, brittle solidified oil products which can experience separation of the liquid oil portion. The crystal habit of a fat can be controlled by source oil selection. Hydrogenated cottonseed oil crystallizes in the β′ crystal form, while almost all of the other oils grown in the US crystallize in the β form.

7.2.4 Cottonseed oil chemical characteristics

Cottonseed oil, like all oils and fats, is made up of glycerol esters with some nonglyceridic material in lesser proportion. It is the chemical composition that defines the chemical and physical properties of all fats and oils, which in turn will determine the suitability of the oil for various processes and applications.

7.2.4.1 Free fatty acid

Oil chemists have known since the 1880s that free fatty acid (FFA) content is a good indicator of crude cottonseed oil quality. Hydrolysis causes the triacylglycerols molecule to split at the ester linkage to form free fatty acids, di- and mono-acylglycerols, and eventually free glycerol. This reaction is normally induced by the presence of moisture and accelerated by heat. It can also be promoted by certain enzymes (lipases). The liberated free fatty acids have a distinct flavor and odor which are more disagreeable when the fatty acid chain length is shorter than 14 carbons. Cottonseed oil which contains mostly C_{16} and C_{18} fatty acids does not become unpalatable until the FFA level exceeds 1.0%.

Crude oil from the best quality cottonseed will have a FFA content of 0.5–0.6%. During a good season the FFA content will be less than 1.0%; however, during unfavorable climatic conditions the FFA content may average 5% or higher. Dry weather during cotton picking favors low FFA development. The oil in moist seeds, either in the field or in storage, undergoes rapid hydrolysis and extremely poor oil may contain 15–25% FFA. Since the refining process neutralizes or reduces free fatty acids to a level of 0.05%, this impurity has a direct relationship with refining loss. For chemical refining the quantity of sodium hydroxide for neutralization is based on the FFA level of the crude cottonseed oil. Refining losses as low as 2.5–3.0% are encountered with cottonseed oils containing 0.5–0.6% FFA but oils with high free fatty acid contents may have refining losses as high as 40–50% (Bailey 1948).

7.2.4.2 Peroxide value

The oxidation of oils is a major cause of their deterioration. Hydroperoxides formed by the reaction between oxygen and unsaturated fatty acids are the primary products of this reaction. Hydroperoxides themselves have no flavor or odor but break down rapidly to form aldehydes, many of which have a strong, disagreeable flavor and odor. The peroxide concentration, usually expressed

as peroxide value (PV), is a measure of oxidation or rancidity in its early stages. Peroxide value measures the concentration of substances, in terms of milli-equivalents of hydroperoxide per 1000 g of sample, that oxidize potassium iodide to iodine. AOCS Method Cd 8-53 (AOCS 1999) is the official method for peroxide value determinations.

7.2.4.3 AOM stability

The unsaturated fatty acids in all fats and oils are subject to oxidation, a chemical reaction which occurs with exposure to air. The eventual result is the development of an objectionable flavor and odor. The double bonds and the adjacent allylic functions are the sites of this chemical activity. Oil oxidation rate is roughly proportional to the degree of unsaturation; for example, linolenic fatty acid (18:3) with three double bonds is more susceptible to oxidation than linoleic (18:2) with only two double bonds, which is ten or more times as susceptible as oleic (18:1) with only one double bond. Oxidative deterioration results in the formation of hydroperoxides, which decompose into carbonyls, and dimerized and polymerized gums. It is accelerated by a rise in temperature, oxygen pressure, prior oxidation, metal ions, lipoxygenases, hematin compounds, loss of natural antioxidant, absence of metal deactivators, time and ultraviolet or visible light. Extensive oxidation will eventually destroy the beneficial components contained in many fats and oils, such as the carotenoids (vitamin A), the essential fatty acids (linoleic and linolenic), and the tocopherols (vitamin E).

The active oxygen method (AOM) is the most common analytical method used to measure oxidative stability of fats and oils products. AOM employs heat and aeration to accelerate oxidation of the oil by continuously bubbling air through a heated sample. Periodic peroxide values are measured to determine the time required for the oil to oxidize to a predetermined peroxide value under the AOM conditions. This method requires close attention to detail to produce reproducible results and even then the variation between laboratories is ± 25 for a l00 h AOM sample. Conductivity instruments such as the Rancimat and the Oxidative Stability Instrument have been developed as alternatives to AOM stability analysis. These instruments measure the increase in the conductivity of deionized water resulting from trapped volatile oxidation products produced when the oil product is heated under a stream of air. The conductivity increase is related to the oxidative stability of the products. These instruments provide a more reproducible measurement of oxidation stability with less technician time and attention.

7.2.4.4 Iodine value

The iodine value is a simple and rapidly determined chemical constant which measures the unsaturation of an oil but it does not define the specific fatty acids. The iodine value procedure determines the grams of iodine absorbed by 100 g

of oil. A higher iodine value indicates a greater number of double bonds. The iodine value results for cottonseed oil vary somewhat from year to year, sections of the country, and by growing season. A cooler growing season provides oil with a higher than average linoleic fatty acid (18:2) content and a lower oleic fatty acid (18:1) content; warmer growing seasons reverse this trend. These variations increase or decrease the number of double bonds and so affect the iodine value. Typically, cottonseed oil iodine values range from 103 in Texas to 112 in other regions of the US.

7.2.4.5 Unsaponifiable matter

Unsaponifiable matter includes those substances present in an oil which are soluble in nonpolar solvents but cannot be saponified by alkalis. These include sterols, hydrocarbons, tocopherols, pigments, and other materials of higher molecular weight which are insoluble in water. The level of unsaponifiable matter in good quality cottonseed oil usually ranges from 0.5–0.7%. It may be slightly less in deodorized oils due to slight reductions of sterols with alkali refining and high temperature deodorization.

7.2.4.6 Saponification value

The saponification value is useful in predicting the type of triacylglycerols in an oil by measuring the alkali-reactive groups. It is a measure of the average molecular weight of the fatty acids in the oil. Glycerol esters containing short-chain fatty acids have higher saponification values than those with longer-chain fatty acids. Cottonseed oil saponification values range from 189–198 with an average of 195. Without any other analytical measurement, saponification values overlap too much to identify individual fats or oils. Most oleic and linoleic classification oils have saponification values in the 180–200 range. Saponification value analyses have now been replaced almost entirely in edible oil processing by fatty acid composition obtained by gas liquid chromatography.

7.2.5 Typical analytical characteristics

Edible fats and oils vary considerably in the chemical composition which determines those physical characteristics that provide functionality. Physical, chemical, and performance analyses are the tools available to the fats and oils processor for the evaluation of existing products, development of new products, purchase of raw materials, and identification of specific customer requirements. Typical refined cottonseed oil analytical characteristics including fatty acid and triacylglycerol composition and ranges allowing for the different varieties, growing conditions, and analytical error are shown in Tables 7.1, 7.2 and 7.3.

Table 7.1 Typical refined cottonseed oil analytical characteristics

	Typical	Range
Specific gravity, g/cc at 25/25°C		0.916–0.918
Refractive index at 25°C		1.468–1.472
Iodine value	110.7	99.0–113.0
Saponification number		189–198
Unsaponifiable matter (%)		0.5–0.7
Titer (°C)		30.0–37.0
Melting point (°C)		10.0–16.0
Cloud point (°C)		−1.1–3.3
Pour point (°C)		−3.9–0
Cold test (h)	0	–
AOM stability (h)	15.0	

Table 7.2 Fatty acid composition (wt %)

		Typical	Range
Myristic	14:0	0.8	0.5–2.0
Palmitic	16:0	23.2	17.0–29.0
Palmitoleic	16:1	0.7	0.5–1.5
Stearic	18:0	2.1	1.0–4.0
Oleic	18:1	16.9	13.0–44.0
Linoleic	18:2	55.8	33.0–58.0
Linolenic	18:3	0.3	0.1–2.1

Table 7.3 Triacylglycerol composition (%) (TAG)*

	Gas chromatography (GC)	High-performance liquid chromatography (HPLC)
Palmitic–linoleic–linoleic	25.7	27.5
Linoleic–linoleic–linoleic	16.1	19.0
Palmitic–oleic–linoleic	14.0	14.0
Oleic–linoleic–linoleic	12.9	12.5
Palmitic–palmitic–linoleic	8.7	7.1
Oleic–oleic–linoleic	4.4	3.1
Palmitic–oleic–oleic	3.3	3.1
Palmitic–palmitic–oleic	2.5	2.2
Oleic–oleic–oleic	2.4	1.6
Stearic–linoleic–linoleic	2.4	1.4
Stearic–palmitic–linoleic	2.1	1.5
Stearic–oleic–linoleic	1.5	1.3

*The figures relate to all regioisomers and stereoisomers containing the three fatty acids indicated.

7.3 Cottonseed oil extraction

Cottonseed oil extraction has slowly progressed from edgestone to wedge press to hydraulic press. Hydraulic pressing was the predominant means used to separate the oil from cottonseed for most of the nineteenth century. As cotton spinning, weaving, and ginning operations improved during the eighteenth century and more cottonseed became available for crushing, the labor-intensive hydraulic press operation quickly yielded to the continuous screw press in the early 1900s. Because edible oil commanded a respectable market price and both the hydraulic press and the screw press left nearly 20% of the available oil in the press cake, research activity was initiated to find an acceptable solvent to extract the oil remaining in the cake. This effort led to the pre-press solvent extraction process in the 1930s. This combination of mechanical press and solvent extraction of press cake recovered more than 97% of the available oil in the cottonseed. Further demands in productivity and oil quality brought expander-solvent extraction of cottonseed oil into the crushing business in the 1970s. Toward the late 1980s, more than 80% of cottonseed crushed in the US was accomplished with an expander-solvent extraction process. Depending on the available transportation infrastructure, hardware, solvent, and skilled labor, cottonseed is still being processed by all three processes (screw press extraction, pre-press solvent extraction and expander-solvent extraction) in different parts of the world. The preferred process for cottonseed varies from nation to nation, and even from region to region within the same country (O'Brien and Wan 2001).

7.4 Cottonseed oil processing

Flow sequences for cottonseed oil processing after extraction for six different product groups are illustrated on Figure 7.1. Extracted and filtered cottonseed oil, still in use in some parts of the world, is omitted from this flowchart. Even in 1998, cottonseed oil purchased in local bazaars in Central Asia had no processing beyond extraction, except possibly a filtration process. Such a product would be unacceptable in the western world where consumers expect edible oil products that are:

- light in color
- bland flavored
- have a high smoke point
- maintain a clear appearance both on the grocery shelf and under refrigeration
- contain additives to prolong flavor and frying stability
- are modified to provide a specific performance characteristic
- are attractively packaged for convenient handling.

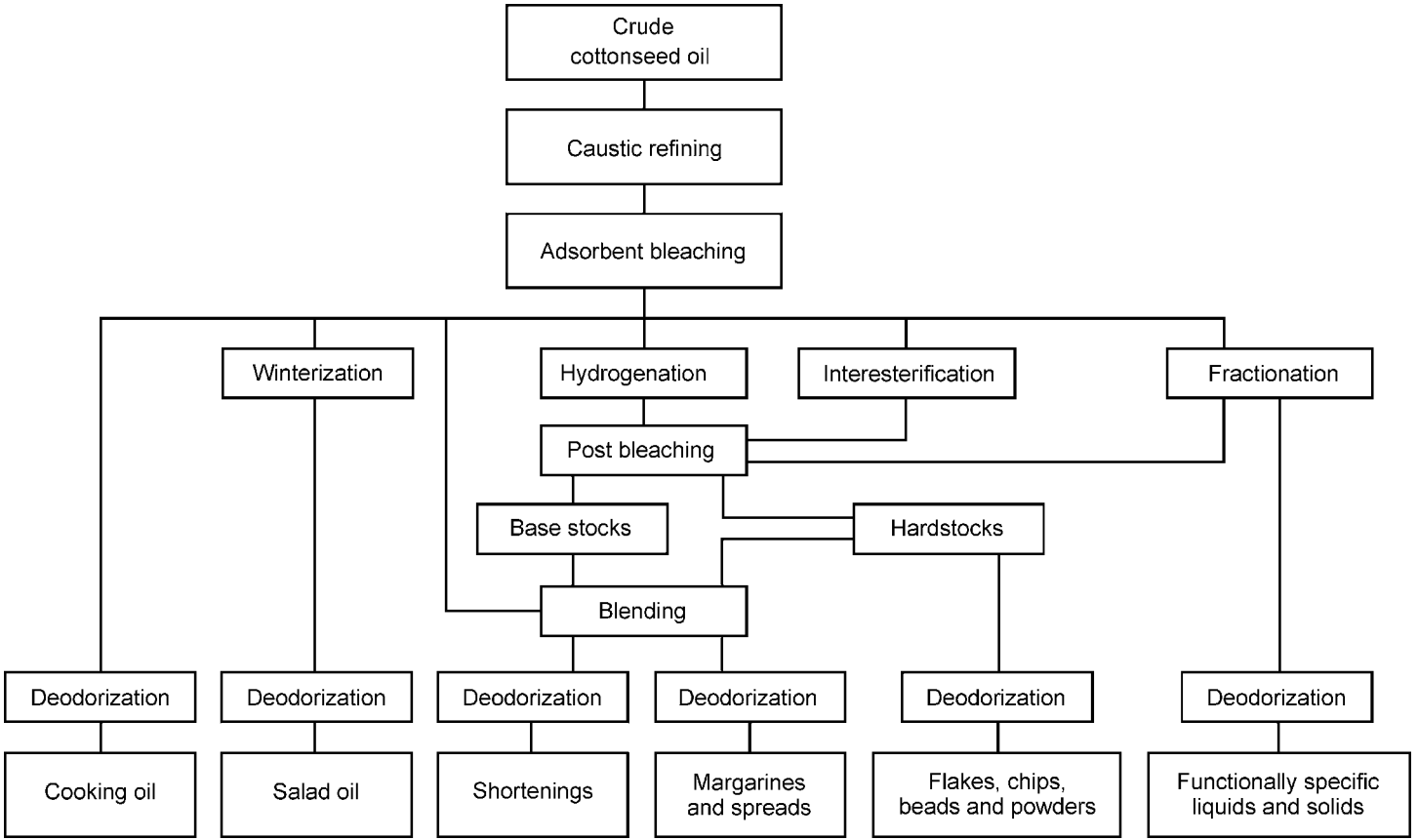

Figure 7.1 Cottonseed oil processing – flow sequence.

The processes responsible for these and other oil product qualities are presented in this section.

7.4.1 Refining

As used here, the term 'refining' refers to any purification treatment designed to remove free fatty acids, phospholipids, gossypol and other gross impurities from cottonseed oil. It excludes other processes such as bleaching or deodorization which are covered later. The refining process probably has more impact on the quality and economic performance of a vegetable oil than any of the other processes used during the conversion of crude oil to a finished product. Inadequately refined oils affect the operation of all succeeding processes and the quality of the finished product. Additional processing and handling required for poorly refined oils increase the cost of finished products beyond those produced from properly refined good quality oil.

Two different refining systems are currently used for vegetable oils: chemical and physical refining. Some shortcomings experienced with physical refining have maintained alkali-refining as the preferred vegetable oil purification technique in the US (Hamm 2001). Some oils, like cottonseed, contain non-glyceride materials that cannot be removed adequately by physical refining. However gossypol and related pigments in cottonseed oil readily combine with caustic soda and are thus removed more effectively by alkali refining.

7.4.2 Pre-bleaching

Bleaching is popularly and correctly regarded as the partial or complete removal of color. However, it is also a purification process to prepare the oil for further processing. Bleaching is relied upon to remove the traces of soap, phospholipids and pro-oxidant metals, remaining after caustic neutralization and water washing, that hinder filtration, poison the hydrogenation catalyst, darken the oil, and adversely affect the flavor of the finished oil. Another function, considered primary by many processors, is the removal of peroxides and secondary oxidation products. These impurities compete for space on the adsorbent surface of the filter media.

The usual method of bleaching is by adsorption of the pigments and other nonglyceride impurities on bleaching earth. In a typical process, the bleaching materials are added to the oil in an agitated vessel either at atmospheric pressure or under a vacuum. The oil is heated to a bleaching temperature of 160–230°F (70–110°C) and held to allow contact time with the bleaching earth. After the adsorbent has captured the impurities it is removed from the oil with a filtration system.

7.4.3 Winterization

When cottonseed oil is required for consumption as salad oil, it must be winterized, that is, much of the more saturated triacylglycerols must be removed so that the material will remain clear when exposed to reduced temperatures, such as those likely to be encountered with refrigeration. If the more saturated glycerol esters in cottonseed oil are not removed it will solidify at temperatures encountered in a refrigerator (around 45°F or 7.2°C).

The descriptive term 'winterization' evolved from the observation that refined and bleached cottonseed oil stored in outside tanks during the winter months physically separated into solid and liquid fractions. Topping or decanting the clear oil from the top of the tanks provided oil that remained liquid without clouding for long periods at cool temperatures. A need for liquid oil with these characteristics developed from the introduction of the refrigerator for home use and the requirements of the mayonnaise and salad dressing industry. The indoor process developed to simulate the natural winter process consisted of a chilled room held at 42°F (5.6°C) with deep, narrow rectangular tanks to provide the maximum surface exposure to cooling. Warm, dry, refined and bleached cottonseed oil pumped into the chill room tanks began to cool, and stearin crystallized immediately but slowly. Convection heat transfer simulated the outside storage conditions. Agitation was avoided because it fractured the crystal, causing formation of small, soft crystals that were difficult to filter. Cooling at this temperature, which simulated mild winter conditions closely, required 3 days to produce the desired large crystals for filtering. After the oil temperature equated with the room temperature, it was held for several hours to allow the stearin or hard fraction to precipitate more fully. The stearin was separated from the liquid oil by filtering with plate and frame presses. Normally, the oil was gravity fed to the filters to avoid breaking up the crystals. Winterization is still performed using the classical technique described above. However, most processors have made modifications to the equipment and process to improve efficiency, such as employing measures jacketed, enclosed tanks equipped with programmable cooling and agitation, better filtration, and improved pumping methods.

7.4.4 Fractionation

Cottonseed oil has melting points spanning a range from −13.3° to 35°C (8° to 95°F) due to its triacylglycerol composition. This range of melting points limits the applications for cottonseed oil. Application potential can be increased with fractionation, a process by which oil is separated into two or more portions. The three commercial processes used commercially for the fractionation of edible fats and oils are: dry fractionation, solvent fractionation, and aqueous detergent fractionation. Dry fractionation, which includes winterization, dewaxing,

hydraulic pressing, and crystal fractionation processes, is probably the most widely used method. Solvent or aqueous detergent fractionation processes provide better separation of specific fractions for the more sophisticated fats and oils products.

Some processors have employed solvent fractionation systems to produce salad oil, which has three major advantages over the product obtained by traditional winterization. These are: (i) a considerably lower viscosity, which allows a faster crystal growth for more rapid stearin separation; (ii) the salad oil produced has a better resistance to clouding at cool temperatures for longer cold tests; and (iii) less liquid oil is trapped in the stearin component giving higher salad oil yields. An operational continuous solvent process was described by Cavanagh (1961) for winterization of cottonseed oil.

Fractionation technology, in particular solvent fractionation, has been utilized to produce some very highly specialized edible oil products. High stability liquid oils, with AOM stability of 350 h minimum without the benefit of added antioxidants, and cocoa butter equivalents are two examples of products that can be produced with fractionation technology. Fractionation technologies may also be employed to produce base stocks for utilization as components in finished products for various applications.

7.4.5 Hydrogenation

The hydrogenation process is an important tool for the edible fats and oils processor. With hydrogenation, cottonseed oil can be converted from liquid oil into a plastic or solid fat more suitable for some applications. There are two reasons to hydrogenate a fat or an oil: (i) to convert naturally occurring oils into physical forms with melting and handling characteristics more suited to the desired product functionality, and (ii) to improve oxidative stability and so extend organoleptic acceptability. Hydrogenation involves the chemical addition of hydrogen to the double bonds in the unsaturated fatty acids but is accompanied by double bond movement and stereomutation. The reaction is carried out by mixing heated oil and hydrogen gas in the presence of a catalyst.

Cottonseed oil requires less hydrogenation to attain the same degree of hardness than other linoleic oils due to its fatty acid composition. Typically, an unhardened cottonseed oil is composed of 2.5% stearic and 22–23% palmitic as the principal saturated fatty acids. The unsaturated fatty acids are composed of approximately 18% oleic, 54% linoleic and less than 1% each of linolenic and palmitoleic. During hydrogenation neither the original stearic nor the palmitic fatty acids are changed. If the hardening reaction is completely selective, before any hydrogen reacts with oleic acid the linoleic fatty acid would have to be completely converted to oleic or other 18:1 isomers. On the disappearance of the linoleic acid, the oleic acid and its isomers will next absorb hydrogen to be converted to the fully saturated stearic fatty acid. This complete degree of

selectivity is never attained in practice. How closely it is approximated depends upon the catalyst type and dosage, temperature and pressure.

7.4.6 Interesterification

The least-known, least-used processing technique (in the US) available to the fats and oils processor for modification of the physical properties of an oil is interesterification, also often referred to as rearrangement. The interesterification process alters the distribution of the fatty acids in the triacylglycerols—producing products with melting and crystallization characteristics different from the original oil or fat. Unlike hydrogenation, interesterification neither affects the degree of saturation nor causes isomerization of the fatty acid double bond. It does not change the fatty acid composition of the starting material but rearranges the fatty acids on the glycerol molecule. The process of interesterification can be considered as the removal of fatty acids from the triacylglycerol molecules, shuffling them, and then replacement in then glycerol esters at random. This change in the distribution of the fatty acids affects the structural properties and melting behavior or the fats and oils. Commercially, interesterification has been utilized for the production of confectionery fats, margarine oils, cooking oils, frying fats, shortenings, and other special application fats and oils products.

Two types of chemical interesterification process are used: random and directed. The triacylglycerol distribution for cottonseed oil is considered to be non-random because the saturated fatty acids are positioned predominately in the *sn*-1 or *sn*-3 positions with the unsaturated fatty acids in the *sn*-2 position. Random rearrangement shuffles the fatty acid distribution to effect a typical melting point increase from 50.9–93.2°F (10.5–34°C) (Norris 1947). With directed interesterification, carried out at lower temperatures, a solid fat may be produced using natural cottonseed oil as the feedstock. The fully saturated triacylglycerols crystallize and are precipitated. This disturbs the equilibrium in the liquid fraction which will be re-established. The unsaturated portion that finally remains may be used as a salad oil, as most of the saturated fatty acids have been removed (Jones and King 1996). Interesterification can be utilized to produce base stocks, similar to those produced with hydrogenation or fractionation, or after blending to formulate shortenings, margarines, high-stability liquid oil products, and other speciality products for the food processor.

7.4.7 Post-bleaching

A separate bleaching operation for oils that have been hydrogenated, fractionated or interesterified has three purposes. It removes all traces of any catalyst used in the preceding process, any undesirable colors generated by the preceding process, and any peroxide and secondary oxidation products. Post-bleach systems

are usually batch systems to enable them to accommodate a wide variety of products.

7.4.8 Blending

Various base stocks are blended to produce the specified composition, consistency, and oxidative stability for the edible fats and oils products, such as shortenings, frying fats, margarine oils, specialty products, and even some salad oils. The base stocks may be composed of natural oils and/or modified oils produced with hydrogenation, fractionation, or interesterification processes. Blends are made to meet both the composition and consistency identified by the product developers and quality assurance requirements. The consistency controls can include specific limits for solid fat index, iodine value, melting point, fatty acid composition, or other parameters specific to the physical characteristics of the particular product. The blending process requires storage tanks to inventory the base stocks and scale tanks and/or meters to proportion the base stocks accurately for each different product. The blend tanks should be equipped with agitators and heating coils to assure a uniform blend (O'Brien 1998).

7.4.9 Deodorization

Edible fats and oils retain undesirable flavors and odors after refining and develop other undesirable organoleptic properties during bleaching, hydrogenation, fractionation and interesterification. Deodorization is a vacuum-steam distillation process operated at elevated temperatures to remove free fatty acids and other volatile odoriferous components that cause the undesirable flavors and odors. Additional deodorization benefits include heat-bleaching to destroy carotenoid pigments, pesticide removal, and reduction of cyclopropenoid fatty acids to a negligible level, all of which ensure oil purity. Deodorization is the last major processing step where flavor, odor, and many of the other qualities of the edible fat and oil product can be controlled. From this point onward, all of the efforts are directed toward retaining the quality of the deodorized product.

The odoriferous substances in oils are free fatty acids, peroxides, aldehydes, alcohols and other organic compounds. Experience has shown that the flavor and odor removal correlates well with the reduction of free fatty acids. Therefore, all commercial deodorization consists of steam stripping the oil for free fatty acid removal. Currently, batch, semi-continuous, and continuous systems of various designs are utilized to produce deodorized oils. All of the systems utilize steam stripping with four interrelated operation variables: vacuum, temperature, stripping steam rate, and holding time.

During high temperature deodorization polyunsaturated acid can be converted to *trans* isomers. Since this is more likely with linolenic acid than with linoleic acid, it is not a major problem with cottonseed oil.

7.5 Cottonseed oil utilization

Shortening, margarine, liquid oils, and other speciality processed fats and oils products have become essential ingredients in food products prepared in the home, in restaurants, and by food processors. Formerly, cottonseed oil was the major oil source in the US for all four food product categories. The US vegetable oil industry was developed with cottonseed oil as the original source oil and it dominated this market for almost 100 years. Many of the prepared food products available today were developed with a shortening, margarine or an oil product containing cottonseed oil. Soybean oil became the dominant vegetable oil in the world due to availability and economics, not to overall performance. Unlike other source oils, cottonseed oil is a more universal source oil for the provision of the desired functionality for most products; in fact, cottonseed oil or another β' crystal former is necessary in product formulations with soybean, sunflower, canola and corn oils, to produce a smooth, plastic, consistency.

7.5.1 Liquid oils

Clarity at or below ambient room temperature is the primary characteristic of a liquid oil. Natural vegetable oils that are liquid at room temperatures in temperate climates, $75 \pm 5^{\circ}$F ($23.4 \pm 3^{\circ}$C), contain high levels of unsaturated fatty acids with low melting points. Fatty acids with one or more double bonds and 18 carbon atoms are the most important unsaturated fatty acids for liquid oils. Oleic (18:1), a monounsaturated fatty acid, is the most widely distributed and most stable C_{18} unsaturated fatty acid. Linoleic (18:2) and linolenic (18:3) are the most widely distributed di- and triunsaturated fatty acids. Both of these polyunsaturated fatty acids are termed essential because they cannot be synthesized by animals, including man, and must be supplied in the diet. Complete exclusion of the essential fatty acids from the diet results in scaly skin, loss of weight, kidney lesions and eventually death.

Three major oil types have been developed which maintain different degrees of clarity and/or oxidative stability at and below room temperature in temperate climates. The definition for each of these classifications is given below.

Cooking oils. Edible oils that are liquid and clear at room temperature, 75°F (23.9°C), may be used for cooking. Cooking oils are typically used for pan frying, deep fat frying, sauces, gravies, marinates and other non-refrigerated food preparation where a clear liquid oil has application. Cooking oils usually congeal or solidify at refrigerator temperatures. Refined, bleached and deodorized cottonseed oil can only be classified as a cooking oil rather than a salad oil because it contains saturated fatty acids that cause it to cloud and solidify at refrigerated temperatures.

Salad oils. Edible oils that are suitable for the production of a mayonnaise or salad dressing emulsion remain liquid at refrigerated temperatures of 40°F (4.4°C). This requirement has been defined in terms of a minimum cold test of $5\frac{1}{2}$ hours; this measurement requires that a sample of the oil remain clear and brilliant while submerged in an ice bath. Cottonseed oil must have a portion of the more saturated triacylglycerols removed to meet the requirements of a salad oil, and this is normally achieved through winterization.

High stability oils. These edible oils that are clear at room temperature and also possess exceptional oxidative and flavor stability. High stability oils will withstand the abuse during AOM testing for periods in excess of 75 h and some longer than 300 h as opposed to a 15 h AOM result for cottonseed cooking oils. High stability oils can be produced by partial hydrogenation followed by fractionation or by genetic engineering of the oilseed.

7.5.1.1 Cooking and salad oil sources

Currently, cooking and salad oils are the only edible fat and oil products with increased consumption figures. Cottonseed oil was the principal cooking and salad oil used in the US until the late 1950s. As a source oil, it lost its dominance for usage in shortenings and margarines in the 1940–1950 era, but remained the preferred liquid oil due to the flavor problems associated with soybean oil. Demand for cottonseed salad and cooking oil decreased both in amount and market share after technology was developed to overcome the soybean oil flavor problems. One of the factors that led to the decreased cottonseed oil consumption in the US was that the export markets provided high returns. These exports helped to maintain the premium pricing for cottonseed oil marketed domestically. The major usage for liquid cottonseed oils in the US is as a cooking oil to prepare snack foods. The unique cottonseed oil flavor imparts a pleasant, stable flavor to potato chips and other salty snacks unattainable with other frying oils that lack the nutty fried flavor note.

7.5.1.2 Liquid oil markets

Liquid oils enter into three major areas of food preparation: retail, food service, and food processor. For some uses there is a similarity in product requirements, but there are also major differences in performance requirements in the three areas. Package sizes are obviously different, with the smallest designed for home use and the largest for food processor shipments of 150–180 thousand pound (7.5–9 tonnes) in tank cars. The retail market consists of bottled oils sold in grocery stores or other retail outlets for home use. The food service industry is composed of restaurants, hotels, institutions and other mass feeding operations. In many cases, food service oils are specialized products designed for the intended use, such as frying, salads and sauces. The food processor market is made up of manufacture of food products sold through retail outlets or utilized

by the food service industry. The food processor oils are normally specifically designed for the individual operation to provide the desired performance for the product as well as for the process.

7.5.2 Shortening

Shortening is an American invention developed with cottonseed oil to replace lard. Cottonseed oil was plentiful and inexpensive in the later decades of the nineteenth century, following the growth of the cotton industry in the US. As the shortening product developed it expanded from a limited application to include baked and other product types. In 1948, H. C. Black defined shortening as a semi-solid plastic material made wholly from fats and oils for use in cooking, baking, and frying (Black 1948). Today, shortening includes many other edible fats or oils products designed for a wide variety of prepared foods. With this broader application, shortening consistencies vary from wide workable ranges to brittle products with sharp melting characteristics, from very firm consistencies to liquid or products that can be pumped, or from creamy, smooth textures to grainy structures, all depending upon the requirements of the application.

In most cases, products identified as shortening are all fat; however, there are exceptions such as the roll-in shortenings that may contain moisture. In some cases, a fat or oil system may be identified as a shortening to distinguish it from a margarine product. Currently, a description for shortening would be: processed edible fats and oils that affect flavor, oxidative stability, shelf life, eating characteristics, nutrition, and the visual appeal of prepared foods by providing emulsification, lubricity, structure, aeration, moisture barrier, flavor medium and/or heat transfer (O'Brien 1998, 2000; Bell 1991).

The first shortenings, prepared by blending liquid cottonseed oil with stearins, were no better than the lard product they imitated. Introduction of the hydrogenation process enabled cottonseed oil processors to develop shortenings that outperformed the natural lard products to become eventually the desired product and permit premium pricing. Speciality shortening development was enhanced with the introduction of mono-and diacylglycerol emulsifiers in 1933. A plentiful supply of lower cost soybean oil and the advanced technologies developed during World War II made it impossible for cottonseed oil to maintain its dominant position for shortenings. However, it could not be totally replaced; cottonseed oil has some definite advantages over soybean and most other vegetable oils, one being its β'-crystal habit. A smooth consistency, fine texture, wide plastic range, good creaming properties, and a tolerance to high temperatures have become the standard for shortening. Most of these desirable characteristics are contributed by the tiny, needle-like β'-crystals. These pack together into dense, fine-grained, rigid structures to form three-dimensional networks capable of trapping a large amount of liquid oil. Soybean oil, as well as most of the other available vegetable oils, has a β-crystal habit and this produces large, coarse, high-melting, self-occluding crystals that clump, allowing separation of the

liquid oil, and responsible for a visible grainy appearance. A β′-crystal form can be induced with the addition of hydrogenated cottonseed oil, or another oil with a β′ crystal habit, usually at levels of 10% or higher.

Most shortenings are identified and formulated according to usage. Table 7.4 and Figure 7.2 illustrate the diverse SFI or solid–liquid relationships among

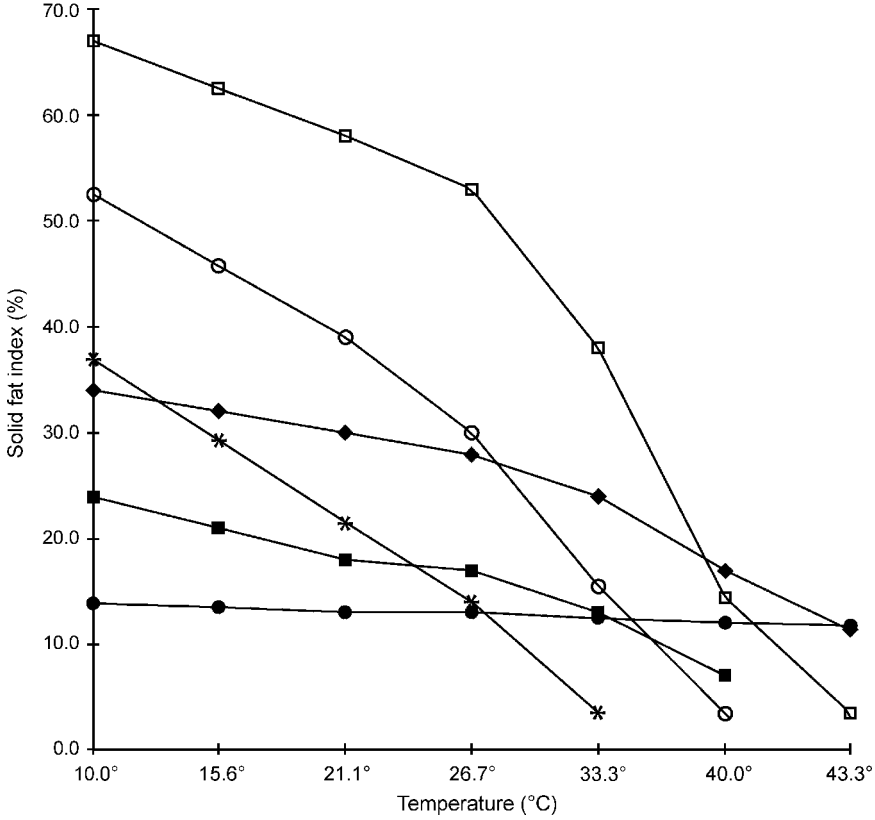

Figure 7.2 Shortening solids fat index profiles. Key: —●—, liquid bread; —■—, bakery all purpose; —◆—, puff pastry; —✱—, non dairy; —○—, frying; —□—, chips.

Table 7.4 Shortening solids fat index profile (see Figure 7.2)

	Liquid bread	Bakery all purpose	Puff pastry	Non dairy	Frying	Chips
10.0°C	14.0	24.0	34.0	37.0	52.5	67.0
15.6°C	13.5	21.0	32.0	29.25	45.8	62.5
21.1°C	13.0	18.0	30.0	21.5	39.0	58.0
26.7°C	13.0	17.0	28.0	14.0	30.0	53.0
33.3°C	12.5	13.0	24.0	3.5	15.5	38.0
40.0°C	12.0	7.0	17.0		3.5	14.5
43.3°C	11.75		11.3			3.5

different fats and oils products. The SFI slopes in Figure 7.2 indicate the differences in plastic range necessary to perform the desired function in the finished food products. Shortenings with the flattest SFI slopes have the widest plastic range for working at cool as well as elevated temperatures. The all-purpose and puff pastry shortenings in Figure 7.2 have the widest plastic range of the plasticized or solidified products. The frying and non-dairy shortenings illustrated have relatively steep SFI slopes which will provide a firm, brittle consistency at room temperature but are fluid at only slightly elevated temperatures. The very flat SFI slope is associated with a fluid opaque liquid or 'pumpable' shortening that has become popular due to the convenience offered, savings in handling costs, and lower saturated fatty acid levels. Liquid shortening systems can be produced with cottonseed oil, but the most successful products have been prepared with β-crystal forming hard fats that produce a stable fluid product with less processing. The most recent addition to the shortening classification is shortening chips. These specialty products are modifications of fat flakes, which were limited previously to hard fats or almost fully saturated fats. Shortening chips are formulated with steep SFI content to provide solid to liquid ratios high enough to flake, but low enough for good eating characteristics after melting into the food product (O'Brien 1998).

7.5.3 Margarine and spread

The physical and functional aspects of a margarine product are primarily dependent upon the characteristics of the major ingredient—the margarine oil. Margarine consistency, flavor and emulsion stability depend upon crystallized fat. Hydrogenation is the preferred process utilized to change the solid–liquid relationship of margarine base stocks. A direct relationship exists between the solid fat content and the structure, consistency and plasticity of the finished margarine. Solids fat index (SFI) values at 50°, 70° and 92°F (10.0°, 21.1° and 33.3°C) are utilized by most margarine manufactures for consistency control. The SFI values are indicative of the crystallization tendencies and the finished product quality: 50°F SFI indicates spreadability and moldability; 70°F SFI indicates room temperature consistency; and 92°F SFI indicates mouth feel.

7.5.3.1 Consumer margarine oil formulations

The major uses for consumer margarines and spreads continue to be as a table-spread, cooking ingredient, and seasoning agent. Consumer margarines are formulated by blending two or more base stocks with different degrees of hardness. This permits the margarines to be spread directly out of the refrigerator and to maintain a solid consistency at room temperature. For quite some time, hydrogenated cottonseed oil was a component of almost all vegetable oil margarines to induce a β′-crystal habit and so prevent graininess. However, this usage was curtailed with the development of more spreadable margarines, use

of multiple base stocks, and uniformly low cold storage temperatures which slowed the transition of margarines formulated with soybean and corn oils to the β-form.

7.5.3.2 Industrial margarine and spreads

Food service and food processor margarine and spreads are usually considered industrial products. The most popular food service margarine is the consumer block margarine formulations used for cooking and seasoning. Individual serving or portion control spread products are also popular food service dining room products. Bakers' margarine, formulated with an all-purpose shortening type base utilizing hydrogenated cottonseed oil to obtain the desired β′-crystal for consistency, is used by many food service kitchens for their baking requirements.

Food processor margarines and spread products are formulated for more specific uses than either the food service or consumer products. The block margarine formulations are packaged in 50 pound or 25 kilo cube cases for use in prepared foods. Margarines are also formulated and plasticized with Danish pastry roll-in capabilities to take advantage of the flavor, color and moisture incorporated into the emulsion. Spread type products were used by food processors before the consumer had accepted them, but for different applications. One of the applications is for self-basting of meat and poultry products during baking. Another is a biscuit topping with special dairy flavor notes and buttermilk curd. Others employ different flavors, spices, or other special ingredients for specific applications, product, or process. Hydrogenated cottonseed oil bases are utilized in many food processor margarine and spread formulations to obtain the desired performance.

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8 Groundnut (peanut) oil

Timothy H. Sanders

8.1 Peanut production, history and oil extraction

Groundnuts are produced on a significant basis in more than 30 countries, with worldwide production figures estimated to be in excess of 20 million tons. The three largest producers of groundnuts are India, China, and the US. In recent years, these countries accounted for approximately 65% of the world production (USDA, FAS 2001; see also Chapter 1). The plant is a legume native to South America and was cultivated as early as 2000–3000 BC (Hammons 1973). Although grown for many centuries, the economic importance of groundnuts and groundnut oil have increased rapidly only in the past century. Groundnut oil is expressed from the seed of *Arachis hypogaea* L., commonly known as groundnut, peanut, or earth nut because the seeds develop underground. Near the middle of the nineteenth century, oil mills in France began importing groundnuts from West Africa for crushing. The excellent quality of groundnut oil was the reason that mills for crushing were soon located throughout European countries, and then throughout the world. The world production of groundnut oil accounts for about 7–10% of the world vegetable oil total. Although uses in various countries differ greatly, overall more than 50% of all groundnuts produced are crushed for oil. Because oil use is so high in India, 75–80% of the groundnuts produced in that country are crushed for oil. In contrast, only 10–12% of recent groundnut production in the US was used for crushing (*Soya and Oilseed Bluebook* 2000). This low percentage is indicative of the economic importance of the nuts themselves as a food crop in the US. Because groundnuts have a high content of digestible protein and unsaturated oil and an exceptional roasted nutty flavor, they have substantial value as a nutritious and flavorful food commodity. More than one-third of the groundnuts produced are used as food on a worldwide basis. In the US, a high percentage of the limited number of groundnuts used for oil extraction have been separated from edible stocks because of the potential for aflatoxin. After minimal oil extraction, the pressed cake, which is low in oil and high in protein, may be used for animal food if aflatoxin is kept below acceptable levels.

Aflatoxin is a potentially carcinogenic compound produced by *Aspergillus flavus* and *Aspergillus parasiticus* which can invade peanuts, corn, cottonseed and other commodities. Control and testing programs are in place in technologically advanced countries, and the concentrations of aflatoxin are usually quite low in edible peanuts; however, the same may not be true in developing

countries. Aflatoxin is generally associated with the protein portion of peanuts and therefore is generally not found in refined oil. Crude or lightly processed oil containing fines may contain some aflatoxin.

Unacceptable pressed cake and much of the material remaining after physical and chemical extraction is relegated to fertilizer usage. Residue from oil processing may contain from 1–7% oil depending on whether the extraction was accomplished by hydraulic press, expeller, and/or solvent extractors. With inefficient equipment, the percentage oil remaining in the residue may be even higher. Pressed cake from edible-grade groundnuts with low oil content may be ground into flour for human consumption. In many parts of the world, extraction efficiency and lack of hygienic conditions yield residues unfit for human consumption. In these situations, the residue is utilized either for animal feed or as fertilizer (Woodroof 1983).

8.2 Oil uses

Throughout the world, frying and cooking constitute by far the greatest use of peanut oil. Peanut oil is also used in preparation of shortenings, margarines and mayonnaise. Some salad oil use is found, and the oil is suitable for use in pourable dressings because of the length of time solids are held in suspension in the oil. Peanut oil solidifies from 0–3°C and thus does not meet the strict terminology for salad oil (Young 1996). A high smoke point of 229.4°C is one of the major reasons peanut oil is used in deep-fat frying (Woodroof 1983). This high temperature allows food to cook quickly with a crisp coating and little oil absorption. Crude oil usually has a nut-like aroma but after refining the oil becomes odorless. Off-flavor and odor development is very limited during frying with groundnut oil. However, degradation of glycerides occurring during frying results in an increase of free fatty acids (FFA) and a decrease in smoke point. Early attempts to use peanut oil as diesel fuel or as an additive were successful but not viable economically (Young 1996). In India, peanut oil is used in the manufacture of vanaspati, a vegetable ghee substitute (Salunke and Desai 1986). Peanut oil is the main ingredient in this hydrogenated fat that resembles natural butter and ghee in appearance and texture. Speciality uses of peanut oil include use in soap to provide long-lasting lather, but because the oil is highly unsaturated it is prone to rancidity. Peanut oil is also regarded as a excellent emollient or non-drying, skin conditioning oil, similar in these properties to olive and castor oils. Highly aromatic peanut oil and peanut extract are high-value products with a strong roasted peanut flavor and nut aroma. These products have applications in flavor compounds, confections, sauces, baked goods, breakfast cereals, flavorings, frozen dairy desserts and flavor compound bases.

Peanut oil is generally subjected only to standard extraction procedures and uses of peanut oil generally do not require even limited hydrogenation. However,

hydrogenated vegetable oils are added at a 1–2% level to peanut butter as a stabilizer. Because of current nutritional interest in *trans*-fatty acids, major US brands of peanut butter were examined for the presence of *trans*-fatty acids but no *trans*-fats were detected in any of the samples using an analytical system with a detection limit of 0.01% (Sanders 2001).

8.3 Composition of groundnut oil

8.3.1 Oil in seed

Although a range of 36–56% has been reported for oil content, groundnuts commonly contain 40–50% oil. Oil content is commonly considered to be about 48–50% and is generally independent of market type or growth habit (Cobb and Johnson 1973). Triacylglycerol content of the oil is generally 95% with some variation among varieties. Maturation of the seed results in increases in total oil, triacylglycerol, and ratio of oleic acid to linoleic acid (O/L), while free fatty acids, polar lipids, monoacylglycerols, and diacylglycerols decrease (Sanders 1980a,b) (Table 8.1). The relative proportions of many components affecting shelf life of oil change dramatically as peanuts mature. Immature peanuts have a substantially lower shelf life than mature peanuts because of oil structure and composition including O/L ratio. Both O/L ratio and oven stability increase with maturity (Sanders 1982). The consistent relationship of these components to shelf life leaves little doubt as to the relationship of maturity and shelf life. Diacylglycerol and polar lipid fractions generally account for an additional 2% of the oil weight. Some reports suggest that total oil percentage decreases after full maturation as lipids are utilized for respiration. Factors such as maturity, environment, cultural practices, variety and soil temperature affect oil content and composition.

Table 8.1 Influence of maturity on quantity and composition of selected oil components of Florunner peanuts

Maturity stage[a]	Oil (% dry weight)	Triacylglycerol[b]	FFA[b]	Diacylglycerol[b]	Polar lipid[b]
5	25.3	85.3	4.5	4.7	2.0
6	30.8	89.3	3.1	3.5	1.4
7	34.4	88.3	2.5	3.6	1.9
8	42.8	90.8	1.8	3.0	1.6
9	45.6	92.6	1.3	2.2	1.3
10	46.7	94.3	0.9	2.0	1.0
11	48.4	94.8	0.7	1.9	0.7
12	48.2	95.8	0.7	1.7	0.6

[a]Relative maturity ranking based on internal shell color. At stage 5 seed are soft and watery, at stage 12 they are fully mature.
[b]Relative weight percent.

8.3.2 Fatty acids

Groundnut oil contains a high proportion of unsaturated fatty acids, in particular oleic (18:1) and linoleic (18:2). Palmitic (16:0), stearic (18:0), arachidic (20:0), 11-eicosenoic (20:1), behenic (22:0), and lignoceric (24:0) are also found in peanut oil, but only palmitic acid exceeds 10%. The long chain fatty acids are usually found at about or slightly less than 2%. With maturation, the percentage of oleic acid increases while linoleic acid percentage decreases slightly. Oxidative stability of groundnut oil is highly correlated with the ratio of oleic acid to linoleic acid (Fore *et al*. 1953). This ratio generally increases with seed maturity and oil stability increases simultaneously. Fatty acid composition values for peanut oil have been reported to vary widely (Worthington *et al*. 1972), as indicated in Table 8.2. The fatty acid composition of specific lipid classes in groundnut are also somewhat variable. The composition of three groundnut varieties and composition of lipid classes from those varieties are shown in Table 8.3 (Sanders 1980b). The fatty acid composition of the triacylglycerol is similar to that of whole oil since the fraction comprises about 95% of the total. Free fatty acid fractions consistently contain higher percentages of palmitic acid than did the triacylglycerol fractions. Long chain fatty acids (C_{20}–C_{24}) were generally more predominant in the *sn*-1,3-diacylglycerol than in other fractions and only traces of these long chain fatty acids are found in the *sn*-1,2 (2,3) diacylglycerol fraction. The phospholipid fractions contained the highest concentrations of palmitic acid.

Cooler production climates result in a greater degree of unsaturation, a lower O/L ratio, and thus a shorter shelf life. Factors of temperature, irrigation, and maturity have also been variously described as affecting degree of unsaturation. Oil composition is affected by mean temperature at critical growth periods (Holaday and Pearson 1974). The relationships examined may provide at least partial explanation for observed problems with oxidative stability in peanuts grown in cooler climates or with cooler temperatures during the latter weeks of the growing season. Holaday and Pearson (1974) demonstrated highly significant variations in oil production from year-to-year for all three major peanut types, highly significant differences among the same varieties grown

Table 8.2 Major fatty acids in groundnut oil (%wt)

Fatty acid	Percentage
Palmitic	7.4–12.5
Stearic	2.7–4.9
Oleic	41.3–67.4
Linoleic	13.9–35.4
Arachidic	1.2–1.9
Behenic	2.1–3.6
Lignoceric	0.9–1.7

Table 8.3 Fatty acid composition (mole %) of various lipid classes in oil from three peanut varieties: Florunner, Starr and Florigiant

Variety	Lipid class	16:0	18:0	18:1	18:2	20:0	20:1	22:0	24:0
Florunner	TAG	11.4	2.3	51.9	28.5	1.2	1.2	2.4	1.2
	FFA	16.9	3.0	45.0	30.1	1.1	1.2	1.9	0.8
	sn-1,3-DAG	13.8	2.6	51.5	25.1	1.2	1.6	2.4	1.4
	sn-1,2(2,3)DAG	13.6	1.5	48.6	36.3	–	–	–	–
	MAG	16.1	3.3	47.9	27.4	0.7	0.6	3.2	0.8
	PL	21.3	3.4	45.1	28.9	–	–	0.7	0.7
	WO	11.0	1.8	51.7	29.9	1.0	1.1	2.4	1.1
Starr	TAG	14.1	3.3	44.6	32.1	1.5	0.8	2.7	0.9
	FFA	21.0	4.2	40.4	29.9	1.2	0.4	2.2	0.8
	sn-1,3-DAG	17.7	3.8	48.2	22.9	1.5	1.2	3.4	1.3
	sn-1,2(2,3)DAG	15.5	2.5	48.9	33.1	–	–	–	–
	MAG	17.9	2.4	46.5	27.8	0.8	0.8	2.4	1.4
	PL	22.3	3.6	44.8	24.6	0.8	1.0	1.6	1.2
	WO	14.0	2.6	43.9	34.2	1.3	0.8	2.5	0.8
Florigiant	TAG	11.2	3.5	52.7	26.6	1.5	0.9	2.3	1.2
	FFA	16.1	3.9	46.6	28.2	1.6	1.0	1.9	0.7
	sn-1,3-DAG	13.2	3.9	52.1	22.2	2.4	1.7	3.4	1.2
	sn-1,2(2,3)DAG	12.6	2.2	48.9	35.8	–	–	0.3	0.3
	MAG	16.7	4.4	48.4	26.8	0.8	–	2.3	0.6
	PL	22.1	3.8	42.8	29.0	0.4	–	1.0	0.9
	WO	11.0	2.8	54.3	27.2	1.3	0.9	2.0	0.8

TAG = triacylglycerol; FFA = free fatty acid; DAG = diacylglycerol; MAG = monoacylglycerol; PL = polar lipid; WO = whole oil.

in different commercial production area, and highly significant interactions between location and year of production.

8.3.3 High-oleic peanut oil

Peanut lines with a high-oleic acid trait have been identified, and this trait has been incorporated into commercial peanut varieties. The original two lines identified had approximately 80% oleic and 2% linoleic acid (Norden *et al*. 1987). The lines developed with the high-oleic acid trait have O/L ratios of approximately 30 and the lines do not have meaningful differences in oil content, flavor, color or texture. Oxidative stability comparisons were made on extracted, neutralized, and bleached oil from high oleic (75.6% oleic and 4.7% linoleic) and conventional lines (56.1% oleic and 24.2% linoleic), differing only in fatty acid composition. These showed up to about 15 times greater oxidative stability in the high oleic oil (O'Keefe *et al*. 1993). Use of high-oleic oil in roasting of peanuts resulted in slight increases in shelf life as measured by oxidative stability and peroxide value, and the degree of improved shelf life was related to the O/L ratio of the peanut roasted (Sanders 2000, unpublished).

8.3.4 Triacylglycerol structure

Of the many triacylglycerol species in peanut oil, the species OOL, OOO, OLL, POL, and POO comprise the greatest proportions (Singleton and Pattee 1987), (O = oleic, L = linoleic, P = palmitic and these three letter symbols include all triacylglycerols with the three acyl groups indicated). This is expected since oleic acid, linoleic acid, and palmitic acid are the major fatty acids in peanut oil. Triacylglycerol species distribution has been utilized by the US Customs Service as one method of identification of some international origins of peanuts (Pettitt *et al*. 1992). Observations for distinguishing between the two production locations were:

- the ratio OOO/OOP was less than 1.0 for Chinese peanuts and approximately 1.5–1.7 for the Argentine peanuts
- PSL (S = stearic) was not measurable in Chinese peanuts and was present at about 0.2% in Argentine samples
- in Chinese samples, OOB (B = behenic) accounted for about 0.4% of the total triacylglycerols while in the Argentine samples it accounted for about 1.1%
- the percentage of OOO was about 10% in Chinese samples versus about 14% in Argentine samples.

The percentage ranges of triacylglycerol species for Argentine and US samples often overlap; however, origin identification was possible through trace element analysis.

Several studies have demonstrated that environment factors affect not only the fatty acid composition of peanut oil, but also, although apparently indirectly, the spatial arrangement of those acids on the triacylglycerol molecule (Sanders 1979; Sanders 1982). Triacylglycerol composition and structure are important in the areas of nutrition, oil stability and possible physiological effects. Table 8.4 provides data demonstrating the differences in triacylglycerol structure reasonably expected among different varieties of peanuts. The data shown in Table 8.4 indicate a nonrandom distribution of fatty acids among the *sn*-1, *sn*-2 and *sn*-3 positions of the triacylglycerols. The percentages of palmitic and stearic acids were generally very low for the *sn*-2 position, higher for *sn*-3, and highest for *sn*-1. The long chain (C_{20}–C_{24}) fatty acids were located almost exclusively at the *sn*-3 position. The *sn*-2 position of triacylglycerols from all the varieties was high in unsaturated fatty acids. The general pattern of fatty acids found at the *sn*-1 and *sn*-3 positions were similar for all varieties, although the mole percentages of each acid at the two positions frequently differed widely. Mole percentages of palmitic, stearic, and linoleic acids were always higher for the *sn*-1 than for the *sn*-3 position, while those of oleic acid were consistently higher for the *sn*-3 position. The patterns of fatty acid distribution at *sn*-2 differed not only from those at *sn*-1 and *sn*-3, but with variety as well.

Table 8.4 Stereospecific analyses of triacylglycerols from three peanut varieties

Variety	Compound or position	16:0	18:0	18:1	18:2	20:0	20:1	22:0	24:0
Florigiant	TAG	10.8	2.9	53.1	27.3	1.8	1.0	1.9	1.1
	1	20.1	4.9	50.7	22.6	0.5	0.7	0.4	0.3
	2	2.2	0.7	51.5	45.3	0.1	0.3	0.1	–
	3	10.3	3.2	57.2	14.0	4.8	2.0	5.3	3.0
Florunner	TAG	11.4	2.1	50.9	29.1	1.6	1.1	2.4	1.3
	1	20.7	3.5	49.5	24.4	0.3	0.7	0.5	0.5
	2	2.1	0.6	47.8	48.8	0.1	0.4	0.1	0.1
	3	11.4	2.3	55.5	14.1	4.4	2.3	6.5	3.4
Starr	TAG	14.2	3.3	43.3	33.0	1.8	1.1	2.7	0.7
	1	24.2	4.9	40.4	28.4	0.4	0.6	0.7	0.3
	2	2.4	0.8	39.5	56.9	0.1	0.2	0.1	–
	3	16.0	4.2	50.0	13.8	4.8	2.4	7.3	1.8

Plots of the percentage of a fatty acid in the total triacylglycerol against the percentage of that fatty acid at one of the positions of the triacylglycerol obtained from Table 8.4 and from additional varieties were subjected to linear regression analysis and determination of correlation coefficients (Sanders 1982). Major saturated, monoene, and diene fatty acids of corn triacylglycerols exhibited a concentration effect in all cases except for saturated acids in the *sn*-2 position (de la Roche *et al*. 1971). Peanut triacylglycerols exhibited this same pattern, and the low concentrations of the long chain fatty acids in the triacylglycerol were significantly correlated with percentages found at the *sn*-3 position only. This may be due to the general restriction of the saturated acids (16:0 and 18:0) from the *sn*-2 position and of the long chain acids from the *sn*-1 and *sn*-2 positions. The concentration of a fatty acid in the total triacylglycerols appeared to affect placement of that fatty acid on glycerol similarly for individual varieties of peanut. The variation in percentage of a fatty acid at any position indicates possible differences in the concentration of various triacylglycerols in the oil.

8.3.5 Phospholipids

The concentration of phospholipids in peanut oil is only about 1%. This class of compounds has been shown to be synergistic with tocopherols in delaying onset of lipid oxidation. The major phospholipids of peanut oil are phosphatidic acids (PA), phosphatidylglycerols (PG), phosphatidylethanolamines (PE), phosphatidylinositols (PI), and phosphatidylcholines (PC). The phospholipid content and concentrations have been shown to be affected by maturity and post-harvest treatment as shown in Table 8.5 (Singleton and Stikeleather 1995). The higher concentrations of PA and PC in immature peanuts might be explained on the basis that these are precursors of other phospholipids. Both excessive heat

Table 8.5 Effect of post-harvest treatment on total phospholipids

Treatment	Phospholipid (% area)					Total Phospholipid (mg/100 g dry wt)
	PA	PG	PE	PI	PC	
Control	2.2	2.5	13.3	15.7	66.4	500
Immature	4.5	2.3	14.0	7.6	71.7	700
Heat cured	9.5	1.1	16.0	15.4	58.1	900
Freeze-damaged	28.3	14.1	15.2	33.5	8.8	250

PA = phosphatidic acid; PG = phosphatidylglycerol; PE = phosphatidylethanolamine; PI = phosphatidylinositol; PC = phosphatidylcholine.

and freezing affect membrane stability as a result of significant differences in the phospholipid content and distribution. The large increase in PA and great decrease in PC with freezing of non-dried peanuts may be related to the fact that freezing induces phospholipase-D activity, particularly of PC. Hokes (1977) found that oven stability of peanut oil was related to the solvent used for extraction of phospholipids and that removal of phospholipids from the oil by precipitation reduced oven stability. The relative amounts of polar lipids extracted by different solvents might explain some variation in oven stability.

8.3.6 Sterols

Peanuts contain β-sitosterol, campesterol, stigmasterol, Δ^5-avenasterol, Δ^7-stigmasterol, Δ^7-avenasterol, and brassicasterol (Table 8.6). These sterols, which are secondary alcohols with 27–29 carbon atoms, are crystalline solids at room temperature. β-Sitosterol, the major component in peanut sterols, has been shown to inhibit cancer growth (Awad *et al.* 2000) and may offer protection from colon, prostate and breast cancer. Unrefined peanut oil contains approximately

Table 8.6 Sterol content of unsaponifiables of peanut oil and whole peanuts

	Peanut oil (mg/100 g)	Whole peanuts (mg/100 g)
Total sterol	337	220
β-Sitosterol	217	142
Campesterol	49	24
Stigmasterol	36	23
Δ^5-Avenasterol	26	NR
Δ^7-Stigmasterol	6	NR
Δ^7-Avenasterol	2	NR
Brassicasterol	trace	NR
Other	–	31

NR = not reported.

200 mg sitosterol/100 g of oil and this value is comparable to soybean oil that contains approximately 220 mg sitosterol/100 g (Awad *et al*. 2000).

8.3.7 Antioxidants

Data on tocopherol content and individual fatty acids from 31 cultivars for four years was used in a multiple regression equation for the prediction of stability of cold pressed oil. This revealed that 87% of the stability could be correlated with the ratio of total tocopherol to % linoleic acid. In a multi-year study of oil composition factors of peanuts from several origins, data indicated that tocopherol content was consistently different in peanuts from various origins (Sanders *et al*. 1992). Higher tocopherol content was consistently found in peanuts produced in the US compared to those produced in China or Argentina. The highest levels reported in US peanuts on a whole seed basis were almost 250 ppm, while the lowest levels were about 100 ppm. In extracted peanut oil, tocopherol content has been demonstrated to be as high as 650 ppm depending on the variety of peanut and growing conditions. The three-year study on peanuts from the US, China, and Argentina reported on levels of the pro-oxidant metals copper and iron. Copper content was always significantly lower in US peanuts and iron content was generally lower. These factors along with higher O/L ratios resulted in greatest oil oven stability and thus, the overall potential for longer shelf life for peanuts produced in the US. There is a consistently close relationship of oil quality factors such as O/L ratio, FFA, peroxide value, total carbonyls, tocopherols, copper and iron to most measures of shelf life. This suggests that any of these factors at inappropriate levels will contribute to shorter shelf life of products.

8.4 Chemical and physical characteristics of groundnut oil

8.4.1 General

Peanut oil characteristics compiled from several references are provided in Table 8.7. Unrefined peanut oil has a bland but slightly beany, nut-like flavor which is removed during refining.

8.4.2 Color

As peanuts mature, oil color becomes lighter as β-carotene and lutelin, which are responsible for the yellow color, become more diluted. Although oil color may be used to assess maturity, other methods are preferred because many factors, such as curing temperature and duration, influence oil color. Color measurement is frequently done by visual comparison under a Commission Internationale de l'Eclairage (CIE) standard light source. The Gardner color is determined using a Gardner-delta color comparator, which has a scale between 1 and 18.

Table 8.7 Chemical and physical characteristics of peanut oil

Characteristic	Value
Flavor and odor	Bland
Color (visual)	Light yellow
Color (Gardner, maximum)	4
Melting point	0–3°C
Smoke point	229.4°C
Specific gravity (21°C)	0.915
Free fatty acid (as oleic acid, maximum)	0.05%
Iodine value	82–106
Peroxide value (maximum)	10 meq peroxides oxygen/kg oil
Acetyl value	8.5–9.5
Heat of fusion (unhydrogenated)	21.7 cal/g
Refractive index (n_D 40°C)	1.46–1.465
Unsaponifiable lipids	0.40%

8.4.3 Melting point

At refrigeration temperatures (0–3°C), peanut oil sets to a gel. In contrast to safflower, soybean, corn and olive oils, peanut oil is not filterable during winterization.

8.4.4 Percentage of free fatty acid (FFA)

Peanut oils generally have low levels of FFA. The highest content is found in very immature seed (0.8%) and the percentage decreases to about 0.05% in fully mature seed. Improper handling, moisture, fungal invasion and other factors contribute to hydrolysis of triacylglycerols and cause significant increases in FFA. Neutralization in the refining process removes FFA, but crude oil used in many parts of the world may contain high FFA with resulting rapid deterioration in quality, flavor and stability.

8.4.5 Iodine value (IV)

The iodine value is a measure of the relative degree of unsaturation in oils as determined by the uptake of appropriate halogen compounds. Because melting point and oxidative stability are related to the degree of unsaturation, iodine value provides an estimation of these quality factors. The greater the iodine value, the more the unsaturation and the higher the susceptibility to oxidation. Peanut oil (IV 82–107) is more saturated than corn (IV 103–128), cottonseed (IV 99–113) or linseed (IV 155–205) oils; however, it is considerably less saturated than coconut (IV 7.7–10.5), palm (IV 44–54), or butter (IV 25–42) oils.

8.4.6 Peroxide value

Elevated peroxide values indicate that lipid oxidation has taken place. It is measured as reactive oxygen in terms of milliequivalents per 1000 g fat. In raw

peanuts, once the cell structure is disrupted by pressing or other means, lipoxygenase promotes oxidation of the linoleic acid to form hydroperoxides. These oxidation products are correlated with reduced flavor scores and cardboard or painty flavor defects. Peroxide value is often used as an indicator of peanut quality related to oil oxidation.

8.4.7 Acetyl value

The acetyl value is the number of mg of KOH required to neutralize the acetic acid produced by the hydrolysis of 1 g of acetylated fat and is a measure of free hydroxyl groups present in the oil. The acetyl number of peanut oil (8.5–9.5) is lower than other vegetable oils but higher than coconut oil, palm oil, and the animal fats and oils.

8.4.8 Heat of fusion

The heat of fusion, or latent heat, is the quantity of heat required to change 1 g of solid to a liquid with no temperature change. This latent heat increases with increasing molecular weight. The heat of fusion of peanut oil is 21.7 cal/g.

8.4.9 Unsaponifiable material

The unsaponifiable matter in peanut oil is mainly sterols (largely β-sitosterol and campesterol).

8.5 Health issues

8.5.1 Cardiovascular disease

Early work with animals suggested a high atherogenic potential when peanut oil was fed in relatively high doses. Because chemical treatment to randomize peanut oil resulted in a decrease in atherogenicity, triacylglycerol structure was believed to be involved (Kritchevsky *et al*. 1973). However, Ahmed and Young (1982) indicated that the Kritchevsky study did not provide adequate proof of this claim, due either to lack of inclusion of other vegetable oils for comparison or lack of adequate data for sound statistical analysis. In the past ten years, consistent data in numerous epidemiological studies indicate an amazingly high 30–50% reduction in cardiovascular disease in people who ate nuts, including peanuts, four to five times each week. Numerous clinical studies have indicated consistent reduction in total and LDL cholesterol in subjects consuming diets of peanuts and peanut oil. In a recent study, subjects consumed one of five diets: a low fat diet, one including olive oil, one including peanuts and peanut butter, one including peanut oil, and a typical American diet. Results showed that the diet including peanuts and peanut butter, the one including peanut oil, and the diet including olive oil (all low in saturated fat and cholesterol and high in

monounsaturated fat) lowered total cholesterol and LDL cholesterol. Further, each of these three diets lowered triacylglycerol levels without lowering the beneficial HDL cholesterol (Kris-Etherton *et al*. 2001).

8.5.2 Allergy

In recent years, concern for food allergies in general has increased, and concern for peanut allergy is no exception. For unknown reasons, peanut allergy is associated with a higher incidence of fatal food-induced anaphylaxis than any other food allergy. Immediate hypersensitivity to foods occurs in 6–8% of children and about 1% of adults. In the US, a recent survey suggested that 0.7% of children are allergic to peanuts in varying degrees. Avoidance is the only current method of dealing with food allergy. Significant research efforts are underway in dealing with peanut allergy. Several peanut allergens have been identified and all are proteins (Burks *et al*. 1998). Refined peanut oil where all protein has been removed is not allergenic; however, oils contaminated with peanut protein may indeed produce significant allergic reactions in peanut-sensitive individuals. Cold-pressed oils are more likely to contain peanut proteins than hot-pressed oils.

Note

The use of trade names in this publication does not imply endorsement by the US Department of Agriculture of the products named, nor criticism of similar ones not mentioned.

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9 Olive oil

Dimitrios Boskou

9.1 Introduction

Olive oil is a major component of the diet of the countries surrounding the Mediterranean Sea. For the people living in this region, olive oil is the main source of fat in their cuisine. In the past few years the oil has also become more popular among consumers in Northern Europe, the US and Canada, in particular, although these new consumers are not always familiar with the properties and characteristics of this natural product. Growing enthusiasm for the Mediterranean diet and for olive oil is due largely to studies indicating that this diet plays a positive role in the prevention of certain diseases, especially coronary heart disease. Chemical and analytical work to elucidate the structure and to quantify minor constituents of olive oil is now progressing rapidly. Much work has been also carried out by nutritionists on the key functional components. This chapter examines what makes olive oil chemically different from other culinary fats. The discussion does not cover olive oil chemistry and technology completely. It aims to highlight the issues related to production, compositional characteristics and properties that make this oil so distinct.

9.2 Extraction of olive oil from olives

Virgin olive oil is obtained from the fruits of the olive tree (*Olea europaea*) by mechanical or other physical means, under conditions that do not cause any changes in the oil.

The oil is first released from the olives by crushing: in pressure systems, stone mills are generally used and in continuous centrifugation plants, metal crushers (hammer, roller, disc). After it has been crushed the olive paste is mixed. Malaxation (stirring the olive mass slowly and constantly) lasts about 30 minutes. The main constituents of the paste after malaxation are olive oil, small pieces of kernel (pit), water and cellular debris. Separation is achieved by pressure, centrifugation, or selective filtration processes.

Important factors in the production of good quality olive oil are the harvesting period, maturity of the fruit, the mode of harvesting (hand picking, nets, other means), storage of olives before processing, leaf removal, mode of crushing and kneading, and the system of extraction. The essentials of the four methods of extraction that are in use today are briefly described below. For a complete

coverage of the subject the reader should consult the extended reviews by Di Giovacchino (1996), Hamatschek (1995), Fedeli (1996) and Kiritsakis (1998).

9.2.1 Pressure

Pressure is the oldest method of extraction. It is still in use though not widespread. It was largely replaced in the 1970s and 1980s by centrifugation methods, which helps to cut processing costs and to reduce olive storage time.

In the pressure system, the paste is pressed to release an oily must (oil and water from the olives). The liquid separates from the solid phase through drainage. A cake (pomace) is formed between the mats and this is dried and used for the production of olive residue oil. Oil and water are further separated by centrifugation (see Figure 9.1).

Pressure systems yield good quality oil when the fruits themselves are in good condition and the filtering diaphragms are properly cleaned. Otherwise, oils are produced with a high level of undesirable components, such as *n*-octane, 2-methyl-propanol, 3-methylbutanol and acetic acid.

9.2.2 Centrifugation (three phase system)

The crushed olives are mixed with water. A horizontal centrifuge separates the mass into pomace and must and the latter is further separated into oil and water (Figure 9.2).

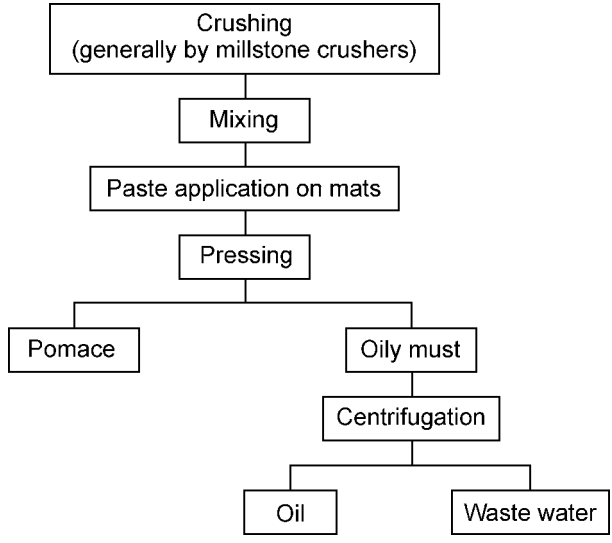


Figure 9.1 Flow chart for olive extraction by pressing.

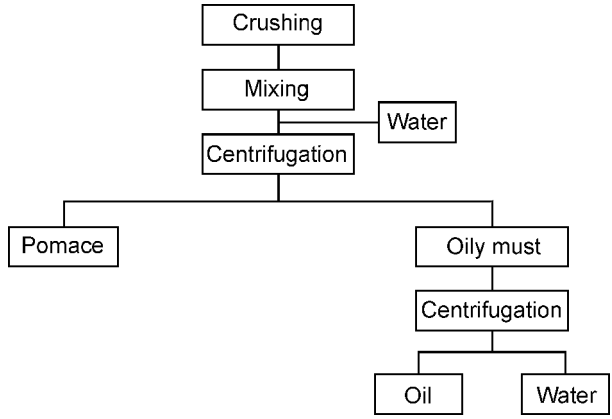


Figure 9.2 Flow sheet for olive extraction in a three phase centrifugal system.

9.2.3 Two phase decanters

Water is not added in two phase decanter extraction. The crushed olives are directly separated into oil and a mixture of water and husks. This system reduces significantly the amount of waste water and so protects the environment. The oil so produced is more stable because the level of natural antioxidants is higher. However, the pomace has a high moisture content (57–58%) and this makes its transportation more costly.

9.2.4 Percolation (selective filtration)

A steel plate is plunged into olive paste. When it is withdrawn it will be coated with oil because of the different surface tension between oil and water. The system is combined with a continuous horizontal centrifuge to increase capacity.

9.2.5 Processing aids

The oil yield and the quality of the oil can be improved by enzymes with pectinolytic and cellulosolytic activity (Di Giovacchino 1996). Micronised mineral talc is used in Spain for hard pastes to increase oil yields. Talc reduces oil/water emulsions and increases the recovery of free oil. However the use of coadjuvants is not in accordance with the legal definition of virgin olive oil and the oil must be obtained from the fruits solely by mechanical or other physical means.

9.2.6 Extraction of pomace oil (olive-residue oil)

Mechanical processsing of olive paste leaves two residual products: husks (pomace) and water. Residual oil in the pomace varies depending on the mode

of extraction. It is usually 6–8% in pressure systems and 3–5% in the three phase extraction systems. The recovery of the oil from the husks is achieved by extraction with hexane. This is undertaken in plants at another location, involving transportation of the byproduct, which presents a cost problem because of its high moisture content (25–58%).

The raw oil extracted from the husks is dark green, with high acidity and a bad flavour. It has to be neutralised, bleached, and deodorised before it is edible. Due to the solvent extraction, olive-residue oil contains some minor constituents at higher levels than those found in olive oils (waxes, sterols, erythrodiol and uvaol). This is the reason for designating pomace oil as a distinct product.

9.3 Olive oil composition

Olive oil is primarily a mixture of triacylglycerols, with some free fatty acids, mono- and diacylglycerols, and non-glyceridic constituents (0.5–1.5%). The free fatty acid content varies with the type of olive oil (extra virgin, fine virgin, ordinary, mixture of refined with virgin) and is an important quality criterion in fixing the grade.

9.3.1 Fatty acids and triacylglycerols

The fatty acid composition of olive oil ranges from 7.5–20% palmitic acid, 0.5–5% stearic acid, 0.3–3.5% palmitoleic acid, 55–85% oleic acid, 7.5–20% linoleic acid, and 0.0–1.5% linolenic acid. Myristic, heptadecanoic and eicosanoic acids are found only in trace amounts (Table 9.1). Recently, Scano and co-workers (1999), using ^{13}C nuclear magnetic resonance spectroscopy, detected and quantified *cis*-vaccenic (11-18:1) and eicosenoic acids.

Fatty acid composition may differ from sample to sample, depending on the place of production, the latitude, the climate, the variety, and the stage of maturity of the fruit. Greek, Italian, and Spanish olive oils are low in linoleic and palmitic acids and have a high percentage of oleic acid. Tunisian olive oils are higher in linoleic and palmitic acids and lower in oleic acid. Table 9.2 presents values of fatty acid composition for Greek olive oils from a study of the State Chemical Labaratory in Athens.

Triacylglycerols found in significant proportions in olive oil are OOO (40–59%), POO (12–20%), OOL (12.5–20%), POL (5.5–7%) and SOO (3–7%) (Boskou 1996). Smaller amounts of POP, POS, OLnL, LOL, OLnO, PLL, PLnO and LLL are also encountered (Regulation 282/98, Official Journal of European Communities, L 28.5/4-2-1998). These three letter symbols represent all the isomeric triacylglycerols containing the three acyl groups indicated where P = palmitic, O = oleic, S = stearic, L = linoleic and Ln = linolenic acid.

Table 9.1 Fatty acid composition of olive oil

Fatty acid		Composition (%)[a]
Lauric	12:0	Not detected
Myristic	14:0	0.0–0.1
Palmitic	16:0	7.5–20.0
Palmitoleic	16:1	0.3–3.5
Heptadecanoic	17:0	0.0–0.5
Heptadecenoic	17:1	0.0–0.6
Stearic	18:0	0.5–5.0
Oleic	18:1	55.0–83.0
Linoleic	18:2	3.5–21.0
Linolenic	18:3	0.0–1.5
Arachidic	20:0	0.0–0.8
Eicosenoic	20:1	Not specified
Behenic	22:0	0.0–0.2
Lignoceric	24:0	0.0–1.0

[a]By gas liquid chromatography, Codex Alimentarius 1997.

Table 9.2 Fatty acid composition (% wt of methyl esters) of Greek olive oils (production 1992–93)

Acid	Minimum	Maximum	Mean
14:0	0.00	0.10	0.02
16:0	7.9	12.3	10.5
16:1	0.5	0.9	0.6
17:0	0.00	0.17	0.05
17:1	0.04	0.29	0.09
18:0	2.0	3.2	2.6
18:1	68.8	82.8	76.9
18:2	4.6	14.5	7.5
18:3	0.5	0.9	0.6
20:0	0.3	0.6	0.4
20:1	0.2	0.4	0.3
22:0	0.0	0.2	0.2
24:0	0.0	0.2	0.1

Values obtained from the analysis of 78 samples.

According to Santinelli and co-workers (1992), the 1-random, 2-random, 3-random distribution theory is not always applicable to olive oil. Like other vegetable oils, olive oil has a high concentration of oleic acid and a low concentration of palmitic and stearic acids in position 2 of the triacylglycerol molecules.

9.3.2 Mono- and diacylglycerols

The presence of partial glycerides in olive oil is due either to incomplete triacylglycerol biosynthesis or hydrolytic reactions. In virgin olive oil, the concentration

of diacylglycerols range from 1–2.8% and monoacylglycerols are present in much smaller quantities (less than 0.25%). Storage conditions affect the distribution of fatty acids. 1,2-Diacylglycerols present in fresh oil tend to isomerise to the more stable 1,3-diacylglycerols. The extent of this rearrangement gives information about the age and storage conditions of the oil.

9.3.3 Other constituents

The various classes of minor constituents can be divided into two groups. The first group consists of fatty acid derivatives such as mono- and diacylglycerols, phospholipids, waxes and esters of sterols. The second group includes classes of compounds not related chemically to fatty acids: hydrocarbons, aliphatic alcohols, free sterols, tocopherols, chlorophylls, carotenoids and polar compounds such as tyrosol and hydroxytyrosol.

Some minor constituents are present only in the crude oil. Refining removes phospholipids and phenols; it also causes significant quantitative and qualitative changes in the other classes.

Most of the minor constituents of olive oil are present in the 0.5–1.5% of unsaponifiable matter.

9.3.3.1 Tocopherols

Tocopherols are important fat-soluble vitamins. They contribute to the stability of an oil and have an important role as quenchers of free radicals *in vivo*. Blekas and co-workers (1995) and Blekas and Boskou (1998) examined the role of α-tocopherol and its contribution to olive oil triacylglycerol stability. They found that α-tocopherol acts as an antioxidant at all levels but the antioxidant effect is greater at low (100 mg/kg) than at higher concentrations (500 and 1000 mg/kg). In the presence of more effective antioxidants such as *o*-diphenols, α-tocopherol did not show any significant antioxidant activity during the period of low peroxide accumulation but acted well when the primary oxidation products reached a critical level.

The tocopherol content is highly variable. Concentrations may range from 5–300 mg/kg. Usual values for good quality oils lie between 100 and 300 mg/kg. Recent studies for the determination of tocopherols gave values ranging from 98–370 mg/kg in Greek oils (Psomiadou *et al.* 2000) and 36–314 mg/kg in Italian oils (Lo Curto *et al.* 2001).

The main component of the tocopherol mixture is α-tocopherol which makes up 95% of the total. The other 5% of the mixture consists of β- and γ-tocopherols. All tocopherols occur in the free (non-esterified) form. The vitamin E(mg): PUFA(g) ratio in olive oil is approximately 1.8. In countries with a high annual *per capita* consumption, a significant percentage of the daily requirement for vitamin E is covered by olive oil. Refined, bleached, and deodorised olive oils have markedly reduced tocopherol content because of losses during processing.

9.3.3.2 Hydrocarbons

Two hydrocarbons are present in olive oil in considerable amounts, squalene and β-carotene (see Section 9.3.3.3).

Squalene. Squalene is a highly unsaturated aliphatic hydrocarbon ($C_{30}H_{50}$) with important biological properties. It is a metabolic precursor of cholesterol. A rich source of squalene is shark liver oil. Squalene is also present in human tissue in small amounts and in some vegetable oils.

The presence of squalene in olive oil probably makes a significant contribution to the health effects of the latter (Gapor Md Top and Rahman 2000). A chemopreventive effect of squalene on some forms of cancer has been reported by Rao and co-workers (1998) and also by Smith and co-workers (1998). The abstract of a patent was published in 1999 for the production of a functional food from olive oil and grain germ. The patent reports a process for mechanical extraction of oil from a mixture of extra virgin olive oil and grain germ (presumably wheat germ or maize germ). According to Eyres (1999), the inventor aims at making functional food with optimal nutritional properties by combining the beneficial effects of the minor constituents present in these oils such as squalene from olive oil and tocopherols from the germ oil.

Squalene has been shown to possess moderate antioxidant properties (Manzi *et al.* 1998) but loss during storage of the oil in the dark is greater than that of β-tocopherol. According to Psomiadou and Tsimidou (1999), squalene plays only a limited role in olive oil stability.

Squalene, found in virgin olive oil at concentrations ranging from 0.7–12 g/kg, accounts for more than 50% of the unsaponifiable fraction of the oil. The squalene content is dramatically reduced during the process of refining (Lanzon *et al.* 1994).

Other hydrocarbons reported to be present in olive oil are C_{14}–C_{30} *n*-alkanes, some *n*-alkenes, and terpene hydrocarbons—mainly α-farnesene. The level of these hydrocarbons is approximately 150–200 mg/kg (Lanzon *et al.* 1994). There is also a limited presence of aromatic polycyclic hydrocarbons (such as naphthalene and phenanthrene) but it is not quite clear to what extent they are natural constituents or contaminants (Tiscornia *et al.* 1982, Moret *et al.* 1997).

9.3.3.3 Pigments

Carotenoids. The main carotenoids present in olive oil (Figure 9.3) are β-carotene and lutein. 5,6-Epoxyxanthophylls such as violaxanthin and neoxanthin and their isomers with a 5,8-furanoid group (auroxanthin, neochrom) have also been reported to occur in very small quantities.

Total carotenoids may range between 1 and 20 mg/kg, but values do not usually exceed 10 mg/kg. Psomiadou and Tsimidou (2001) reported a lutein

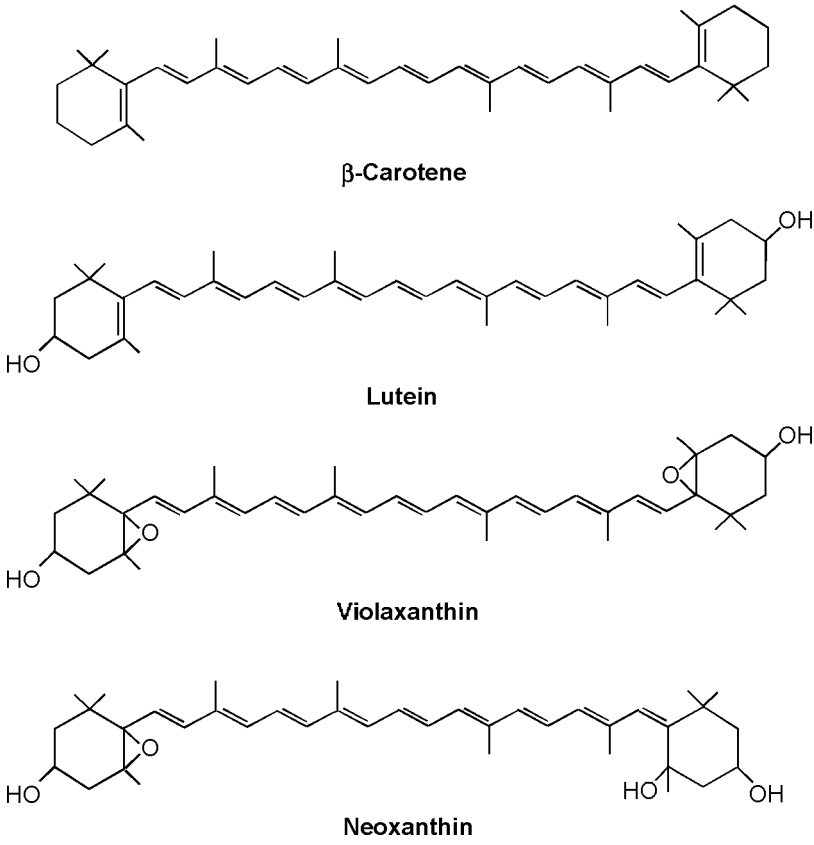


Figure 9.3 Structures of carotenoids in olive oil.

content between 0.2 and 3.4 mg/kg and β-carotene content between 0.4 and 5.1 mg/kg in a series of samples from various regions in Greece.

Carotenoids are singlet oxygen quenchers and protect the oil from photo-oxidation. Their role in the oxidative stability of olive oil has not yet been fully eludicated. There is probably a relation between carotenoids and the mode of action of polar phenols and α-tocopherol (Psomiadou and Tsimidou 1998).

Chlorophylls. Chlorophyll pigments are responsible for the greenish hues in virgin olive oil. Their content may range from 10 to 30 mg/kg. The main chlorophyll present in packed oil is pheophytin a. Chlorophyll a occurs in the oil just after production. Minguez-Mosquera and co-workers (1990) reported the presence of chlorophyll a, chlorophyll b, pheophytin a and pheophytin b in fresh oils. Psomiadou and Tsimidou (2001) found no chlorophyll a and only

traces of chlorophyll b and pheophytin b in a number of oils from various cultivars and various regions in Greece. The main pigments were pheophytin a and its unidentified derivatives, probably the pyro-derivative (abstraction of the carboxymethyl group) and a hydroxy-derivative formed by allomerisation.

In the absence of light, chlorophylls may act as weak antioxidants. However, in the presence of light they act as strong oxidation promoters. The pro-oxidant effect of chlorophylls and pheophytins on the photo-oxidation of refined oils has been widely demonstrated. In natural olive oils a pronounced effect of the action of singlet oxygen may not be observed, and this has to be attributed to the presence of singlet oxygen quenchers in natural olive oil.

9.3.3.4 Sterols

Four classes of sterols occur in olive oil: common sterols (4-α-desmethylsterols), 4-α-methylsterols, 4,4-dimethylsterols (triterpene alcohols) and triterpene dialcohols.

Desmethylsterols. This is the major class of sterols in olive oil at levels of 100–200 mg/100 g oil (Figure 9.4). Some of the total sterol fraction is present as esters with fatty acids. β-Sitosterol makes up 75–90% of the total sterol fraction. Other sterols found in considerable amounts are Δ^5-avenasterol (5–36%) and campesterol (approximately 3% of the total sterol fraction). Other 4-desmethylsterols, present in olive oil and found only in trace or very small amounts, include cholesterol, campestanol, stigmasterol, Δ^7-campesterol, chlerosterol (24S-24-ethyl-$\Delta^{5,25}$-cholestadien-3β-ol), sitostanol, $\Delta^{5,24}$-stigmastadienol, Δ^7-stigmasterol and Δ^7-avenasterol.

Virgin olive oil shows a remarkable resistance to oxidation and polymerisation during domestic deep-frying of potatoes or in other uses at frying temperatures. Compared to vegetable oils such as sunflower, cottonseed oil, corn and soybean oil, olive oil shows a significantly lower rate of alteration as demonstrated by measurements of viscosity, total polar compounds and loss of

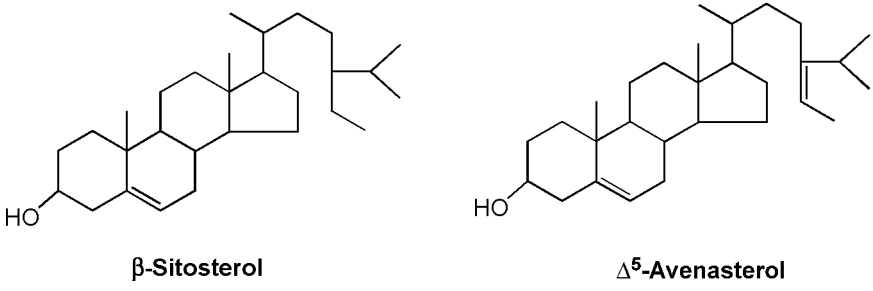


Figure 9.4 β-Sitosterol and Δ^5-avenasterol, the two major desmethylsterols of olive oil.

tocopherols. A possible explanation for the resistance of olive oil to rapid deterioration at elevated temperatures is its low iodine value and also the presence of Δ^5-avenasterol. This sterol has an ethylidene side chain which is a structural feature for retarding oxidative polymerisation in heated triacylglycerols (Blekas and Boskou 1999).

4α-Methylsterols. These compounds are intermediates in sterol biosynthesis and are always present in small quantities in olive oil. 4-α-Methylsterols are difficult to quantify accurately because of their complex nature and their occurrence in both free and esterified form. Approximations based on combined thin layer and gas chromatography with internal standards gave values ranging from 20–70 mg/100 g oil (Boskou 1996). The predominating α-monomethyl sterols in olive oil are obtusifoliol (4α,14α-dimethyl-24-methylene-Δ^8-cholesten-3β-ol), cycloeucalenol (4α,14α-dimethyl-9,19-cyclopropane-24-methylene-cholesten-3β-ol), gramisterol (4α-methyl-24-methylene-Δ^7-cholesten-3β-ol) and citrostadienol (4α-methyl,24-ethylidene-Δ^7-cholesten-3β-ol) (Figure 9.5). Other minor sterols identified are: 24-methyl-31-nor-9(11)-lanosterol, 24-methylene-31-nor-9(11)-lanosterol, 24-methyl-31-nor-*E*-23-dehydrocycloartanol, 24-methyl-*E*-23-dehydrolophenol, 24-ethyllophenol, 24-ethyl-*E*-23-dehydrolophenol,

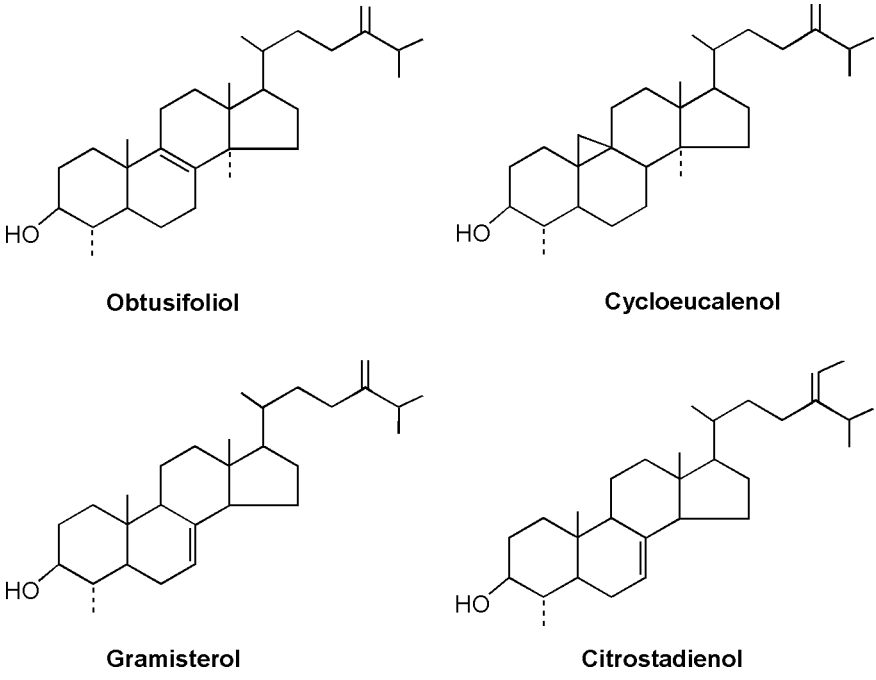


Figure 9.5 Structures of the main 4α-methylsterols present in olive oil.

24-methyl-24(25)-dehydrolophenol, 28-isocitrostadienol, 24-ethyl-24(25)-dehydrolophenol (Itoh *et al.* 1981).

4,4-Dimethylsterols (triterpene alcohols). The main triterpene alcohols present in olive oil are β-amyrin, butyrospermol, cycloartenol and 24-methylene-cycloartanol (Figure 9.6). This sterol fraction is complex and many constituents are still unidentified. Itoh and his co-workers (1981) used argentation thin layer chromatography and GC–MS to identify minor 4,4-dimethylsterols present in olive oil and olive pomace oil (β-residue oil).

New compounds reported are: taraxerol, dammaradienol, germaniol, parkeol, 7,24-tirucalladienol, 24-methylene-24-dihydroparkeol, cyclosadol and cyclobranol. Significant differences were observed by Itoh and co-workers between olive oil and β-residue oil in the compositions of triterpene alcohol fractions particularly in the percentage of 24-methylenecycloartanol. Significant differences were also observed between the distribution patterns of the total and esterified triterpene alcohol fraction in virgin olive oil, especially in the percentages of 24-methylenecycloartanol, butyrospermol and cycloartanol (Boskou 1996).

Triterpene alcohols are present at concentrations ranging from 100–150 mg/100 g oil. Olive husk oil has a much higher content.

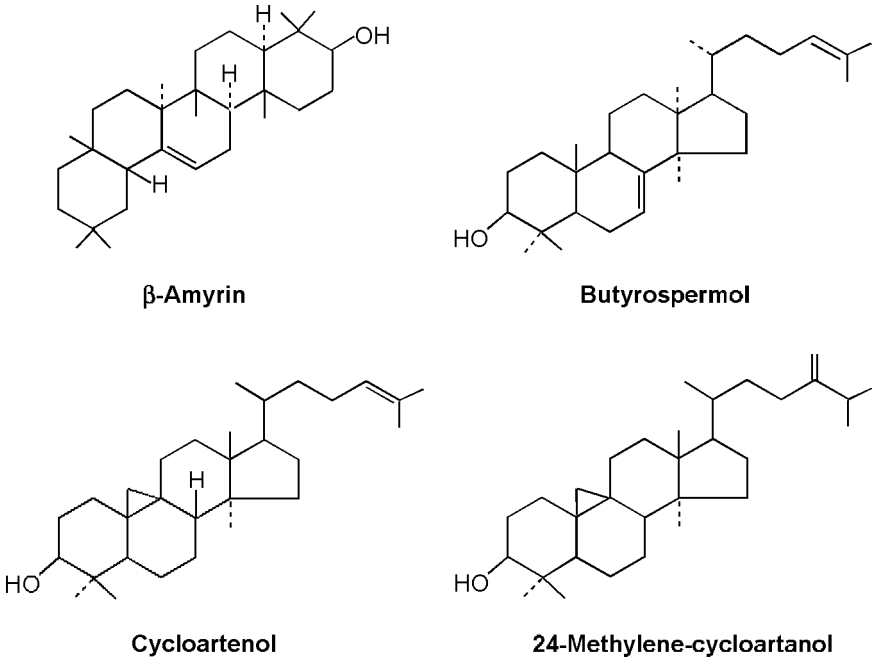


Figure 9.6 Structures of the main 4,4-dimethyl sterols.

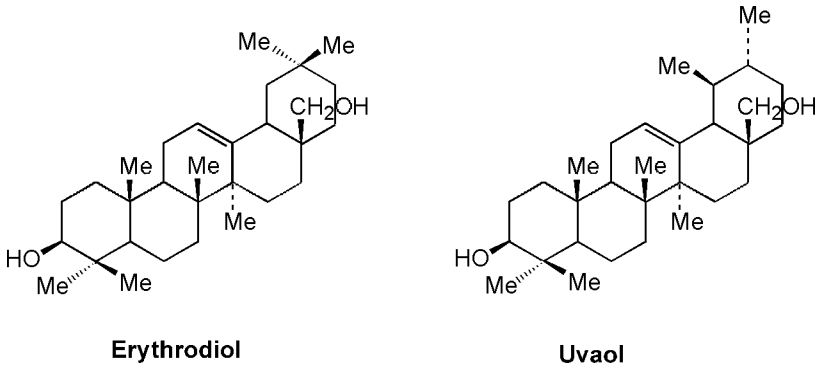


Figure 9.7 The two main triterpene dialcohols in olive oil.

9.3.3.5 Triterpene dialcohols

The two main triterpene dialcohols in olive oil are erythrodiol (homo-olestranol, 5α-olean-12-ene-3β,28-diol) and uvaol (Δ-12-ursen-3β,28-diol) (Figure 9.7).

Absolute amounts of erythrodiol plus uvaol range from 1–20 mg/100 g in olive oil and may be as high as 280 mg/100 g in β-residue oil. Triterpene dialcohols can be extracted and co-chromatographed with the 4-desmethylsterol fraction. Their relative content in the total fraction as determined by GLC is used as a reliable indicator for distinguishing olive oil from β-residue oil (Boskou 1996).

9.3.3.6 Hydroxyterpenic acids

Pentacyclic hydroxyterpenic acids, isolated from the acidic fraction of olive oil by TLC, are also reported to be present in olive oil (Figure 9.8).

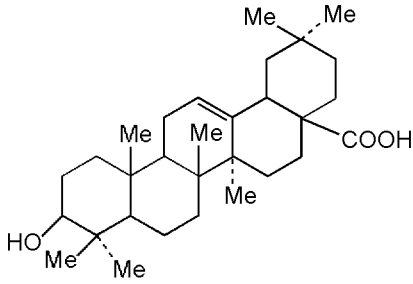
9.3.3.7 Fatty alcohols, waxes and diterpene alcohols

Fatty alcohols. These form an important class of olive oil minor constituents because they can be used to differentiate between various olive oil types. The main linear alcohols present in olive oil are docosanol, tetracosanol, hexacosanol and octacosanol. Odd carbon atom alcohols (tricosanol, pentacosanol, heptacosanol) may be present in trace amounts.

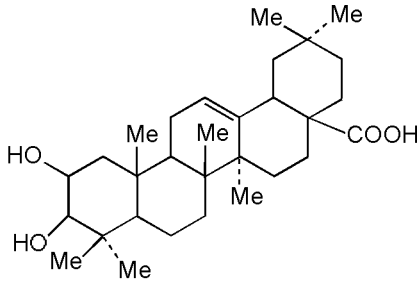
Total aliphatic alcohol content does not usually exceed 35 mg/100 g oil. In olive-extracted oil, the level of fatty alcohols is ten times higher or even greater. Dry climatic conditions and high temperatures may cause high alkanol content of olive oil.

Alcohols in olive oil have been reviewed by Tiscornia and co-workers (1982) and Boskou (1996).

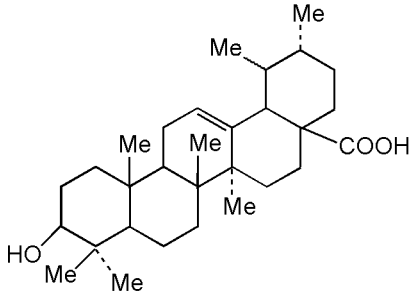
Waxes. Waxes are esters of fatty alcohols with fatty acids. The content of olive oil wax content is very low and does not exceed 35 mg/100 g. Extracted olive oils have a very high wax content and this difference is used officially for the



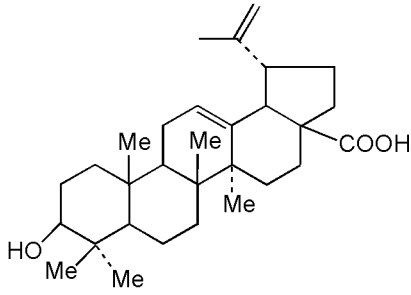
Oleanolic acid



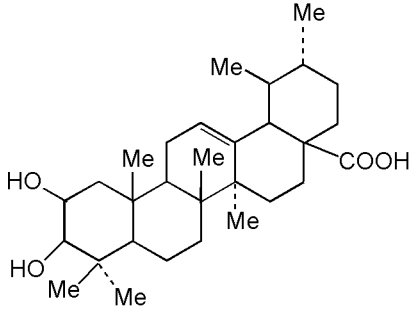
Maslinic acid



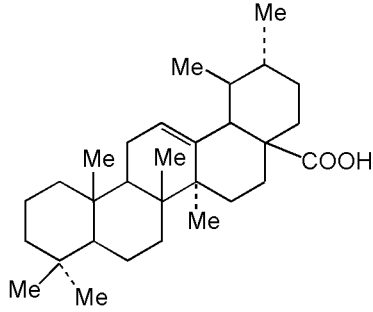
Ursolic acid



Betulinic acid



2α-Hydroxy-ursolic acid



Deoxyursolic acid

Figure 9.8 Pentacyclic hydroxyterpenic acids have also been reported to be present in olive oil.

distinction between pressed oil and β-residue oil. The main waxes detected in olive oil are C_{36}–C_{46} esters but the whole fraction is very complex because of the presence of several types of esters (saturated and unsaturated, straight-chain, even-numbered esters) and also benzyl alcohol, phytyl and geranylgeranyl esters (Reiter and Lorbeer 2001).

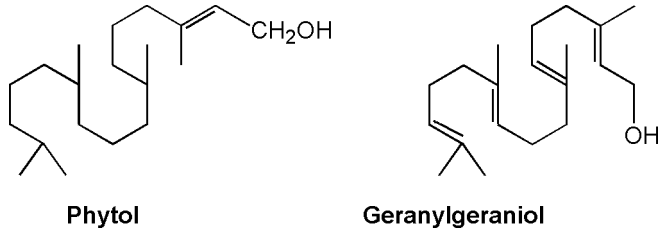


Figure 9.9 Acyclic diterpenoids reported to be present in olive oil.

Diterpenoids. Two acyclic diterpenoids have been reported to be present in the alcohol fraction isolated from olive oil. These are phytol (at a concentration of 120–180 mg/kg) which probably originates from chlorophyll, and geranylgeraniol (Figure 9.9).

9.3.3.8 Polyphenols

Virgin olive oil has a unique place among other vegetable oils because of its minor constituents, and much has been written in the past two decades about their importance. Both completed and ongoing studies associate these constituents with the beneficial role of olive oil in human health (Visioli 2000, Trichopoulou and Vasilopoulou 2000).

The polyphenols are an important class of minor constituents linked both to the flavour of virgin olive oil and to its keeping ability. Many publications deal not only with the nutrition effects of polyphenols, but also with the agronomic factors that influence their presence in olives and in olive oil, the mechanisms that contribute to a longer shelf life, and the importance of the processing conditions.

Phenolic compounds present in olive oil are conventionally characterised as 'polyphenols', though not all of them are polyhydroxy aromatic compounds. They are part of the polar fraction usually obtained from the oil by extraction with methanol–water.

Compounds which often appear in lists of olive oil polyphenols are (in alphabetical order): 4-acetoxy-ethyl-1,2-dihydroxybenzene, 1-acetoxy-pinoresinol, apigenin, caffeic acid, cinnamic acid (not a phenol), *o*- and *p*-coumaric acids, elenolic acid (not a phenol), ferulic acid, gallic acid, homovanillic acid, *p*-hydroxybenzoic acid, *p*-hydroxyphenylacetic acid, hydroxytyrosol, luteolin, oleuropein, pinoresinol, protocatechuic acid, sinapic acid, syringic acid, tyrosol, vanillic acid, vanillin (Boskou 1996, Morales and Tsimidou 2000, Garcia *et al.* 2001, Mateos *et al.* 2001). Tyrosol (4-hydroxy-phenethyl alcohol) and hydroxytyrosol (3,4-dihydroxy-phenethyl alcohol) in their various forms are reported to be the major constituents. The more polar part of the methanol–water extract contains free phenols and phenolic acids (Figure 9.10). The less polar part contains aglycones of oleuropein and ligstroside (the hydroxytyrosol and tyrosol glycosides, Figure 9.11), diacetoxy and dialdehydic forms of the aglycones

(Figure 9.11), flavonoids (luteolin, apigenin, Figure 9.12), the lignans 1-acetoxypinoresinol and pinoresinol (Figure 9.13), elenolic acid and cinnamic acid (Figure 9.14).

Litridou and co-workers (1997) reported the presence of an ester of tyrosol with a dicarboxylic acid. The same investigators demonstrated that the total content of phenols and *o*-diphenols was higher in the less polar part of the methanol–water extracts. Glycosides were found to be present only in trace amounts. In a recent report Garcia and his co-workers (2001) determined the dialdehydic forms of elenolic acid linked to hydroxytyrosol and tyrosol, 1-acetoxy-ethyl-1,2-dihydroxybenzene (hydroxytyrosol acetate), 1-acetoxypinoresinol, pinoresinol, oleuropein aglycone, luteolin, and ligstroside aglycone as phenols with the higher concentration in Italian oils.

The polyphenol content differs from oil to oil. Wide ranges have been reported (50–1000 mg/kg) but values are usually between 100 and 300 mg/kg. The cultivar, the system of extraction, and the conditions of olive oil processing are critical factors for the content of polyphenols.

Polyphenols are important for the flavour and the stability of olive oil. When their content exceeds 300 mg/kg the oil may have a bitter taste. Formation of

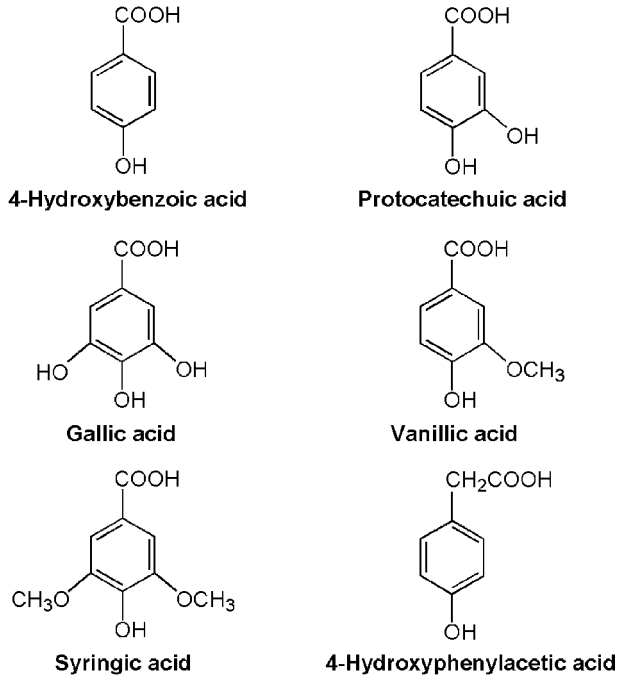


Figure 9.10 Structures of the main phenolic compounds reported to be present in olive oil: phenolic acids.

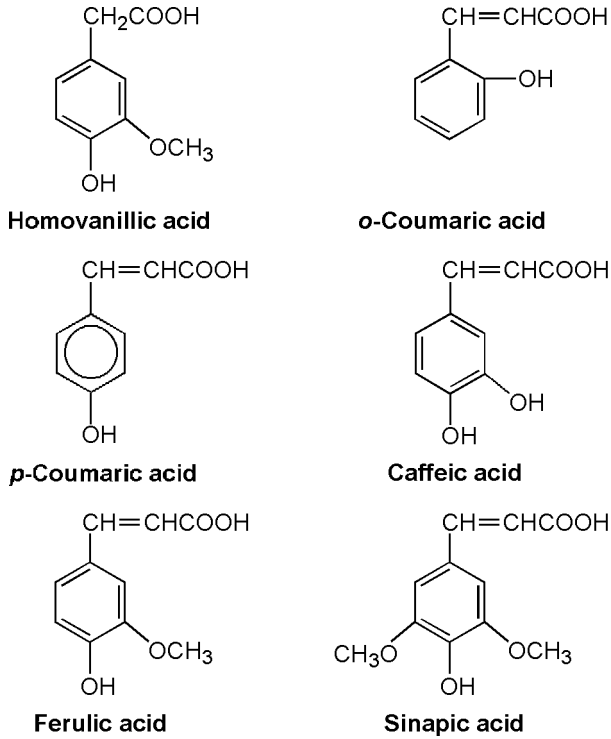


Figure 9.10 (continued)

4-vinylphenol from *p*-coumaric acid by decarboxylation or the presence of esters of cinnamic acid may also contribute to the flavour in a negative way. However, a high polyphenol content appears to be beneficial for the shelf life of the oil and there is a good correlation of stability and total phenol content (Tsimidou *et al.* 1992, Monteleone *et al.* 1998). Among the various phenolic compounds tested for their contribution to the antioxidant effect, hydroxytyrosol was found to be the most potent and more effective than butylated hydroxy toluene (BHT) (Boskou 1996). Gutierrez-Rosales and Arnaud (2001) found that the concentration of hydroxytyrosol, dialdehydic form of elenolic acid linked to hydroxytyrosol and oleuropein aglycone are highly correlated to the oil stability.

9.3.3.9 Volatile and aroma compounds

Olive oil possesses a unique place among vegetable oils largely due to the mode of extraction and to the presence of volatile and non-volatile flavouring compounds. The most important constituents of the aroma of olive oil are C_6 aldehydes and alcohols formed in the fruit from polyunsaturated fatty acids. This takes place on crushing, the first step of processing. The plant tissue

is disrupted and a sequence of lipoxygenase-catalysed reactions occur. The hydroperoxides formed by oxidation of polyunsaturated fatty acids (18:2 and 18:3) are decomposed by a specific lyase yielding aldehydes of six or nine carbon atoms and C_{12} or C_9 oxo-acids. The aldehydes formed are transformed to the corresponding alcohols by reducing enzymes with dehydrogenase activity or to hexyl esters with specific transferases.

Today, more than 100 constituents have been identified and the mechanisms for their formation have been explained. The most important classes of volatiles are hydrocarbons, alcohols, aldehydes, esters, phenols, phenol derivatives, oxygenated terpenes and furan derivatives (Boskou 1996, Reiners and Grosch 1998, Morales and Aparicio 1999, Morales and Tsimidou 2000).

Some of the volatile compounds are odourless (e.g. octane), while others, at least in the concentrations found, make only a very small contribution to the aroma. In a series of papers Grosch and his collaborators (Guth and Grosch 1991, Blekas *et al.* 1994, Blekas and Guth 1995) indicated that only a small fraction of the complex mixture of volatiles causes the characteristic odour of olive oil. To measure the potency of odorants, they applied a technique called 'aroma extract dilution analysis' (AEDA). This is a screening method applied to the volatiles distilled in high vacuum. An aliquot of the sample is diluted in diethyl ether and analysed by capillary gas chromatography while the effluent of the capillary is sniffed. The aliquot is then diluted in a volume 1:1 and the

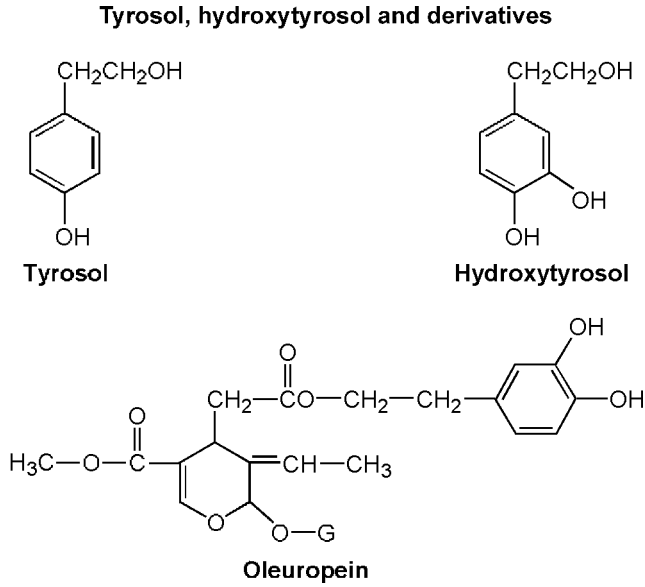
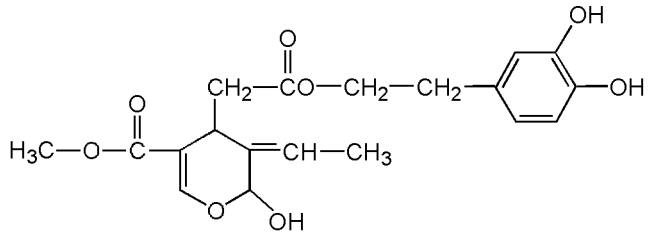
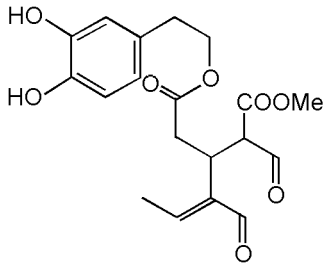


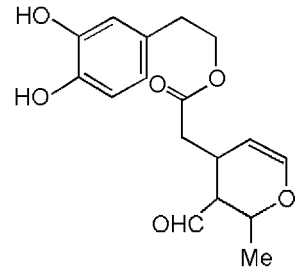
Figure 9.11 Structures of the main phenolic compounds reported to be present in olive oil: tyrosol, hydroxytyrosol and derivatives.



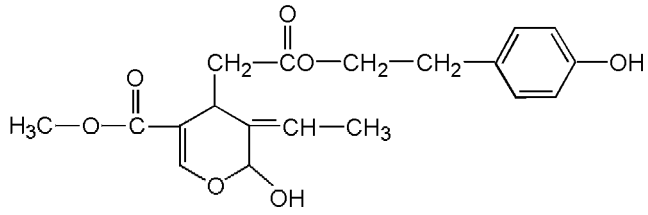
Oleuropein aglycone



Dialdehydic form of oleuropein aglycone



Decarboxymethyl form of oleuropein aglycone

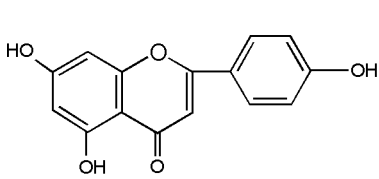


Ligostroside aglycone

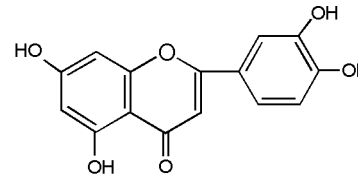
Figure 9.11 (continued)

new sample is analysed again. The procedure continues until odour is no longer detected. In this way the flavour dilution factor (FD-Factor) is estimated. FD-Factors are relative measures and are proportional to the odour activity value (OAV) which is the ratio of concentration to odour threshold of the compound in an odourless oil. Grosch and his co-workers concluded that the compounds mainly contributing to four basic flavour notes are:

- green: (*Z*)-3-hexenal
- fruity: ethyl 2-methylbutyrate, ethyl isobutyrate, ethyl cyclohexylcarboxylate
- fatty: (*Z*)-2-nonenal
- blackcurrant: 4-methoxy-2-methyl-2-butanethiol.

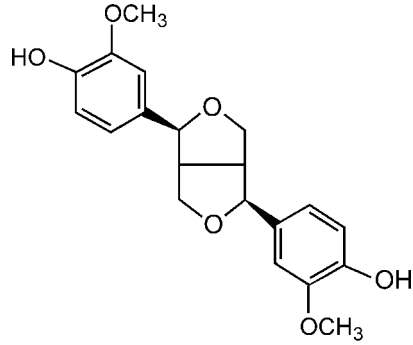


Apigenin



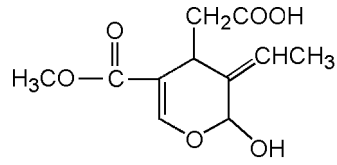
Luteolin

Figure 9.12 Structures of the main phenolic compounds reported to be present in olive oil: flavonoids.

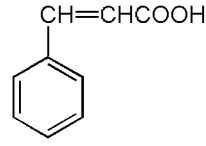


Pinoresinol

Figure 9.13 Structures of the main phenolic compounds reported to be present in olive oil: lignans.



Elenolic acid



Cinnamic acid

Figure 9.14 Closely related non phenolic compounds extracted with phenols.

Other important odorants are given below (Blekas and Guth 1995, Reiners and Grosch 1998, Morales and Aparicio 1999):

- green — hexanal, (*E*)-2-hexenal, (*E*)-3-hexen-1-ol, (*E*)-2-hexen-1-ol, (*Z*)-3-hexen-1-ol.
- fruity — (*E*)-2- hexenal, hexyl acetate, (*Z*)-3-hexenyl acetate, ethyl 2-methylpropanoate, (*Z*)-3-hexenyl acetate.
- fatty — heptanal, (*E*)-2-nonenal, (*E*)-2-octenal, (*Z*)-3-nonenal, (*E*)-2-decenal
- grassy — hexanal, (*Z*)-3-hexen-1-ol
- soapy — nonanal, octanal
- deep fried — 2,4-decadienal
- sweet — phenyl acetaldehyde, hexyl acetate
- astringent–bitter — (*E*)-2-hexen-1-ol, (*E*)-2-hexenal.

OAVs were calculated for potent odorants in oils from Italy, Spain and Morocco by Reiners and Grosch (1998). After quantification, the concentrations of the odorants were divided on the basis of their nasally determined threshold values in sunflower oil. High OAVs were shown by the following compounds:

- oils from Italy: acetaldehyde, acetic acid, propanal, 1-penten-3-one, (*E*,*Z*)-2,4-decadienal, (*Z*)-3-hexenyl acetate, *trans*-4,5-epoxy-(*E*)-2-decenal, (*Z*)-3-hexenal, and (*E*)-2-hexenal
- oils from Spain: acetaldehyde, acetic acid, *trans*-4,5-epoxy-(*E*)-2-decenal, 4-methoxy-2-methyl-2-butanethiol, ethyl 2- and 3-methyl butyrate, and 3-methyl butanal
- oils from Morocco: acetaldehyde, (*E,Z*)-2,4-decadienal, *trans*-4,5-epoxy-(*E*)-2-decenal, (*Z*)-3-hexenal, ethyl 2- and 3-methyl butyrate, ethyl cyclohexylcarboxylate, and ethyl isobutyrate.

9.3.3.10 Phospholipids

Experimental work for the determination of phospholipids in olive oil is rather limited. Freshly produced virgin olive oil was found to contain 40–135 mg/kg (Tiscornia *et al.* 1982). Crude pomace oil has higher levels of phospholipids. Phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol and phosphatidic acid are the main phospholipids present in unprocessed oil. Phospholipids are partly bound to lipoproteins.

9.3.3.11 Metals

Transition metals, especially iron and copper, are known as pro-oxidant factors, because they generate free radicals. In virgin olive oil traces of iron and copper may originate from the soil and fertilisers or through contamination

from the processing equipment and storage vessels. The use of stainless steel equipment is necessary to avoid metal contamination. Concentrations of iron reported for virgin olive oil usually range between 0.5 and 3 ppm (Boskou 1996). Values reported for copper are 0.001–0.2 ppm. The iron and copper content is related, at least in part, to the system used for the extraction of oil. Oils obtained by classical systems were found to have higher percentages of these two metals compared to oils extracted by the centrifugal and percolation techniques.

Other metals present in virgin olive oil (chromium, manganese, tin, nickel and lead) do not exceed a few ppb.

9.3.4 Effect of processing of oils on the composition of virgin olive oils

9.3.4.1 Aroma compounds

Olive oil crushing and kneading are important factors for aroma compounds. Lercker and co-workers (1999) found that after crushing, Italian olives the volatile fraction contained approximately 20% *trans*-2-hexenal and after 70 min of kneading, the percentage was increased to 50%. Hexanal content was also increased but its level remained significantly lower than that of hexenal. When kneading was over a different tendency was observed—an increase in hexanal and a decrease in hexenal. The authors concluded that strong enzyme activity and extended kneading periods generate desirable aroma compounds at the expense of stability through loss of antioxidants.

Morales and Aparicio (1999) studied the conditions of extraction and showed that a temperature of 25°C and a malaxing time of 30–45 min produce volatiles contributing to the best sensory quality. Higher temperatures (> 35°C) with minimum malaxing time (< 30 min) produce oils with pleasant green notes.

Ranalli and his co-investigators (2001) examined three Italian olive varieties and four malaxation temperatures (20, 25, 30 and 35°C). The results of the study indicated that by malaxing the paste at 30°C a satisfactory oil output is obtained and the oil has a pleasant green flavour. Generally, malaxation times shorter than 45 min and low malaxation temperatures produce oils with better aromas and higher (*E*)-2-hexenal/hexanal ratios. The temperature of malaxation is critical because of the behaviour of hydroxyperoxide lyase, which affects the production of volatiles through the lipoxygenase pathway.

9.3.4.2 Polyphenols

The content of polyphenols depends on the extraction system. Pressure systems and two-phase decanters yield oil with a higher polyphenol content and longer induction periods. In the three-phase centrifugal systems the paste is thinned with water and part of the phenols is lost in the water (Di Giovacchino 1996).

The type of crushing of the fruits also seems to be important. Stone mills give oil with a lower polyphenol content while hammer crushes give oils with a characteristically high content of phenols. This suggests a difference in the enzymatic hydrolytic activity during crushing and may be used to upgrade the quality of extra virgin olive oils. Olives yielding oils with a very high content of polyphenols can be processed in a stone mill to avoid enhancement of 'bitterness' and 'pungency'. For olives giving 'sweet' oils with a low level of polyphenols it is better to use the hammer system (Caponio *et al.* 1999).

Other factors affecting the polyphenolic content are the screen size of the metal crushers and the use of pectolytic enzymes.

9.3.4.3 Other minor constituents

From the rest of the minor constituents, carotenoids and chlorophylls are affected by the extraction system. Their level is higher in the oils obtained by centrifugation, because of the metallic crushers used in this system, which release more of the pigments. Aliphatic alcohols and waxes content may increase if the temperature of the paste is too high (Cert *et al.* 1999).

9.4 Refining and modifications

9.4.1 Olive oil and olive pomace oil refining

Refining is applied to olive pomace oil and non-edible grades of virgin olive oil with high acidity and unacceptable sensory characteristics. Alkali refining, bleaching and deodorisation are the standard procedures. Physical refining may be also used but the temperatures applied can lead to *trans* fatty acids and promote interesterification reactions. The latter increases the percentage of saturated acids at the β-position of triacylglycerol molecules. Attempts are now being made to deodorise olive oil using nitrogen as stripping gas (Ruiz-Mendez and Dobarganes 1999). The use of nitrogen is expected to increase the free fatty acid vaporisation efficiency and also to reduce losses of unsaponifiables and triacylglycerols.

Olive-residue oil needs two additional steps: degumming and winterisation. Degumming is necessary for olive pomace oil because it contains up to 2% phospholipids and this is achieved by treatment with phosphoric or citric acid to form hydrated phospholipids. Winterisation removes waxes and high melting triacylglycerols. The process is based on freezing (5–8°C), 'maturing' to increase the size of crystals, and addition of 5% water. The mixture of oil and water is placed in a centrifuge which separates the aqueous phase with the wax from the dewaxed oil. Further washing with warm water and centrifugation eliminates the residual impurities (mainly soaps). When winterisation is carried out in hexane solution the operation is performed before bleaching.

9.4.2 Refining and minor constituents

Refining is applied to remove constituents (pigments, free fatty acids, oxidation products) that make the oil unsuitable for edible purposes. However, alkali treatment, bleaching earths, and the high temperatures used in the deodorisation step may cause unwanted losses of tocopherols. Some changes taking place during refining are useful for checking the identity of refined olive oils and controlling admixtures with natural olive oil.

9.4.2.1 Sterols

Alkali refining may cause a reduction of sterols up to 15%. Losses are also observed during decolorisation and deodorisation. Free 4α-methylsterols and triterpene alcohols undergo severe changes during bleaching. Isomerisation of the side chain and opening of the 9β-19-cyclopropane ring may occur. The intensity of bleaching can be assessed by the presence of steradienes formed from dehydration of sterols. The determination of these hydrocarbons is an effective means to detect refined oils labelled as non-refined. The main steradienes found are stigmasta-3,5-diene (from β-sitosterol), campesta-3,5-diene (from campesterol) and 3,5,22-stigmastatriene (from stigmasterol).

9.4.2.2 Fatty acids and triacylglycerols

In the various stages of refining, conjugated double bonds and geometrical isomers are formed. Conjugated dienes absorb at 232 nm and trienes at 268 nm. *Trans* fatty acids are detected by capillary gas chromatography or by argentation thin layer chromatography combined with gas chromatography. In addition to geometrical isomerisation, long deodorisation periods and high temperatures may result in interesterification with a consequent increase in palmitic acid at the 2-position of the triacylglycerols.

9.4.2.3 Alkanols

The content of linear alcohols increases during refining through the liberation of alcohols from waxes.

9.4.2.4 Tocopherols and squalene

Tocopherols and squalene are eliminated when the olive is processed. Deodorisation sludges are rich in squalene and can be used as a source of this hydrocarbon for industrial purposes. Squalene losses are accompanied by formation of squalene isomers.

9.4.2.5 Phenolic compounds

These compounds are very polar and dissolve in the water used in the various refining steps and lost.

9.4.2.6 Other constituents

Various other constituents are drastically reduced or disappear completely. These are pigments, phospholipids, aroma compounds, and contaminants such as metals, aromatic hydrocarbons and insecticide residues. While volatile hydrocarbons disappear others, such as diterpenes, may be formed by degradation of phytol.

9.4.3 Hardening and interesterification

Olive oil is too valuable to be hydrogenated, since even non-edible oils (lampante) are usually more expensive than commodity seed oils. Small quantities may be neutralised, decolorised, and hydrogenated when there is a surplus of raw material. To obtain a plastic product suitable for the preparation of cooking fats or margarines, olive oil has to be hydrogenated under conditions that favour isomerisation. Finished products usually have a low percentage of diene acids and a rather high level of geometrical and positional isomers.

Interesterification of blends of refined olive oil and tristearin give zero-*trans* plastic fats with a higher percentage of unsaturated fatty acids than hydrogenated olive oil. Gavriilidou and Boskou (1991) interesterified blends of refined olive oil and glycerol tristearin on a laboratory scale using sodium methoxide as catalyst. The rearranged fats had properties very close to those of soft tube and packed margarines. Blends of refined olive oil and partially hydrogenated palm oil were subjected to chemical and enzymic interesterification by Alpaslan and Karaali (1998). The products were similar to those of package margarines but higher in monounsaturated fatty acids.

9.5 Regulations

Criteria for quality and genuineness of the various olive oil types are described in the Norm of the Codex Alimentarius (1993) and EU Commission Regulation 2568/91 and its amendments. An important amendment of the basic regulation is Reg 2472, which summarises most of the changes since 1991 and is valid from February 1998 (European Commission 1997).

The Codex Alimentarius standard includes limits for acidity, volatile matter, insoluble impurities, peroxide value, colour, odour, taste, iron, copper, K_{270}, ΔK, permitted additives, contaminants (lead, arsenic, halogenated solvents), refractive index, saponification value, iodine value and unsaponifiable matter. Physical and chemical constants, such as iodine value and saponification value, are not found in the EU regulation. This is explained by the fact that more definite information is obtained by determining fatty acid composition, sterol and wax composition, *trans* fatty acid content, stigmastadiene, and so on.

9.5.1 Olive oil classification

The descriptions and definitions given below are included in EU regulation 356/1992 based on the 1986 International Agreement of Olive Oil and Table Olives adopted by olive oil producing countries.

- *Virgin olive oil*. The oil obtained from the fruit of the olive tree (*Olea europaea*) only by mechanical or other physical means under conditions, particularly thermal, that do not lead to alteration in the oil and which has not undergone treatment other than washing, decantation, centrifugation and filtration.
- *Extra virgin olive oil*. This type has absolutely perfect flavour and odour, and a maximum acidity, in terms of oleic acid, of 1 g/100 g.
- *Fine virgin olive oil*. This type has absolutely perfect flavour and odour, and a maximum acidity, in terms of oleic acid, of 2 g/100 g.
- *Semi-fine virgin olive oil (or ordinary virgin olive oil)*. This type has good flavour and odour, and a maximum acidity, in terms of oleic acid, of 3.3 g/100 g, with a 10% margin of tolerance.
- *Virgin olive oil not fit for consumption as it is*. This oil, designated virgin olive oil lampante, is intended for refining or for technical purposes. It has an off-flavour and/or off-smell and acidity, in terms of oleic acid, of more than 3.3 g/100 g.
- *Refined olive oil*. This oil, which is obtained from virgin olive oil by refining methods which do not lead to alteration in the initial triacylglycerol structure, has a maximum acidity, in terms of oleic acid, of 0.5 g/100 g.
- *Olive oil*. This oil, which consists of a blend of virgin olive oil (except lampante) and refined olive oil, has a maximum acidity, in terms of oleic acid, of 1.5 g/100 g.
- *Crude olive pomace oil (crude olive residue oil)*. This oil, to the exclusion of oils obtained by re-esterification processes and any mixture with oils of other kind, is obtained by treating olive pomace with solvents.
- *Refined olive pomace oil*. This oil, which is obtained from crude olive pomace oil by refining methods not altering the initial triacylglycerol structure, has acidity of no more than 0.5 g/100 g.
- *Olive pomace oil*. This oil, which is a mixture of refined olive residue oil and virgin olive oil (except lampante), has a maximum acidity, in terms of oleic acid, of 1.5 g/100 g.

Identity and quality characteristics of the above types of olive oil are given in Tables 9.3 and 9.4. Theoretical ECN42 values in Table 9.4 are calculated from the fatty acid composition and the 1,3-random, 2-random distribution theory using an appropriate computer programme. The difference between this theoretical value and a real value obtained by HPLC replaced trilinolein content. K_{232} and K_{270} are specific UV extinctions of 1% solution of the fat in a specified solvent,

Table 9.3 Standards of the Commission of the Codex Alimentarius (1993)

Type	Volatile matter at 105°C (%) max	Insoluble impurities (%) max	Traces of metals (ppm) max		Peroxide value (meq·O_2/kg) max	Iodine value	Refractive index (20°C)	Saponification value (mg KOH/kg)	Unsaponifiables (g/kg) max	Contaminants (ppm) max		
			Fe	Cu						Pb	As	Solvents
Virgin olive oil	0.2	0.1	5	0.4	20	75–94	1.4677–1.4705	184–196	15	0.1	0.1	0.2
Lampante	0.3	0.2	5	0.4	Non-Specified	75–94	1.4677–1.4705	184–196	15	0.1	0.1	0.2
Refined olive oil	0.1	0.05	5	0.4	10	75–94	1.4677–1.4705	184–196	15	0.1	0.1	0.2
Olive oil (a mixture of refined and virgin olive oil)	0.1	0.05	5	0.4	20	75–94	1.4677–1.4705	184–196	15	0.1	0.1	0.2
Crude olive residue oil	1.5	Non-Specified			Non-Specified							
Refined olive residue oil	0.1	0.05	5	0.4	10	75–92	1.4680–1.4707	182–193	30	0.1	0.1	0.2
Olive residue oil (mixture of refined residue oil and virgin olive oil)	0.1	0.05	5	0.4	20	75–92	1.4680–1.4707	182–193	30	0.1	0.1	0.2

Table 9.4 Olive oil characteristics, European Commission (1997)

Category	Acidity* (%)	Peroxide value (meq · O_2/kg)*	Halogenated solvents (mg/kg)*[a]	Waxes (mg/kg)	Saturated fatty acids in triacylglycerols position 2 (%)	Stigmasta-dienes (mg/kg)[b]	Difference between HPLC and theoretical calculation of ECN42	K_{232}*	K_{270}*	K_{270} after alumina[c]	Delta-K*	Panel test*
1. Extra virgin olive oil	≤ 1.0	≤ 20	≤ 0.20	≤ 250	≤ 1.3	≤ 0.15	≤ 0.2	≤ 2.50	≤ 0.20	≤ 0.10	≤ 0.01	≥ 6.5
2. Virgin olive oil	≤ 2.0	≤ 20	≤ 0.20	≤ 250	≤ 1.3	≤ 0.15	≤ 0.2	≤ 2.60	≤ 0.25	≤ 0.10	≤ 0.01	≥ 5.5
3. Ordinary virgin olive oil	≤ 3.3	≤ 20	≤ 0.20	≤ 250	≤ 1.3	≤ 0.15	≤ 0.2	≤ 2.60	≤ 0.25	≤ 0.10	≤ 0.01	≥ 3.5
4. Virgin lampante olive oil	> 3.3	> 20	> 0.20	≤ 350	≤ 1.3	≤ 0.30	≤ 0.3	≤ 3.70	> 0.25	≤ 0.11	–	< 3.5
5. Refined olive oil	≤ 0.5	≤ 5	≤ 0.20	≤ 350	≤ 1.5	–	≤ 0.3	≤ 3.40	≤ 1.20	–	≤ 0.16	–
6. Olive oil	≤ 1.5	≤ 15	≤ 0.20	≤ 350	≤ 1.5	–	≤ 0.3	≤ 3.30	≤ 1.00	–	≤ 0.13	–
7. Crude olive-residue oil	> 0.5	–	–	–	≤ 1.8	–	≤ 0.6	–	–	–	–	–
8. Refined olive-residue oil	≤ 0.5	≤ 5	≤ 0.20	–	≤ 2.0	–	≤ 0.5	≤ 5.50	≤ 2.50	–	≤ 0.25	–
9. Olive-residue oil	≤ 1.5	≤ 15	≤ 0.20	> 350	≤ 2.0	–	≤ 0.5	≤ 5.30	≤ 2.00	–	≤ 0.20	–

*An asterisk after the characteristic signifies, with regard to the quality of the oil, that:

- in the case of virgin lampante olive oil, the limits laid down (with the exception of that for K_{232}) do not all have to be complied with simultaneously
- in the case of other virgin olive oils, failure to comply with one or more of the limits is to entail a change of category within the virgin olive oil group

[a]Overall upper limit for compounds detected by electron capture detector. For compounds detected individually the upper limit is 0.10 mg/kg.

[b]Sum of isomers that could (or could not) be separated by capillary column.

[c]To check the presence of refined oil, if the K_{270} exceeds the limit for the category concerned, it shall be determined again after passage over alumina.

Notes: The results of the tests must be expressed to the same number of decimals as the specified for each characteristic. The last digit shall be increased by one unit if the following digit is greater than 4. An oil is to be placed in a different category or declared not in conformity in terms of purity if any one of the characteristics lies outside the limit laid down.

Table 9.4 (continued)

Category	Minor fatty acids						Sum of the trans-oleic isomers (%)	Sum of the trans-linoleic and trans-linolenic isomers (%)	Chole-sterol (%)	Brassi-casterol[a] (%)	Campe-sterol (%)	Stigma-sterol (%)	β-Sito-sterol (%)	Δ-7-Stigma-sterol (%)	Total sterols (mg/kg)	Erythrodiol and uvaol (%)
	Myri-stic (%)	Linole-nic (%)	Arachidic (%)	Eico-senoic (%)	Behenic (%)	Lignoceric (%)										
1. Extra virgin olive oil	≤ 0.05	≤ 0.9	≤ 0.6	≤ 0.4	≤ 0.2	≤ 0.2	≤ 0.05	≤ 0.05	≤ 0.5	≤ 0.1	≤ 4.0	< Camp.	≥ 93.0	≤ 0.5	≥ 1000	≤ 4.5
2. Virgin olive oil	≤ 0.05	≤ 0.9	≤ 0.6	≤ 0.4	≤ 0.2	≤ 0.2	≤ 0.05	≤ 0.05	≤ 0.5	≤ 0.1	≤ 4.0	< Camp.	≥ 93.0	≤ 0.5	≥ 1000	≤ 4.5
3. Ordinary virgin olive oil	≤ 0.05	≤ 0.9	≤ 0.6	≤ 0.4	≤ 0.2	≤ 0.2	≤ 0.05	≤ 0.05	≤ 0.5	≤ 0.1	≤ 4.0	< Camp.	≥ 93.0	≤ 0.5	≥ 1000	≤ 4.5
4. Virgin lampante olive oil	≤ 0.05	≤ 0.9	≤ 0.6	≤ 0.4	≤ 0.2	≤ 0.2	≤ 0.10	≤ 0.10	≤ 0.5	≤ 0.1	≤ 4.0	–	≥ 93.0	≤ 0.5	≥ 1000	≤ 4.5
5. Refined olive oil	≤ 0.05	≤ 0.9	≤ 0.6	≤ 0.4	≤ 0.2	≤ 0.2	≤ 0.20	≤ 0.30	≤ 0.5	≤ 0.1	≤ 4.0	< Camp.	≥ 93.0	≤ 0.5	≥ 1000	≤ 4.5
6. Olive oil	≤ 0.05	≤ 0.9	≤ 0.6	≤ 0.4	≤ 0.2	≤ 0.2	≤ 0.20	≤ 0.30	≤ 0.5	≤ 0.1	≤ 4.0	< Camp.	≥ 93.0	≤ 0.5	≥ 1000	≤ 4.5
7. Crude olive-residue oil	≤ 0.05	≤ 0.9	≤ 0.6	≤ 0.4	≤ 0.3	≤ 0.2	≤ 0.20	≤ 0.10	≤ 0.5	≤ 0.2	≤ 4.0	–	≥ 93.0	≤ 0.5	≥ 2500	≥ 12
8. Refined olive-residue oil	≤ 0.05	≤ 0.9	≤ 0.6	≤ 0.4	≤ 0.3	≤ 0.2	≤ 0.40	≤ 0.35	≤ 0.5	≤ 0.2	≤ 4.0	< Camp.	≥ 93.0	≤ 0.5	≥ 1800	≥ 12
9. Olive-residue oil	≤ 0.05	≤ 0.9	≤ 0.6	≤ 0.4	≤ 0.3	≤ 0.2	≤ 0.40	≤ 0.35	≤ 0.5	≤ 0.2	≤ 4.0	< Camp.	≥ 93.0	≤ 0.5	≥ 1600	> 4.5

[a] Δ-5,23-Stigmastadienol + Clerosterol + Sitosterol + Sitostanol + Δ-5-Avenasterol + Δ-5,24-Stigmastadienol.

Note: The results of the tests must be expressed to the same number of decimals as that specified for each characteristic. The last digit shall be increased by one unit if the following digit is greater than 4. An oil is to be placed in a different category or declared not in conformity in terms of purity if any one of the characteristics lies outside the limit laid down.

in a thickness of 1 cm. Panel test expresses the assessment of trained tasters, on a 0–9 scale.

It is clear from the tables that olive oils, and especially virgin olive oil, are strictly regulated. This is related to their high prices, and to the fact that natural olive oil has always been the subject of fraud by mixing less expensive vegetable oils and olive residue oil.

Some of the parameters and designations are now being examined by EU experts. A lot of changes are being discussed to adjust legislation to recent developments in the production and trade of the product. Some of the points which are now being considered for modification are :

- acidity of extra virgin olive oil (reduction from 1% to 0.8%)
- banning the category 'ordinary virgin olive oil' with 3.3% acidity limit; edible virgin olive oils will have a maximum 2% acidity in terms of oleic acid, a change that will improve quality, since the use of high acidity oils with flavour defects in mixtures will be significantly diminished
- the term 'olive oil' (a mixture of virgin and refined): the word 'standard' has been proposed; this type of oil will have acidity of 1% instead of 1.5%
- designation of 'repasso', which for the time being is not regulated (repasso is an inferior quality oil obtained from a second processing of the pomace from the two phase decanters)
- adoption of the IOOC method for the panel test.

These limits and definitions, once they are incorporated into EU legislation, will also be adopted and included in the new Norm of the Codex Alimentarius in the year 2003.

9.6 Cloudy olive oil

Extra virgin olive oil is produced in a form of an emulsion or dispersion, which can persist for several months before full deposition of a residue. Today, there is a growing interest in cloudy (veiled) extra virgin olive oil, which some consumers consider as more 'green' and not over-processed. However, this is not correct because the additional 'processing' is only precipitation and filtering.

Veiled oils have longer induction periods compared to filtered oils. It is, therefore, believed that the material in suspension–dispersion that 'veils' extra virgin olive oil plays a significant stabilising role against oxidation, although there is little evidence concerning the chemical nature of the material which forms the stable dispersion system. Another possible explanation might be the presence of emulsifiers. There are compounds in the oil with a low solubility in water which act as tensioactive solutes. Mono- and diacylglycerols and galactolipids belong to this category. Bianco and his co-workers (1998) identified two digalactosyl glycosides in freshly produced oils: the α-1,6-digalactosyl derivative of the

1,2-glycerol diester of linolenic acid and the α-1,6-digalactosyl derivative of the glycerol linolenate–oleate diester. The physicochemical characteristics of such compounds and the stable emulsions formed may allow an increase in the transfer of hydrophilic phenolic compounds (mainly *o*-diphenols), which are strong antioxidants.

A lipoxygenase activity has been detected in freshly prepared olive oils (Georgalaki *et al.* 1998). Taking into consideration the higher stabilities of cloudy oil, it can be postulated that the polar phenolic compounds present act not only as primary antioxidants, but also as inhibitors of oxidising enzymes.

9.7 Consumption and culinary applications

In the past five years, world olive oil production was approximately 2.5 million tonnes (see Chapter 1). The main producing countries are Spain, Italy, Greece, Tunisia, Turkey, Syria, Morocco, Algeria, Portugal and Jordan. There is a smaller amount of production in Argentina, Croatia, Israel, Lebanon, Libya, Palestine and France, and even smaller in Cyprus, Mexico, and the US.

World consumption during the period 1996–2000 averaged 2.37 million tonnes (International Olive Oil Council 2001). The share of this consumption is: EU 71%, US 6%, Syria 4%, Turkey 3%, Algeria 2%, Tunisia 2%, Morocco 2% and others 9%. Spain, Italy and Greece, the main producing countries, have the highest total consumption and the highest per capita per year consumption. The following per capita consumption were reported for 1999: Greece > 20 kg, Spain and Italy about 13 kg, Portugal 6.7 kg, Syria and Tunisia 5.5 kg, Jordan 5 kg, Libya 4 kg, and Lebanon 2.6 kg. In Australia, France, Morocco, Algeria, Israel, and Turkey per capita consumption is 1–1.5 kg. In the rest of the world (Central and Northern Europe, the US, Canada, South America) the figure is below 1 kg/capita/year.

Virgin olive oil has a remarkable stability and can be stored for 18 months or more. The resistance to development of rancidity is combined with a wide array of flavour notes and colour hues, as well as distinct features due to differences between the olive cultivars from which the oil is extracted. These qualities offer opportunities for a variety of culinary applications with little or no processing.

Olive oil contributes flavours that are reflected throughout the whole dish. A good quality olive oil blends perfectly with green vegetables. Traditional dishes are prepared with seasonal vegetables, various greens, parsley and grains. In vegetarian dishes, olive oils with herbal flavours are usually preferred. For salads a pronounced hint of apple is suitable, while for grilled meats a peppery flavour is desirable. Other dishes such as pies, mayonnaise and fried eggs require different flavours for those who appreciate sensorial characteristics like mouth feel, bouquet, taste and aftertaste, and have developed their own personal preferences. ‘Freshly cut grass flavour’, ‘flowery aroma’, ‘pepperiness’ and

other such comments are very likely to be heard, not only in oil-tasting parties, but even in common discussions of consumers with a sophisticated palate.

The taste of olive oil is very often complemented by the sharp taste of vinegar, lemon or tomato. A simple traditional salad dressing is an instantly beaten mixture of olive oil and lemon juice, a rich source of both lipid-soluble and water-soluble vitamins.

In salads or in cooking, olive oil is usually mixed with herbs and spices, which are also important elements of the Mediterranean diet. Herbs like oregano, rosemary, or thyme and others from the plants of the *Lamiaceae* family are rich sources of phenolic compounds with strong antioxidant activity (Nakatami 1994, Tsimidou and Boskou 1994, Antoun and Tsimidou 1997, Exarchou *et al.* 2001). These herbs maintain the nutritional value of the food and enhance the shelf life of the food product.

9.7.1 Olive oil in frying

Olive oil shows remarkable stability during domestic deep-frying of potatoes or in other uses requiring frying temperatures (Boskou 1999). When compared to other vegetable oils such as sunflower, cottonseed, corn, and soybean oil, olive oil has a significantly lower rate of alteration. This increased stability to thermal oxidation explains why the oil can be used for repeated frying. The reason for the resistance of olive oil to rapid deterioration at elevated temperatures is its fatty acid composition and the presence of natural antioxidants, such as tocopherols, squalene and Δ^5-avenasterol (Boskou 1996, Blekas and Boskou 1999). The polar antioxidants found in virgin olive oil may also make a contribution to the increased stability to thermal oxidation and polymerisation.

These properties of olive oil are well-known to people of the Mediterranean basin, who traditionally use good quality olive oil for frying but only for a limited number of times. According to Varela (1992), deep frying in olive oil offers a means to improve the lipid intake profile, since during the frying process there are important changes in fat composition because of the olive oil penetration into the fried food. Western diets using blended oils containing animal fats are rich in saturated fats and also in the linoleic acid (*n*-6) series. If, however, meat is cooked in olive oil there is a favourable change in saturated to polyunsaturated fatty acids ratio. A better combination is to cook fish with olive oil. If sardines, for example, are fried in olive oil, the nutritional benefits of the oil are combined with the *n*-3 series fatty acids from the fish (Cuesta *et al.* 1998).

9.7.2 Other uses

Small quantities of refined olive oil and virgin olive oil may be added to soft margarines prepared from hydrogenated or interesterified vegetable oils.

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10 Corn oil

Robert A. Moreau

10.1 Composition of corn oil

10.1.1 Introduction—the corn oil industry

Unlike most other vegetable oils, corn oil (maize oil) is obtained from seeds (kernels) that contain only 3–5% oil. Obtaining oil directly from the kernels is technically possible, but 'corn kernel oil' would be costly to produce, due to the low levels of oil in the kernels. Because corn kernels contain high levels of starch (60–75%), a process of 'wet milling' was developed to isolate pure starch efficiently from corn kernels. The first corn wet mill in the US started to produce corn starch in 1842, and by 1860 several corn wet mills were in operation (Anonymous 1996). During industrial wet milling, the non-starch portions of the kernel are separated into four fractions: steepwater solubles (about 7%), fiber (about 10%), corn gluten meal (about 6%), and germ (about 7%) (Moreau *et al.* 1999a). The steepwater solubles and the fiber fractions are blended together to produce an animal feed called 'corn gluten feed', which contains about 21% protein and 60–70% fiber. The high fiber content restricts its use mainly to feeds for ruminants. Corn gluten meal contains about 60% protein and low fiber (< 1%), and is a premium feed for nonruminants (poultry and swine). Corn germ is rich in oil (> 30%), and is the source of all commercial corn oil which could more accurately be called 'corn germ oil'. The US produces 57% of the world's supply of corn oil (see Chapter 1).

Unlike those oilseeds, where solvent extraction alone can be used to obtain oils, extraction after flaking of wet milled corn germ produces substantial amounts of 'fines' that interfere with the efficiency of the extraction process. Traditionally, oil is removed from the wet milled germ using a conditioning (heating) process, followed by mechanical expelling (prepress) and hexane extraction. Extrusion has recently been employed as a means of germ preparation for solvent extraction, producing a crude corn oil of high quality and high yield (Maza 2001). Others have demonstrated that corn germ can be effectively extracted by supercritical fluid extraction (Ronyai *et al.* 1998). Within the US, most of the crude corn oil is currently produced by four wet milling companies and refined corn oil is produced by only three of these (Anonymous 2001a). It was estimated that in 1996 about 90% of commercial corn oil in the US was from wet milled germ and the remainder from dry milled germ (Anonymous 1996).

Oil is usually obtained from dry milled corn germ by full press (via an expeller). List and co-workers (1984) compared some of the chemical components in corn oil from wet milled germ versus dry milled germ and reported lower levels of free fatty acids, lower levels of phosphorus, and higher levels of tocopherols in the latter.

Although several 'high oil' corn hybrids are available and are becoming increasingly popular, most of the crop has been used for animal feed (with the increased fat providing more calories). Little or none has been wet milled to obtain starch, corn oil and other products. A process for extracting oil from the flaked kernels of high oil (> 8%) corn hybrids was recently patented (Ulrich *et al.* 2001). An interesting aspect of this proprietary process is that it uses the popular flaking and extraction machinery that is usually employed for soybean oil processing.

10.1.2 Common corn oil refining steps and effects on oil composition

The major component of crude corn germ oil is triacylglycerol (TAG), but the crude oil also contains other minor nonpolar and polar lipid components (Table 10.1). Free fatty acids, pigments, volatile compounds, phospholipids, and waxes are the major undesirable components in crude corn oil and these are removed by appropriate refining steps. Whereas soybean oil processing usually is preceded by water degumming, during corn oil processing, degumming is usually not included if corn oil is going to be processed through alkali refining (degumming is necessary if physical refining is used). In corn oil processing, most companies remove free fatty acids by alkali refining, which involves adding base and subsequently neutralizing (and sequestering) the free fatty acid soaps (and phospholipids) into a byproduct called 'soapstocks' (Strecker *et al.* 1996). Alternatively, free fatty acids can be removed by a process called physical refining or steam refining. This involves treating the oil at high temperature and vacuum to volatilize the free fatty acids. Physical refining is only advisable if the oil is of high quality—otherwise the oil becomes dark and has poor stability (personal communication, R. Ormsbee). Physical refining begins by removing phospholipids by a water degumming step (Antoniassi *et al.* 1998). Failure to remove the phospholipids adequately (by either alkali refining or degumming) results in a corn oil that will form dark colors and off-flavors when heated (Anonymous 1996). After a subsequent bleaching step, the next step in physical refining is a steam distillation at high temperature and very low pressure (vacuum) which volatizes the free fatty acids. Leibovitz and Ruckenstein (1983) reported higher yields of oil with physical refining than with alkali refining. Others have noted that oils that contain phytosterol esters (especially ferulate-phytosterol esters, such as those found in corn fiber oil and rice-bran oil) are extensively hydrolyzed during conventional alkali refining, but remain relatively intact during physical refining (personal communication, R. Nicolosi). Other

Table 10.1 Polar and nonpolar lipid classes in corn germ oil, corn kernel oil and corn fiber oil

Oil	TAG	FFA	St:E	St	FPE	Tocols	GL	PL	Reference
Germ oil (crude)	95.6	1.7	nr	1.2*	nr	0.06	nr	1.2	Orthoefer and Sinram 1987
Germ oil (crude)	96.8	0.31	0.47	0.48	0.01	0.17	nr	nr	Moreau *et al.* 1999a
Germ oil (RBD)	98.9	0.03	nr	1.1*	nr	0.05	0	0	Orthoefer and Sinram 1987
Kernel oil (crude)	nr	nr	0.76–3.09	0.54–1.28	0.047–0.839	0.023–0.127	nr	nr	Moreau *et al.* 2001
Fiber oil (crude)	84.5	2.11	5.61	1.17	4.11	0.76	nr	nr	Moreau *et al.* 1999a
Fiber oil (crude)	nr	nr	2.9–9.2	1.9–4.3	6.5–9.5	nr	nr	nr	Singh *et al.* 2000

Figures are % wt of total lipids.

*Value is after saponification, meaning that it is the sum of St and St:E.

Abbreviations: nr, not reported; TAG, triacylglycerols; FFA, free fatty acids; St:E, phytosterol fatty acyl esters; St, free phytosterols; FPE, phytosterol ferulate esters; Tocols, tocopherols and tocotrienols; GL, glycolipids; PL, phospholipids; and RBD, refined, bleached and deodorized oil.

strategies for removing free fatty acids from crude oil have included liquid–liquid extraction and a new method involving solvent extraction in a perforated rotating disk (Pina and Meirelles 2000). Deodorization of corn oil involves treatment at high temperature (> 200°C) and vacuum (around 2–10 mm Hg), and it removes undesirable odors and flavor components (Orthoefer and Sinram 1987). Unfortunately, the deodorization process also removes some phytosterols and tocopherols. The byproduct of deodorization (the deodorizer distillate) is a major industrial source of tocopherols and phytosterols. The latter serve as precursors in the synthesis of some steroid pharmaceuticals and are sometimes hydrogenated to phytostanols. A recent study compared the levels of tocopherols and phytosterols in industrial deodorizer distillates obtained from chemical and physical refining of corn, canola, sunflower and soybean oils (Verleyen *et al.* 2001). Pigments are usually removed by treating the oil with acid-activated bleaching clay (Strecker *et al.* 1996). Another refining step that ensures physical stability of oils at low temperature is dewaxing or winterization. This involves cooling the oil to 5–10°C, and removing precipitates by filtration (Leibovitz and Ruckenstein 1983).

10.1.3 The composition of crude corn oils–comparison of germ, kernel and fiber oils

Although all commercial corn oil is produced from corn germ oil, considerable research has been devoted to the study of extracting the entire corn kernel to produce corn kernel oil and extracting corn fiber (a byproduct of wet milling) to obtain corn fiber oil (Table 10.1). The levels of total phytosterols (the sum of free phytosterols and phytosterol fatty acyl esters) in corn germ oil averages a little more than 1%, which is higher than the levels found in most other common vegetable oils (Orthoefer and Sinram 1987). Some of these phytosterols are removed during refining, but even after refining, the levels of phytosterols in commercial corn oil are still about 1% (Table 10.1). Hojilla-Evangelista and co-workers (1992) at Iowa State University developed a process, the sequential extraction process (SEP), which involves the ethanol extraction of whole flaked corn kernels, and then additional steps to fractionate proteins and starch. Although analyses of their SEP oil (a type of corn kernel oil) have not been published, we have reported data on the composition of hexane-extracted corn kernel oil. We found (Moreau *et al.* 2001) that it contains higher levels of the three phytosterol lipid classes (free phytosterols, phytosterol fatty acyl esters, and phytosterol ferulate esters) than does germ oil (Table 10.1). Moreau and co-workers (1996) reported that a unique oil, very rich in the two phytosterol esters (their chemical properties will be described in a later section) could be extracted from corn fiber. Corn fiber oil contains the highest levels of natural

phytosterols and phytostanols (see section 10.1.6) of any known plant extract (Hicks and Moreau 2001).

10.1.4 Fatty acid composition of corn triacylglycerols

Edible oils are often compared by examining their fatty acid profiles. In the 1950s and 1960s a marketing slogan for corn oil was that it was 'high in polyunsaturates', mostly attributed to its high content of the essential fatty acid linoleic acid (18:2). An essential fatty is one that is required by humans but cannot be biosynthesized and must therefore be obtained in the diet (Table 10.2). Another desirable feature of corn oil is that it contains relatively low levels ($< 15\%$) of saturated fatty acids and very low levels of linolenic acid (18:3). This last is especially susceptible to oxidation, leading to rancidity. Although the levels of linoleic acid in US corn oil average about 60%, its levels in corn oil produced outside the US are closer to 50%, with most of the difference being accounted for by higher amounts of oleic acid (Strecker *et al.* 1996).

Several studies have reported that when the same corn hybrids are grown in multiple locations, the corn oil produced from plants grown in cooler regions have higher levels of linoleic acid (White and Weber 2002). It was also noted that the average levels of linoleic acid in US commercial corn oil increased from 57.8 to 62.0% between 1974 and 1986 (White and Weber 2002).

In response to the current demand for high monounsaturated vegetable oils, recent efforts have been devoted to developing corn hybrids that produce corn germ oils with high levels of oleic acid. A 'high oil/high-oleic acid' corn hybrid was recently patented (Leto and Ulrich 2001). In addition to the extensive literature on the fatty acid composition of crude and refined corn germ oil, there also have been reports on the fatty acid composition of crude corn kernel oil (Goffman and Böhme 2001) and of crude corn fiber oil (Moreau *et al.* 2001). The fatty acid composition of both are very similar to that of corn germ oil (Table 10.2).

10.1.5 Triacylglycerol molecular species

Reversed-phase HPLC techniques have been developed to analyse quantitatively the triacylglycerol molecular species of oils of plant and animal origin. Reports of the triacylglycerol molecular species of refined corn oil led to the identification of 19–27 individual molecular species, with oleate-linoleate-linoleate and linoleate-linoleate-linoleate being the two most abundant molecular species (Table 10.3). Silver ion HPLC was also used to analyse quantitatively the triacylglycerols in corn oil (Neff *et al.* 1994). This procedure separated the triacylglycerols into eleven fractions. The two largest fractions had five and six double bonds with the structures dienoic-dienoic-monoenoic and dienoic-dienoic-dienoic, thus confirming the two most abundant molecular species identified in reversed phase HPLC.

Table 10.2 Fatty acids in refined corn germ oil, corn kernel oil and corn fiber oil

Oil	16:0	18:0	20:0	18:1	18:2	18:3	Reference
Germ oil (RBD) US	11.0 ± 0.5	1.8 ± 0.3	0.2 ± 0.2	25.3 ± 0.6	60.1 ± 1.0	1.1 ± 0.3	Orthoefer and Sinram 1987
Germ oil (RBD) US	9.2–16.5	0–3.3	0.3–0.7	20–42.2	39.4–65.6	0.5–1.5	Firestone 1999
Germ oil (RBD) US	10.90	1.80	nr	24.2	58.0	0.70	Anonymous 2001c
Germ oil (RBD) US	11.0 ± 0.6	1.7 ± 0.3	nr	25.8 ± 0.9	59.8 ± 1.2	1.1 ± 0.4	Strecker *et al.* 1996
Germ oil (RBD) Int	12.9 ± 1.4	2.6 ± 0.6	nr	33.1 ± 2.5	48.8 ± 2.4	1.4 ± 0.4	Strecker *et al.* 1996
Kernel oil (crude) Int	9.2–11.8	1.1–1.7	0.3–0.5	19.5–30.4	53.0–65.3	1.2–2.1	Goffman and Böhme 2001
Corn fiber oil (crude)	13.8 ± 0	1.7 ± 0	0.3 ± 0	23.8 ± 0.1	56.4 ± 0.1	2.6 ± 0	Moreau *et al.* 2000

Figures are mol% of total fatty acids.

Abbreviations: nr, not reported; US, US hybrids; Int, International hybrids; 16:0, palmitic acid; 18:0, stearic acid; 20:0, arachidic acid; 18:1, oleic acid; 18:2, linoleic acid; 18:3, linolenic acid; and RBD, refined, bleached, and deodorized oil.

Table 10.3 Triacylglycerol molecular species in refined corn germ oil

TAG molecular species	Area (%)[a]	Area (%)[b]	Area (%)[c]
LLO	19.98	21.5	23.0
LLL	17.79	25.4	22.6
LLP	13.71	14.7	15.2
OOL	11.82	10.7	10.6
PLO	10.85	10.0	10.4
PPL	2.48	2.5	1.7
OOP	3.48	2.9	2.4
LLS	2.64	2.2	1.8
LOS	1.77	1.8	1.3
OOO	4.35	2.8	3.2
PPO	1.55	0.9	0.4
PLS	0.78	0.8	0.4
LLLn	0.91	1.2	0.8
LnLO	2.20	0.9	2.3
OOS	0.56	0.6	0.5
POS	0.20	0.3	0.3
PLnL	0.43	0.5	0.5
PPP	0.0	0.0	0.1
OOLn	1.09	0.1	1.0
PLnO	0.0	0.1	0.5
PPS	0.36	0.0	0.1
SSL	0.0	0.1	0.3
LnLS	0.0	0.1	0.0
SSO	0.0	0.0	0.0
PPLn	0.0	0.0	0.2
SSP	0.0	0.0	0.1
SSS	0.0	0.0	0.1

[a]From Strecker *et al.* 1990.
[b]HPLC-Mass Spec values from Byrdwell *et al.* 2001.
[c]HPLD-Flame Ionization Detector Values from Byrdwell *et al.* 2001.
Abbreviations: Ln, linolenic acid; L, linoleic acid; O, oleic acid; S, stearic acid; P, palmitic acid. Symbols such as LOS refer to all the possible triacylglycerols containing these three acids.

10.1.6 Unsaponifiables and phytosterols

Commercial corn oil has been recognized as containing the highest levels of unsaponifiables (1.3–2.3%) of all the commercial vegetable oils (Strecker *et al.* 1996). The three main chemical components in the unsaponifiable fraction of corn oil are phytosterols, tocopherols and squalene.

Corn germ oil contains two phytosterol lipid classes, free phytosterols and phytosterol fatty acyl esters (Table 10.1). Phytosterols have been recognized as one of the twelve most important classes of phytonutrients (Fahey *et al.* 1999). Most chemical identification of phytosterols in vegetable oils has been conducted by saponifying (hydrolyzing with base) the oil and measuring the resulting free phytosterols, usually by GLC (Table 10.4). The major phytosterols

Table 10.4 Phytosterols in refined corn germ oil, corn fiber oil and corn aleurone (values represent free + esterified phytosterols, measured after saponification)

Oil	Campesterol	Stigmasterol	β-Sitosterol	Sitostanol	Δ^5-Avenasterol	Δ^7-Stigmasterol	Δ^7-Avenasterol	Reference
Germ oil (RBD)	18.6–24.1	4.3–7.7	54.8–66.6	nr	4.2–8.2	1.0–4.2	0.7–2.7	Firestone 1999
Germ oil (RBD)	24.3	7.7	61.6	nr	3.8	0.7	0.8	Ham *et al.* 2000
Germ oil (RBD) (free phytosterols)	22.1	5.7	69.8	nr	2.4	nr	nr	Worthington and Hitchcock 1984
Germ oil (RBD) (esterified phytosterols)	16.7	6.8	66.9	nr	8.0	nr	nr	Worthington and Hitchcock 1984
Corn fiber oil (crude)	4.9 ± 0.4	1.4 ± 0.1	34.3 ± 0.1	43.1 ± 0.7	1.8 ± 0	nr	nr	Moreau *et al.* 2000
Corn aleurone oil (crude)	4.7 ± 0.3	tr	20.8 ± 0.1	50.6 ± 0.4	3.5 ± 0.1	nr	nr	Moreau *et al.* 2000

Figures are mol% of total phytosterols.

in corn germ oil are β-sitosterol > campesterol > stigmasterol (Table 10.4). Snyder and co-workers (1999) developed a method to concentrate and fractionate the phytosterols in corn germ oil. Examination of the total phytosterols in corn fiber oil revealed that the major phytosterol was sitostanol (Table 10.4). Sitostanol is a stanol with no carbon–carbon double bonds, whereas phytosterols typically contain at least one such unit. Natural sitostanol is rare in plants, and the only reports of its presence in greater than trace amounts have been in grains (Moreau *et al.* 2001). The sitostanol used in commercial sitostanol-ester margarines is produced by catalytic hydrogenation of the two most common plant phytosterols, β-sitosterol and stigmasterol (Hicks and Moreau 2001). We recently reported that most of the sitostanol in corn fiber oil is present as the ferulate ester, and most of the sitostanol in corn fiber (and in corn kernels) is present in the aleurone layer (Table 10.4). In some grains the aleurone layer is multiple cell layers, but in corn it is a single layer of (phytosterol-rich) living cells (Singh *et al.* 2001).

Worthington and Hitchcock (1984) reported, on the basis of GC examination, that squalene was the major hydrocarbon in corn germ oil and Moreau and co-workers (2000) recorded about 0.2% of squalene in both the fiber and the germ oils.

10.1.7 Tocopherols and tocotrienols

Corn oil has long been recognized as a rich source of tocopherols, with γ-tocopherol being the most abundant tocopherol, followed by α-tocopherol and then δ-tocopherol (Table 10.5). Among the tocopherols, α-tocopherol has received the most attention because of its vitamin E activity, but the other isomers also are known to have valuable antioxidant properties. Recent evidence suggests that γ-tocopherol may be superior to α-tocopherol in preventing the oxidation of low density lipoproteins and delaying thrombus formation (Saldeen *et al.* 1999). Wang and co-workers (1998) recently reported significant levels of tocotrienols (the most abundant was γ-tocotrienol followed by α-tocotrienol) in corn kernel oil. Saponfication of the kernels caused about a two-fold increase in the levels of extractable tocotrienols and γ-tocopherol. In addition to their valuable antioxidant properties, it is currently believed that tocotrienols also possess cholesterol-lowering properties—probably associated with their ability to inhibit cholesterol biosynthesis (Parker *et al.* 1993). We recently reported high levels of γ-tocopherol in corn fiber oil (about 0.36 wt%), noting that heat pretreatment of the corn fiber before extraction caused a nearly tenfold increase in the levels of extractable γ-tocopherol, thereby increasing its concentration in the oil to about 3% (Moreau *et al.* 1999b). These last two references suggest that future research should focus on optimising the pretreatment conditions for extraction of tocopherols and tocotrienols from corn germ (and perhaps kernels and fiber).

Table 10.5 Tocopherols and tocotrienols in corn germ oil, corn kernel oil and corn fiber oil

Oil	α-Tocopherol	β-Tocopherol	γ-Tocopherol	δ-Tocopherol	α-Tocotrienol	γ-Tocotrienol	δ-Tocotrienol	Reference
Germ, crude	191	0	942	42	nr	nr	nr	Strecker *et al.* 1996
Germ, RBD	134	18	412	39	nr	nr	nr	Strecker *et al.* 1996
Germ, RBD	23–573	0–356	268–2468	23–75	0–239	0–450	0–20	Firestone 1999
Kernel, crude	67–276	0–20	583–1048	12–71	46–90	60–133	nr	Goffman and Böhme 2001
Kernel, crude[a]	57.5	nr	600	nr	132.2	242.5	nr	Wang *et al.* 1998
Kernel, crude[b]	120	nr	1330	nr	310	492.5	nr	Wang *et al.* 1998
Fiber oil, crude[c]	nr	nr	3,600	nr	nr	nr	nr	Moreau *et al.* 1999b
Fiber oil[d]	nr	nr	34,933	nr	nr	nr	nr	Moreau *et al.* 1999b

Figures are mg/kg oil, equivalent to ppm.

[a]Measured in crude oil. Values are reported as kernel oil composition, calculated using published mg/g dry wt of kernel, assuming an oil consumption of 4.0% in the kernel.

[b]Measured after saponification. Values are reported as kernel oil composition, calculated using published mg/g dry wt of kernel, assuming an oil consumption of 4.0% in the kernel.

[c]Untreated.

[d]Heat-pretreated.

Table 10.6 *Cis* and *trans* fatty acids in corn oil and corn oil margarines

Oil	% Fat	16:0	16:1	18:0	*c* 18:1	*t* 18:1	*cc* 18:2	*ct* 18:2	*tt* 18:2	*ccc* 18:3	20:0	20:1	Total *trans*	Reference
Corn oil	100	10.9	0	1.8	24.2	0	58.0	0	0	0.7	0	0	0	Anonymous 2001c
Corn oil margarine[a]	80	8.1	0	6.0	17.5	19.7	20.8	0.7	0	2.2	0.26	0	19.7	Anonymous 2001c
Corn oil margarine[a]	81.98	8.99	0	5.16	16.97	19.63	25.69	0.5	0	0.47	0.19	0.16	20.13	Exler *et al.* 2001
Corn oil spread[b]	38.83	3.91	0.02	2.44	9.44	5.20	14.9	0.46	0	0.26	0.19	0.07	5.66	Exler *et al.* 2001
Corn oil spread[c]	19.47	2.03	0.01	0.83	4.75	2.69	7.82	0.1	0	0.17	0.04	0.04	2.79	Exler *et al.* 2001

Figures are g/100 g product (%).
For abbreviations see Table 10.2.
[a]Stick.
[b]Light, tub.
[c]Extra light, tub.

10.1.8 Carotenoids

High levels of carotenoids have been reported in corn kernels, with most (74–86%) being localized in the endosperm, 2–4% in the germ, and 1% in the bran (Weber 1987). The most abundant carotenoids in corn kernels are lutein and zeaxanthin. Consuming foods that are rich in these carotenoids may decrease the risk for age-related macular degeneration (Sommerburg *et al.* 1998). The levels of carotenoids in commercial corn oil are relatively low, partly due to their low concentrations in the germ and partly due to their removal during bleaching. The nutritional value of corn oil carotenoids has not received much attention. Although it is generally believed that carotenoids function as antioxidants, there is some evidence that, under certain conditions, carotenoids in vegetable oils and certain other food matrices may serve as pro-oxidants, especially at higher concentrations (Subagio and Morita 2001).

10.1.9 Trans *fatty acids*

The common unsaturated fatty acids in all vegetable oils exist only in the *cis* configuration. During the production of margarine, spreads and shortenings via catalytic hydrogenation, carbon–carbon double bonds are converted to carbon–carbon single bonds, but the process also catalyzes the production of some *trans* fatty acids (Enig *et al.* 1983). There is considerable variation in the levels of *cis* and *trans* fatty acids in commercial corn oil margarines and spreads (Table 10.6). The levels of *trans* fatty acids range from a low of 2.8 to a high of 20.1 g of total *trans* fatty acids per 100 g of product. Concerns about possible associations between *trans* fatty acids and certain types of cancer (Ip 1997) have caused some groups to seek to reduce or eliminate the levels of *trans* fatty acids in foods. This can be achieved either by using butter, or by using processes other than hydrogenation to raise the melting point of corn oil, thereby producing new types of margarines and spreads (see Section 10.3). With the controversy associated with *trans* fatty acids produced during chemical hydrogenation, some individuals may not realize that a natural group of *trans* fatty acids, conjugated linoleic acid or CLA (the *trans* double bond is produced by anaerobic rumen bacteria during biohydrogenation), have been discovered in dairy and beef products. Current international research indicates that CLA may have several health-promoting properties (Lawson *et al.* 2001). The discovery of these health-promoting properties of some *trans* fatty acids (CLA) may provide an incentive to re-evaluate objectively the risks of the *trans* fatty acids in margarines from corn and other vegetable oils.

10.2 Properties of corn oil

10.2.1 Chemical and physical properties

The important properties of corn oil include its pleasing flavor, its high levels of polyunsaturated (essential) fatty acids, and its low levels of saturated fatty

Table 10.7 Physical and chemical characteristics of corn oil

Property	Value
Iodine value	127–133[a]
Saponification number	187–193[a]
Free fatty acids RBD (%) max	0.05[b]
Color Lovibond	3.0 red max[b]
Gardner	6 max
Refractive index	
20°C	1.4753[a]
26°C	1.4726[a]
Specific gravity	
25/25°C	0.91875[a]
Viscosity (cP)	
40°C	30.80[a]
60°C	18.15[a]
Dielectric constant 26°C	3.954[a]
Surface tension, 25°C (dyn/cm)	34.80[a]
Interfacial tension, k H_2O at 24°C (dyn/cm)	18.60[a]
Thermal conductivity at 130°C (J/s/cm^2/°C)	4.2017×10^{-5}[a]
Unsaponifiables (%)	1–3
Weight per gallon at 60°C (pounds)	7.7[d]
Melting point (°C)	−11 to −8[d]
Smoke point (°C)	230 to 238[d]
Flash point (°C)	332 to 338[d]
Fire point (°C)	366 to 371[d]
Cloud point (°C)	−14 to −11[d]

[a]From Strecker *et al.* 1996.
[b]From Anonymous 2001a.
[c]From Firestone 1999.
[d]From Anonymous 1996.

acids and of linolenic acid (Anonymous 1996). The other main physical and chemical properties of corn oil are summarized in Table 10.7.

10.2.2 Stability

Because frying is a major use of corn oil, numerous studies have compared the stability of corn oil and other vegetable oils during frying (Strecker *et al.* 1996, Gertz *et al.* 2000). One frying study demonstrated that, compared to canola and soybean oils, corn oil produced the lowest levels of oxidation products and retained the highest levels of tocopherols, during five days at continuous frying temperatures (Strecker *et al.* 1990). Another oxidative stability study revealed that corn oil hybrids with higher levels of saturated fatty acids were more stable than traditional corn oils (Shen *et al.* 1999). A new optical assessment study was recently developed, providing a new parameter for assessing the oxidative stability of corn oil during frying (Sebben *et al.* 1998).

10.2.3 Nutritional properties

Over 30 clinical studies during the past forty years have supported the hypothesis that corn oil has cholesterol-lowering properties (Strecker *et al.* 1996). This observation of corn oil's superiority over other vegetable oils in its cholesterol-lowering properties has been termed the 'maize oil aberration', (Meijer 1999). In the 1950s, experts believed that the high levels of polyunsaturated fatty acids in corn oil were the reason for its cholesterol-lowering properties (Anonymous 1996). Others have suggested more recently (Howell *et al.* 1998) that the cholesterol-lowering effect of corn oil is related to the fact that it contains the highest levels of unsaponifiables and phytosterols of any common vegetable oil. However, a recent study, comparing corn oil with cottonseed oil, found that although corn oil contained more unsaponifiable material, cottonseed oil was more effective at lowering total serum cholesterol. The authors attributed this to the specific types of unsaponifiables in cottonseed oil (Radcliffe *et al.* 2001). Lichtenstein and co-workers (1993) reported that hydrogenation of corn oil reduces its cholesterol-lowering properties in humans. Recent clinical studies with phytosterol and phytostanol ester products have indicated that a person must ingest 1.6 to 3.3 g of phytosterols per day to achieve a 5 to 10% reduction in total serum cholesterol (Meijer 1999). To ingest 1 g of phytosterols from corn oil, a person would need to eat about 100 g (about half a cup and about 900 calories) of corn oil per day, an amount that is feasible, but probably not practical. A recent hamster study (van Tol *et al.* 1999), comparing corn oil and olive oil, presented evidence that, although both oils reduced LDL-cholesterol ('bad cholesterol'), olive oil was better at increasing HDL-cholesterol ('good cholesterol'). Other recent studies indicated that corn fiber oil is more effective than corn oil at lowering serum cholesterol in hamsters (Wilson *et al.* 2000). Obviously, more work is required to evaluate the health-promoting properties of corn oil and corn fiber oil.

The antioxidant properties of tocopherols (such as those found in corn oil) may be involved in combating atherosclerosis by preventing the oxidation of low-density lipoproteins (Saldeen *et al.* 1999). Another recent study indicated that the particular ratio of individual tocopherols in corn oil (a high ratio of γ-tocopherol/α-tocopherol) may achieve better protection against DNA damage than α-tocopherol alone (Elmadfa and Park 1999). Others have demonstrated beneficial effects of corn oil on blood pressure, platelet aggregation and diabetes (Strecker *et al.* 1996).

10.3 Major food uses of corn oil

10.3.1 Cooking/salad oil

Of the 1.3 billion pounds (0.65 million tonnes) of refined corn oil consumed in the US in 2000, approximately half was used for cooking and salad oils, and

about a quarter was used for margarines and spreads (Anonymous 1996). Corn oil has long been a popular cooking oil, because of its mild flavor, its oxidative stability (due to low levels of linolenate), and its reputation as a healthy edible oil (due its high levels of polyunsaturated fatty acids). Because it contains higher levels of polyunsaturates than most other commodity vegetable oils (especially soy), corn oil was considered a premium oil and was sold at a premium price. In recent years, with the increased popularity of monounsaturate-rich oils (olive, canola, and now NuSun sunflower oil), corn oil is still considered a premium vegetable oil, but there has been a drop in the price differential between corn oil and other commodity vegetable oils. At the time of this writing the wholesale US prices for refined oils from soy, corn, and cottonseed, were respectively 20, 26, and 27 cents/lb.

10.3.2 Margarines and spreads

Corn oil margarine (common 'stick' margarines containing 80% fat) and corn oil spreads (common 'tub' margarine spreads containing 20–65% fat) are popular food products. In the late 1870s, Unilever began manufacturing margarine in Europe and the US Dairy Company began production of 'artificial butter' in the US (Anonymous 2001b). Sales of corn oil margarine in the US climbed slowly and reached a level of about 1 million pounds (500 tonnes) in 1930 (Anonymous 1996). During the period of 1950 to 1980, when there was growing consumer interest in the health-promoting properties of the polyunsaturates in corn oil, production of corn oil margarine in the US climbed from 15 to 250 million pounds (7500 to 125,000 tonnes) per year (Anonymous 1996). In recent years there has been growing concern about possible harmful effects of the *trans* fatty acids, which can range from 10–20% of the total fatty acids, in margarines and spreads made from corn oil and other vegetable oils (see Section 10.2), and consumer concerns about *trans* fatty acids have become a major issue for margarine manufacturers. Methods have been developed to produce margarines, shortenings, and spreads by interesterifying (List *et al.* 1995) or blending oils. These include a recent patent that details a process to produce '*trans*-free' shortening by blending corn oil and palm fat (Sundram *et al.* 1999). These processes remove the need for chemical hydrogenation and eliminate the formation of *trans* fatty acids. Zero *trans* fatty acid margarines and spreads currently account for a major portion of the sales in several European countries and several manufacturers are now marketing zero *trans* fatty acid margarines and spreads in the US.

10.4 Conclusions

Corn oil's desirable properties include: a mild nutty flavor, high levels of unsaturated fatty acids, low levels of saturated fatty acids and very low levels of

linolenic acid, high levels of desirable unsaponifiables (including phytosterols and tocopherols), and stability during frying. Although consumer focus has been shifting towards 'high-monounsaturate'-oils (olive, canola, and NuSun sunflower oils), additional research is still needed to compare objectively the health-promoting properties of polyunsaturates versus monounsaturates. The food industry currently relies on corn oil margarine and other food products that contain hydrogenated corn oils. Additional research also is needed to evaluate objectively the risks associated with *trans* fatty acid-containing products made from hydrogenated corn oil, especially in light of the recent evidence that at least some types of *trans* fatty acids (conjugated linoleic acids) may have multiple health-promoting properties.

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11 Sesame, rice-bran and flaxseed oils

S. P. Kochhar

11.1 Introduction

There are several minor oilseeds that an important because of their special characteristics, properties, nutritional and health benefits. These include high-γ-linolenic oils (evening primrose, borage or starflower and blackcurrant), 'virgin' olive oil (Chapter 9), and the seed oils from sesame, rice bran, pumpkin, hemp and melon. This chapter deals with three minor vegetable oils, namely sesame seed oil, rice bran oil, and flaxseed (linseed and linola) oil.

11.2 Sesame seed oil

Sesame (S*esamum indicum*, L.) is one of the oldest oilseed crops known to mankind and is the only cultivated S*esamum* species. Sesame seed has been considered to be important because of its high oil content (42–56%) and protein (20–25%), and also because it is a good source of minerals, particularly calcium, phosphorus, potassium and iron (Deshpande *et al*. 1996). Moreover, sesame oil is highly resistant to oxidation and displays several medicinal effects (Weiss 1983; Salunkhe *et al*., 1991; Kochhar, 2000). For instance, it is written in Chinese ancient books that sesame seeds (called 'Chih-Ma' in Chinese) increase energy and prevent ageing. The oil obtained from sesame seeds, called 'Tila' in Sanskrit or simply 'Til' these days, has been used as domestic Ayurvedic medicine in India. Actually the name sesame comes from the Arabic word 'semsin'. Researchers (Bedigian 1984) now believe that the actual origin of sesame was from Sudan where many wild species are found and not India. The magic words 'Open Sesame' relate to its popularity in Arab countries. The seed colour varies from white through various shades of brown, gold, grey, violet and black. Moreover, because of their characteristic flavour and sweet taste, de-hulled sesame seeds are extensively used in baked goods (as a garnish on top of breads, rolls, bread sticks, buns, and some biscuits, and crackers) and in many confectionery products. In the Middle East and some other countries, sesame seeds are used mainly for preparing 'tahini' (sesame butter) and 'halvah' (sweet). In many European countries sesame snack bars produced with honey and homous — a dip-in chilled product made from chick pea flour and sesame paste — are being marketed.

As in many common vegetable oils, the lipids of sesame seeds consist mainly of neutral triacylglycerols with small quantities of phospholipids. However, compared with other vegetable oils, sesame oil contains a relatively high percentage of unsaponifiable matter (1–3%) which includes sterols, sterol esters, (mainly) γ-tocopherol, and unique compounds called sesame lignins (described below). Sesame oil is classified as a polyunsaturated, semi-drying oil containing about 82% unsaturated fatty acids. The major fatty acids, oleic and linoleic, are present in approximately equal amounts in the oil.

11.2.1 World seed production

Sesame, also known as gingelly, beniseed, sim-sim and sesamum, is an important annual crop of many countries. The sesame plant is cultivated in relatively hot and dry regions because the seeds are adaptable and drought-resistant (Salunkhe *et al*. 1991). India, China, Myanmar (Burma), Sudan, and Mexico are the major countries involved in the growing of sesame seed and production of sesame seed oil. It is interesting to note that in Myanmar, the sesame crop matures in about 60 days, in Sudan about 80 days, and in the southern US, Mexico, and India about 80–140 days depending upon the variety (Deshpande *et al*. 1996). The total production of sesame seeds has grown by 57% since 1980. This growth is mainly in Asia where China tripled its production from 225,000 to 725,000 tonnes in 2000 (Woltman 2000). The total production of sesame seed relating to 2000–01 harvest is 3.02 million tonnes (Table 11.1). About 20% of this production is exported, particularly to Japan, EU countries, and South Korea. Some of the seed is used as such or in de-hulled form in a variety of exotic products but the bulk (70%) is crushed to yield oil. Most of the oil is consumed in the major producing countries and only a relatively small amount (23,000 tonnes) is exported.

11.2.2 Oil composition

The fatty acids in sesame seed oil are mainly equal proportions of oleic acid and linoleic acid, with small amounts of saturated acids, and only a little linolenic

Table 11.1 Sesame seed and oil production, disappearance and exports (1000 tonnes)

	Seed			Oil	
	Crop	Export	Crushing	Production	Disappearance
India	700	100	380	152	152
China	820	122	530	228	223
Myanmar	302	33	215	88	88
Sudan	305	115	143	61	59
Total	3016	627	1840	782	780

Source: *Oil World Annual* 2001, ISTA Mielke GmbH, Hamburg, Germany.

acid. Several researchers have reported the fatty acid composition of sesame oils from *Sesamum indicum* seeds (Yermanos *et al*. 1972; Eltinay *et al*. 1976; Spencer *et al*. 1976; Brar 1982; Abdel Rahman 1984). The fatty acids of the oil are mainly oleic acid (18:1, 33–54%) and linoleic acid (18:2, 35–59%), together with palmitic acid (16:0, 8–17%) and stearic acid (18:0, 3–9%). Kamal-Eldin and co-workers (1992b) compared the fatty acid composition and triacylgycerol profiles of different varieties of the cultivated sesame, *S. indicum* with three wild species, (*S. alatum, S. angustifolium* and *S. radiatum*) growing in Sudan, using capillary column GC and HPLC. The oil content of the wild species (29–36%) was much less than that in the cultivated varieties (47–54%). The reported percentage fatty acid ranges of 16:0, 18:0, 18:1 and 18:2 in the *S. indicum* varieties were 9.2–10.9, 5.2–6.7, 36.1–41.3 and 41.3–46.7, and that in wild species 8.7–11.5, 5.6–9.9, 36.3–44.2 and 36.9–44.8 respectively. Table 11.2 presents the Codex Alimentarius ranges of some parameters and fatty acid composition of sesame oil, along with typical data for commercially produced oil. The fatty acid composition of sesame oil was only slightly affected by genotype, agroclimatic conditions, and stages of ripening (Brar 1977, 1980;

Table 11.2 Typical fatty acid composition and Codex ranges of some parameters of sesame seed oil

Parameter	Commercial sample refined (typical)	Codex range (FAO/WHO)
Iodine value	109	104–120
Saponification value	193	187–195
Acid value	0.2	0.6 max[a]
Peroxide value (meq O_2 / kg)	0.6	10.0 max[a]
Fatty acids (% wt)		
14:0	0.1	<0.5
16:0	9.2	7.2–12.0
16:1	0.1	<0.5
18:0	5.8	3.5–6.0
18:1	40.6	35.5–50.0
18:2	42.6	35.5–50.0
18:3	0.3	<1.0
20:0	0.7	<1.0
20:1	0.2	<0.5
22:0	0.2	<0.5
Others	0.2	
Induction period (h at 120°C)	6.0	
Tocopherols (mainly γ)	550 mg/kg	

Source: Codex Standard 26-1981, Supplement 1, 1983.
[a]Non-virgin oil.

Table 11.3 Important characteristics of sesame oil

Parameter	Seegeler (1983)	Weiss (1983)
Refractive index (n_D^{50})	1.463–1.474(25°C)	1.458 (60°C)
Specific gravity (25°/25°C)	0.916–0.921	0.922–0.924
Smoke point (°C)	166	–
Flash point (°C)	375	–
Solidifying point (°C)	–3 to –4	–3 to –4
Titre (°C)	20–25	22–24
Free fatty acids (% oleic)	1.0–3.0	1.0–3.0
Hydroxyl value	1.0–10.0	1.0–10.0
Saponification value	186–199	188–193
Unsaponifiable matter	0.9–2.3	0.9–2.3
Baudouin test*	positive	

*Using BS 684: Section 2.30:1978.

Lee and Kang 1980; Sekhon and Bhatia 1972). The triacylglycerol composition of the *S. indicum* variety comprised 1.5% monounsaturated, 7.7% diunsaturated and 90.8% polyunsaturated triacylglycerols (Kamal-Eldin *et al*. 1992b). The major triacylglycerols were found to be 25.4% LLO, 19.6% LLL, 15.1% LOO, 1.8% PLL and 8.1% PLO (L = linoleic, O = oleic, P = palmitic and each three letter symbol represents all the triacylglycerols containing the three acids indicated). Oil from cultivated *S. indicum* comprised 88.9% triacylglycerols, 6.5% diacylglycerols, 1.2% free fatty acids, 2.8% polar lipids, and 0.6% sterol esters (Kamal-Eldin and Appelqvist 1994a). Fatty acids composition is often used to characterise individual oils, including sesame oil. There are, however, a number of additional parameters of sesame oil presented in Table 11.3, including the Baudouin test that can be useful for characterisation of the oil. Sesame oil is dextro-rotatary, which is unusual for the glycerol esters lacking any optically active fatty acid. Minor components of the unsaponifiable fraction of sesame oil are probably responsible for the optical rotation of the oil.

The unsaponifiable material (1–3%) consists mainly of sterols, tocopherols and sesame lignans. For four cultivated species of *S. indicum*, the level of unsaponifiable material has been reported to be 1.4–1.8% (Kamal-Eldin and Appelqvist 1994b). The sesame oils from these species contained total sterols (0.51–0.76%), including desmethyl sterols (85–89%), monomethyl sterols (9–11%) and triterpene alcohols (dimethyl sterols) (2–4%) respectively. β-Sitosterol (62–67%), campesterol (15–20%), stigmasterol (5–8%) and Δ^5-avenasterol (7–10%) are the major sterols present in both free and esterified forms. The monomethyl sterols, namely gramisterol, citrostadienol and obtusifoliol, were present mainly as esters. The total sterols contained 65% in free and 35% in esterified form. Composition (% wt) data of the desmethyl sterols, monomethyl sterols and dimethyl sterols (tritepene alcohols) of four *Sesamum* species are listed in Table 11.4. Tocopherols of crude sesame oils are generally

Table 11.4 Sterol composition (% m/m) in the sterol fraction of oils from four *Sesamum* species

Desmethyl sterols

Sample	Cholesterol	Campesterol	Stigmasterol	Sitosterol	Δ^5-Avenasterol	Δ^7-Stigmastenol	Δ^7-Avenasterol
S. indicum (4 varieties)	0.0–0.3	15.4–20.3	5.4–8.0	60.3–66.9	6.4–10.6	0.8–2.7	0.3–1.4
S. alatum	0.4	18.3	12.8	36.9	23.5	1.1	0.7
S. radiatum	0.5	10.5	5.6	62.6	13.1	2.5	3.6
S. angustifolium	0.4	10.1	6.5	52.6	23.6	1.7	1.4

Monomethyl sterols

Sample	Obtusifoliol	Unknown (a)	Unknown (b)	Gramisterol	Cycloeucalenol	Citrostadienol	Others
S. indicum (4 varieties)	20.7–28.3	2.6–10.4	0.0–5.4	12.5–27.1	3.7–20.7	15.4–26.0	8.4–17.2
S. alatum	31.0	6.2	5.4	26.1	3.1	12.8	15.4
S. radiatum	16.2	0.0	0.8	14.7	10.7	48.7	8.9
S. angustifolium	12.6	5.4	4.9	16.0	7.6	41.6	11.5

Dimethyl sterols (triterpene alcohols)

Sample	β-Amyrin	Δ^8-Sterol	α- Amyrin	Cycloartenol	Δ^7-Sterol	24-Methylene cycloartanol	Others
S. indicum (4 varieties)	8.6–32.5	0.0–6.7	5.0–15.2	22.5–46.8	tr–9.0	13.1–24.6	0.0–24.0
S. alatum	7.9	8.9	7.0	21.6	2.1	35.9	16.6
S. radiatum	5.1	5.7	11.6	37.5	2.5	30.4	7.2
S. angustifolium	4.8	3.4	7.2	34.1	3.9	20.9	25.7

Source: Kamal-Eldin *et al.* 1992a.

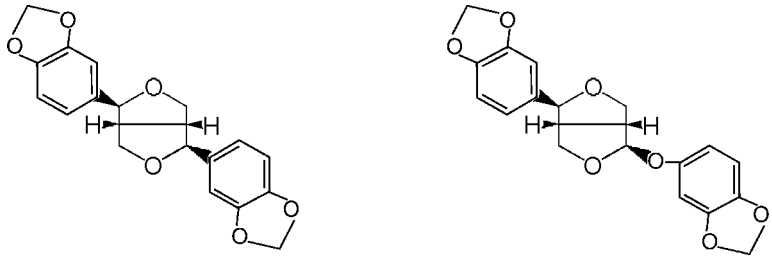

Figure 11.1 Chemical structures of two major lignans present in sesame seed and oil.

in the region of 400 to 700 mg/kg (ppm), of which γ-tocopherol is predominant (96–98%) along with a small portion is δ-tocopherol (2–3%). Sesame seed and its oil contain significant amounts of characteristic lignans, sesamin, and sesamolin. Figure 11.1 shows chemical structures of the two major lignans. A wide range of variation in the levels of sesamin (0.02–1.13%) and sesamolin (0.02–0.59%) was reported in *S. indicum* oils (Fukuda *et al*. 1988a; Tashiro *et al*. 1990; Yoshida and Kajimoto 1994). Kamal-Eldin and Appelqvist (1994b) determined the contents of sesamin and sesamolin in oils from S*esamum indicum* to be 0.55 and 0.50% respectively. The presence of other lignans, sesangolin and 2-episesalatin, in some wild sesame species has also been reported. Two new lignans, sesaminol and sesamolinol, both with antioxidant properties, have been isolated with pinoresinol (Fukuda *et al*. 1986a). The contents of these antioxidative lignans having a phenolic group in sesame seed oil are small (Osawa *et al.* 1985). In commercial crude sesame oils produced from seeds from seven different origins, the percentage of sesamin was 0.31–1.18% and of sesamolin 0.19–0.62% (Kochhar 2001). Traces of sesamol, diasesaminol, and sesaminol were also observed in several of these oil samples. The structural formulae of important antioxidative components present in sesame seed and oil are given in Figure 11.2. In addition, the presence of water-soluble potent antioxidants, four pinoresinols, and two caffeoyl glucosides is reported in sesame seed (Katsuzaki *et al*. 1992, 1993, 1994).

11.2.3 Seed processing and oil refining

The sequence of commercial processing of sesame seed involves (i) cleaning, (ii) cracking, flaking and conditioning, and (iii) cooking and pressing (single or double) for crude oil. The cake still contains 8–10% oil and is either solvent-extracted for crude oil with subsequent refining or used directly as a premium quality cattle feed. Yen and Shyu (1988) reported the effects of various pre-treatments of the seed on oil yield and quality. The smaller the particle size, the

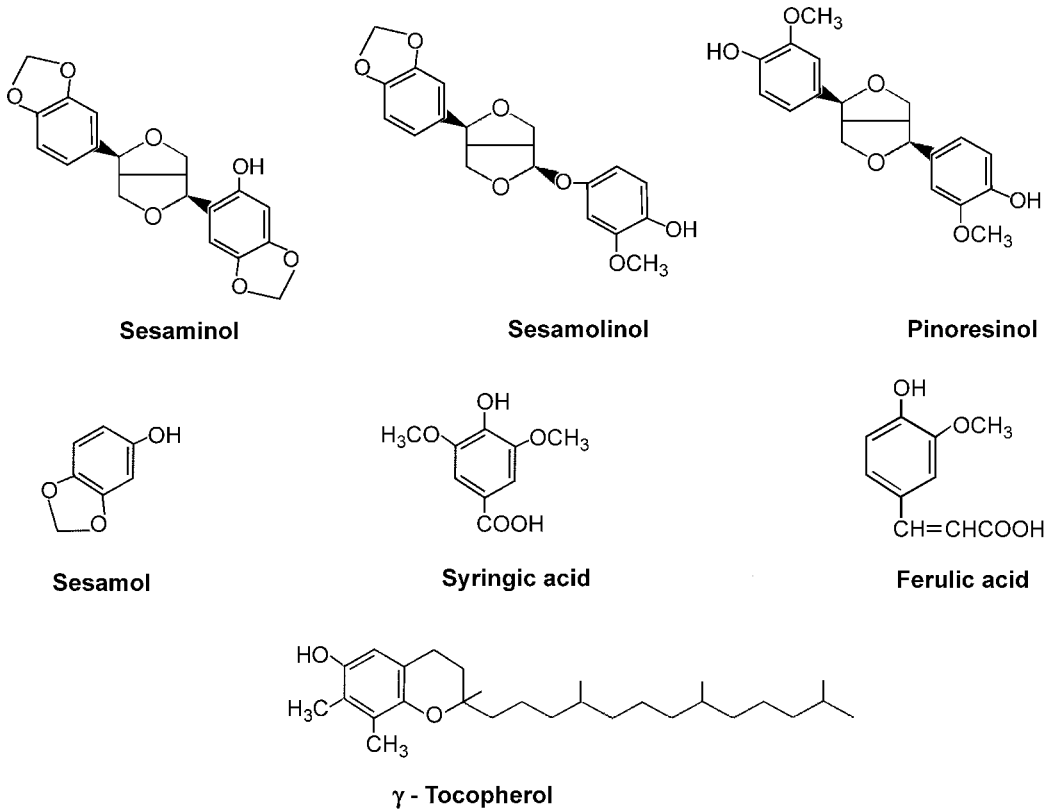

Figure 11.2 Structural formulae of antioxidative components present in sesame seed and oil.

higher the oil yield but with a slight increase in acid value and hydroperoxide level. Oil pressed from de-hulled sesame seeds has the best storage stability.

The sesame hull (about 17%) contains a large amount of undesirable oxalic acid and indigestible fibre. De-hulling sesame seed is therefore essential to improve the quality of the meal so that it can be used of human food. Most de-hulling methods involve the use of water and its subsequent removal from the wet de-hulled seeds. The cost of this drying process raises the price of the de-hulled seeds 30–40% above that of commercial seeds. The de-hulled seed contains significantly more oil (58–64%) and less crude fibre, calcium, iron, thiamin and riboflavin. Oxalic acid, present mainly in the seed coat, is significantly decreased by de-hulling (Narasinga Rao 1985). When the seed is properly de-coated, the oxalic acid content is reduced from about 3% to less than 0.25% of the seed mass (Johnson *et al.* 1979).

In many seed-producing countries, cold-pressed crude oil is favoured and used directly in cooking. Sesame oil may be obtained from roasted sesame seed or from seed cooked with steam. Roasted seed is classified according to roasting temperature (e.g. 140–150°, 160–180° and about 200°C) and time (5–30 min). The expelled oil is filtered and used without further purification. Roasted sesame oil ranges in colour from light to dark brown and has a characteristic roasted flavour, the strength of which depends on the roasting conditions. A large number of nitrogen- and sulfur-containing compounds have been identified among a total of 141 flavour components (Namiki 1995). Each of these seems to contribute to the characteristic flavour of roasted sesame seed and oil, but no single compound has been identified which can be considered responsible for the characteristic roasted sesame flavour. Yoshida (1994) studied the effect of roasting of sesame seeds (120–250°C for 30 min) on the composition and quality of the oil. Acid, peroxide, anisidine and thiobarbituric values rose with increasing temperature. In the roasted oil at 250°C, the glycolipid content per 1000 seeds increased markedly (263 mg) compared with unroasted oil (7 mg) and phospholipids were no longer detectable. γ-Tocopherol and sesamolin remained at up to 90% of their original level after roasting at 180°C, but were almost removed at 250°C.

Roasting at temperatures below 220°C had little effect upon fatty acid composition, but higher temperatures considerably reduced oleic and linoleic acid levels (Yen 1990). Roasted oil is very popular in Chinese, Korean and Japanese cooking because of its flavour. Currently, roasted oil is also available in several supermarkets in the UK and other EU countries. The unroasted oil, also called sesame salad oil, is refined by the traditional steps of degumming, neutralisation, bleaching and deodorisation (Deshpande *et al.* 1996). Han and Ahn (1993) found that refining did not affect sesame oil characteristics but decreased its oxidative stability. The refined oil is pale in colour and pleasant to taste. For use as a base in salad dressing, the oil is generally winterised to remove any higher melting point components. However, for salad oil application, the refined oil

requires no winterisation. Both roasted and unroasted oils are also used for various pharmaceutical purposes.

11.2.4 Sesame antioxidants and oil stability

Compared with other vegetable oils sesame oil is highly resistant to oxidative deterioration. For example, Fukuda and co-workers (1988b) found that croutons fried in roasted or unroasted sesame oil had a better oxidative stability than those fried in safflower oil, corn oil, or a mixture of soybean and rapeseed oils. Fatty acid composition and tocopherol levels do not completely explain the high stability of sesame oil. Refined sesame oil possesses much less antioxidants than roasted sesame seed oil. Yen and Shyu (1989) investigated the effect of roasting conditions (at temperatures of 180°, 190°, 200° and 210°C for 30 min) on the oxidative stability of sesame oil. He found that sesame oil, prepared with roasting at 200°C for 30 min followed by 7 min steam cooking time, had the best oxidative stability. Yoshida and Kajimoto (1994) reported the effect of microwave heating on antioxidant components and oil quality of sesame seeds. During microwave treatment (for 2, 4, 6, 8, 12, 20, 25 or 30 min), the carbonyl and anisidine values increased gradually and the concentration of tocopherols, sesamin and sesamolin decreased gradually, until approximately 20% of these components were lost after treatment of 30 min. However, after microwave treatment for 16–20 min, sesame oil still retained 85% of its antioxidant components. The strong antioxidant activity of roasted oil has been attributed to the sesamol from sesamolin formed during roasting and to the presence of γ-tocopherol. This is not enough, however, to explain the strong antioxidant activity of roasted oil. It was noticed (Namiki *et al*. 1993) that in roasting the antioxidant activity increased significantly with browning, and browning increased significantly above 180°C. It was thus suggested that browning products, formed especially at temperature above 190°C, contributed substantially to the formation of antioxidant components. Most likely, the superior antioxidant efficacy of roasted oil can be explained by the synergistic effect of these known antioxidants with not yet defined/unidentified components.

Marked changes have been found to occur during acid clay bleaching of sesame oil. Sesamolin, though not having any antioxidant properties in itself, is precursor to several phenolic antioxidants. During normal acid-bleaching process at 90–105°C sesamolin is transformed into sesamol, sesaminol and its isomers. The reaction pathway involves scission of sesamolin between acetal oxygen and carbon to produce an oxonium ion and sesamol, and an electrophilic addition of sesamol at the *ortho* position to the oxonium ion to form sesaminol. Four isomers of sesaminol are then formed by intermolecular transformation (Figure 11.3). Traditional deodorisation of the bleached sesame oil, undesirably, removes sesamol almost completely and more than 85% of the original sesamolin and related isomers of sesaminol. This reduces considerably the

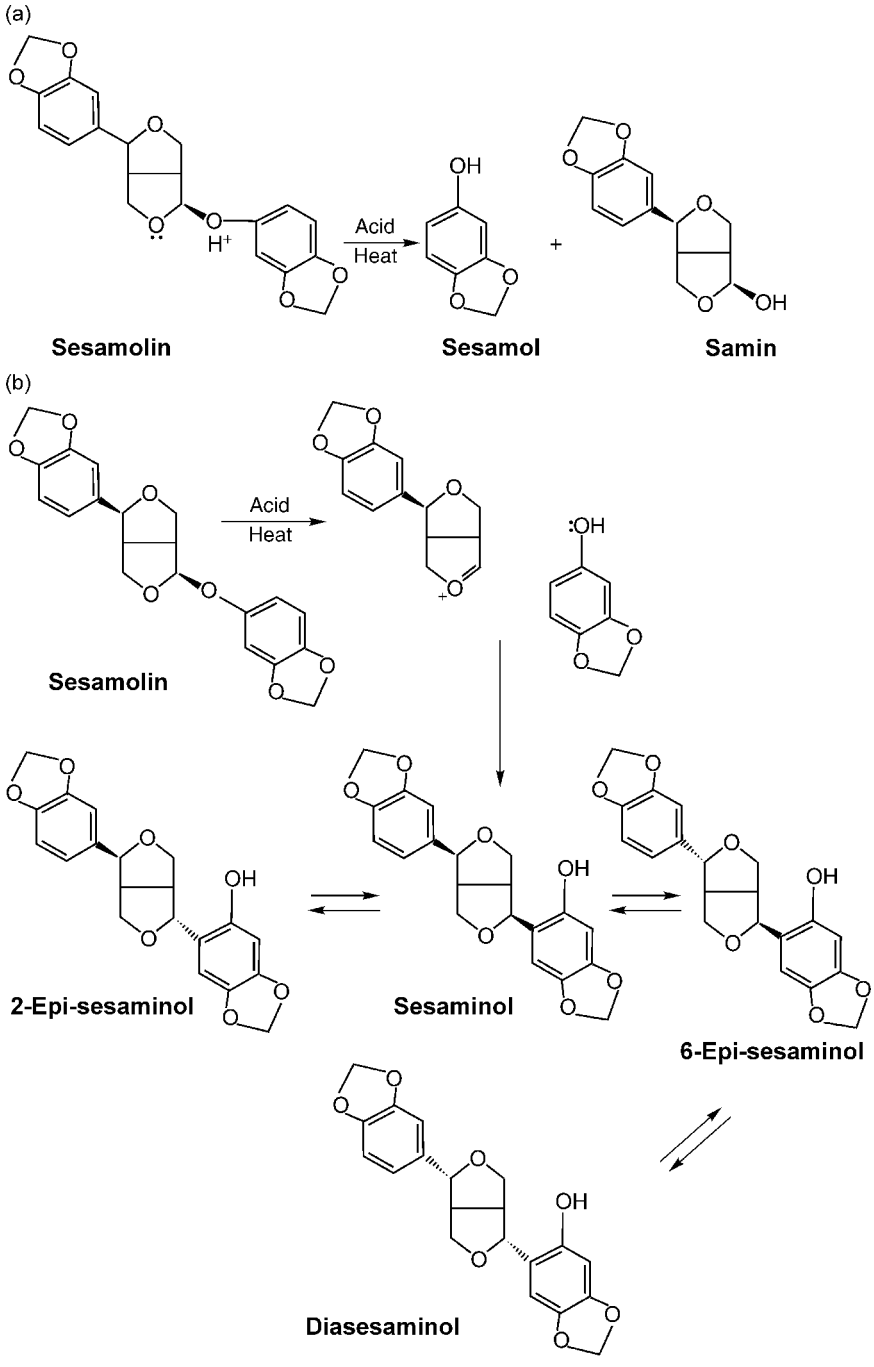

Figure 11.3 Schemes for the formation of sesamol (a) and sesaminol isomers (b) from sesamolin.

Table 11.5 Effects of various refining steps on antioxidants (mg/kg) of sesame oil

Total	Sesamolin	Sesamol	Sesaminol	Episesaminol	γ-Tocopherol	Total
Traditional refining[a]						
Crude oil	5100	43	0	0	335	5478
Neutralised and washed	4248	7	0	0	226	4481
Bleached	0	463	339	480	218	1500
Deodorised	0	17	284	343	184	828
'Dedicated' refining						
Crude oil	6188	2	10	nd	402	6602
Neutralised and washed	6092	tr	tr	nd	401	6493
Bleached	3273	1781	71	36	398	5559
Deodorised	3160	1593	74	36	383	5246

Source: [a]Fukuda *et al*. 1986b; Silkeberg and Kochhar 2000; nd = not detected, tr = trace <0.5 mg/kg.

antioxidant effectiveness of the refined, bleached and deodorised sesame oil. In contrast, it is interesting to report that using a 'dedicated' refining process of sesame seed oil according to the US Patent of Silkeberg and Kochhar (2000) and other worldwide patent applications more than 78% of sesamolin and related potent components and 95% of γ-tocopherol were retained. Table 11.5 compares the data on the effects of normal and 'dedicated' refining on antioxidants of sesame oil. In contrast, using traditional refining, the losses in antioxidants were very high, only 12.5% by weight of the original total of sesamolin, sesaminol and episesaminol and 55% by weight of γ-tocopherol being retained in the refined oil. The levels of sesamin and episesamin, also being formed, are not included in Table 11.5, as they have not been shown to possess any antioxidant function *in vitro*.

Apart from tocopherols, other phenolics and antioxidant precursors, sesame seed oil also contains considerable amounts (0.08–0.26%) of Δ^5- and Δ^7-avenasterols and of citrostadienol which contain an ethylidene group ($CH_3CH=$). These ethylidene-containing side chain sterols have an anti-polymerisation effect that protects the oil at high temperature. The protective effect at elevated or frying temperatures has been ascribed to the formation of an allylic free radical at C_{29} followed by isomerisation to a relatively stable tertiary free radical at C_{24} (Gordon 1989; Gordon and Magos 1983). Gertz and Kochhar (2001) recently suggested that a complex set of non-radical reactions occur, predominantly at frying temperatures. The polymerisation reactions of triacylglycerols during deep-frying could thus be retarded by acid-catalysed reactions involving the ethylidene group-containing sterols and other natural components, such as sesamolin, present in sesame oil. Moreover, the protective effect of such components in sesame oil has been related to the finding that they retard the loss of tocopherols in heated oils, and thus enhance frying life of

the oil and subsequently prolong shelf life of fried snacks on storage. Yen and Lai (1989) showed that instant noodles fried in sesame oil, or in its blend with rice-bran oil or soybean oil, had a better oxidative stability than those fried in rice-bran oil or soybean oil alone. Rice-bran oil (as discussed later) also contains, in addition to a unique group of compounds called oryzanols (a group of ferulic acid esters of triterpene alcohols and plant sterols), a significant amount (0.36%) of ethyldiene side chain sterols. A blend of 'dedicatedly' refined sesame seed oil and 'specially' produced rice-bran oil, called Good-Fry® Constituents, with very high antioxidant potency, is now commercially available for stabilisation of frying oils with natural antioxidants as a replacement for synthetic compounds (Kochhar 2000).

11.2.5 Health effects and future research

Both sesame seed and oil have long been used as health foods to slow down ageing and prevent several ailments (Namiki and Kobayashi 1989). It is thought that the presence of sesaminol and other potent antioxidants in the seed and its oil are not only effective components *in vitro*, but that they may also have an active role in the physiological suppression of lipid peroxidation. Several animal studies and experiments with *in vivo* model systems have demonstrated the positive effects of sesame lignan phenols in suppressing lipid peroxidation equal to or stronger than tocopherol. Sesame lignans display a synergistic effect on the vitamin E activity of γ-tocopherol present in the oil and seed. The mechanism of this synergistic effect is not yet clear. Sesamin lignan shows no or little antioxidant activity *in vitro* experiments. The results of a study in rats showed that sesamin might serve as a natural hypocholesterolemic agent, due to the unique function of sesamin that simultaneously inhibits both cholesterol absorption and synthesis. Recently, a study on the protective role of sesaminol glucoside indicated that the reduction of atherosclerosis by this lignan depends not only on its cholesterol lowering effect, but more heavily on its antioxidant potential for inhibition of LDL oxidative modification in rabbits (Osawa *et al.* 1999). Clinical trials on human subjects are underway to explain and confirm the many health effects of sesame. So the potential beneficial effects of sesame oil and seed ('Open Sesame') are not yet all defined or understood. Further research supported by clinical trials is needed to explore the 'wonders' of sesame seed and its oil in depth.

11.3 Rice-bran oil

Rice (*Oryzae Sativa* L.) is the principal staple food of about half of the world population. It is grown in more than hundred countries, under a variety of climatic conditions (Wadsworth 1992). When harvested from the field, rice is in

the form of paddy (rough rice), where the kernel (white rice) is fully enveloped by the hull. When paddy is milled, the germ and bran layer separate from the endosperm and result in the milling residue which is commonly called 'Bran'. Rice-bran oil is, therefore, a byproduct of rice milling and has been used for centuries in many Southeast Asian countries. Typically, rice-bran oil (simply, rice oil or 'heart' oil) comprises about 20% saturated fatty acids and an even balance of monounsaturated and polyunsaturated fatty acids (40:40). Rice-bran oil contains relatively large amounts of unsaponifiable components (4–5%). In recent years, the oil has gained world wide attention due to the presence of several health beneficial components such as oryzanol and other high-value compounds including tocotrienols and squalene.

11.3.1 Production of bran and oil extraction

Current world production of rice is approximately 500 million tonnes per annum. Most of this is consumed close to the area where it is produced. Milling of rough rice involves drying (11–12% moisture), cleaning, shelling, separation of kernels, bran removal, polishing and glazing to add to consumer appeal. In some areas, rough rice is de-husked at harvest and brown rice (with bran layer still attached) is stored for later milling. The bran contains pericarp, aleurone, germ and some endosperm. The milling operation of paddy produces about 20% husk, 8–10% bran, and approximately 70% starch endosperm (white rice). Rice bran with about 15–30% lipids is a good source of protein, minerals, vitamins, phytin, trypsin inhibitor, lipase and lectin (Orthoefer 1996a; Gopala Krishna 2000). The oil content of rice bran, produced by different milling process, is generally in the range of 15–20%. Parboiled rice bran has a greater lipid content (20–30%) due to less endosperm contamination and outward movement of lipids from aleurone and germ cells to the bran layer (Juliano 1985).

Rice-bran oil contains 2–4% free fatty acids at the time of milling. If not immediately extracted, the lipids in freshly milled rice bran undergo hydrolysis due to the presence of a potent lipase. Development of free fatty acids at the rate of 5–7% per day has been reported in rice bran (Saunders 1986). To obtain good quality rice-bran oil, it is therefore important to stabilise the bran quickly prior to extraction. Sayre and co-workers (1982) reviewed the methods of stabilising rice bran which include dry heat, wet heat, and extrusion. For example, if the bran is subjected to a short-term high temperature heat treatment, immediately after milling, lipase activity is destroyed and 'stabilised' bran is produced. Heat stabilisation at 125–135°C for 1–3 s at 11–15% moisture causes no adverse effect on bran nutritional quality in feeding trials with rats, chicks, and pigs (Shaikh and Brady 1999). The stabilised rice bran is expanded to rice flakes or pellets prior to extraction. Palletising (6–8 mm diameter) not only improves percolation but also minimises the fines in the miscella. Table 11.6 lists the composition of stabilised rice bran. The wet extrusion method involves the

Table 11.6 Composition of stabilised rice bran

Constituent	Range (% wt)
Moisture	2–4
Free fatty acids (as % oleic)	4–6
Oil	18–24
Protein	12–17
Dietary fibre	23–35
Soluble fibre	2–6
Carbohydrates	45–55
Ash	7–10

Source: Shaikh and Brady 1999.

injection of approximately 10% additional water, usually as steam, into the bran. Typically, this is done with an extruder fitted with steam injection ports, which reduces the stabilisation temperature to 120°C. The expansion process yields porous rice-bran pellets that facilitate the percolation of solvent for oil extraction. The stabilised rice-bran flakes are then dried, prior to extraction, usually by passing hot air over a bed of bran pallets. Sayre and co-workers (1985) showed that the stabilisation of rice bran by the extrusion cooking produced high-quality edible grade rice-bran oil.

Hexane is generally used for counter-current extraction of the stabilised bran material in a batch or continuous operation. The pre-treated bran flakes/pellets are placed in the extractor, hexane is pumped in, and allowed to percolate through the bran to extract oil. As waxes are soluble in hot hexane, an extraction temperature between 30–50°C gives optimised oil extraction without excessive wax removal. The extracted oil and hexane miscella are transferred to a solvent recovery unit for the production of crude rice-bran oil. The cake is treated separately with stripping steam in a desolventiser/toaster to remove residual solvent. The lipid composition of good quality, crude rice-bran oil is presented in Table 11.7. The crude oil is usually dark greenish-brown, depending upon the extraction method, bran condition and composition. The colour pigments include carotenoids, chlorophyll and Maillard browning products. Parboiled rice-bran oil is generally darker in colour than that produced from raw rice bran.

Earlier methods for production of oil from rice bran used hydraulic pressing. The cleaned bran is steam cooked, dried, pre-pressed, and finally pressed in an expeller. However oil recovery is lower and the oil may be darker, as higher temperatures and longer retention times are employed in the cooking process. Ramsay and co-workers (1991) studied the supercritical fluid extraction of rice-bran oil and found the oil yield with CO_2 to be slightly lower (18.0%) than that obtained with hexane extraction (20.2%). Recently, aqueous extraction of oil from rice bran has been studied on a laboratory scale (Hanmoungjai *et al*. 2000). Extraction temperature and pH were found to be the main factors influencing oil yield. Enzymatic treatment of rice bran previous to solvent extraction or pressing

Table 11.7 Lipid composition of crude rice-bran oil

Component	% wt
Saponifiable lipids	**90–96**
Neutral lipids	88–89
Triacylglycerols	83–86
Diacylglycerols	3–4
Monoacylglycerols	6–7
Free fatty acids	2–4
Waxes	3–4
Glycolipids	6–7
Phospholipids	4–5
Unsaponifiable lipids	**4.2**
Phytosterols	43[a]
4-Methyl sterols	10
4-Dimethyl sterols (triterpene alcohols)**	28
Hydrocarbons*	18
Tocopherols and tocotrienols	3

*Squalene 16–40%, i.e. 0.12–0.3% in oil.
**Mainly oryzanol.
[a]These figures are % of total unsaponifiable lipids.
Source: Sayre and Saunders 1990; Orthoefer 1996b.

has also been reported (Hernandez *et al*. 2000). Gingras (2000) estimated that the annual production of crude rice-bran could be as high as 3–4 million tonnes but the actual production is probably around 1.0 million tonnes worldwide (Nalewade 2000).

11.3.2 Oil refining and high value byproducts

The composition of the crude oil has a major influence on refining method and conditions used. Rice-bran oil is usually difficult to refine due to high free fatty acid (FFA) levels, waxes, bran fines and pigments. In general, traditional refining of rice-bran oil involve dewaxing, degumming, neutralisation, bleaching to improve colour and steam deodorisation (Orthoefer 1996a). Both waxes and free acids a exert strong effect on refining losses. For example, 5% FFA crude oil could have losses from 12–40% by the cup method. The causes of high refining losses in rice-bran oil are associated with the presence of hydroxy and oxidised compounds as well as the high FFA content (Hartman and Dos Reis 1976).

The simple procedure for wax removal from crude rice-bran oil is to use settling tanks in which the crude oil is gradually cooled, followed by filtering or centrifuging. This removes bran fines and most of the wax. Generally, a temperature of less than 60°C is employed for initial dewaxing. Further dewaxing may be performed in combination with degumming or alkali neutralisation. It is also possible to remove wax from refined bleached oil, but the yields improve if most

of the wax is removed prior to alkali refining (Gingras 2000). Degumming and/or acid pre-treatment with food-grade phosphoric acid or citric acid is carried out to precipitate gums, metals and other undesirable components from the oil. Standard water degummimg is applied if food-grade lecithin is required from this step. Degumming temperatures above 80°C are recommended to keep waxes from crystallising and being removed with the gums. Depending upon the FFA content and the type of refining process, the degummed or acid pre-treated oil is then neutralised with 16–30 Baume caustic with 20–40% excess. Soap-stock separation temperatures in the region of 55–70°C are reported to work well (Orthoefer 1996a). Miscella refining in hexane can also be used to obtain good quality refined oil from high FFA rice-bran oil (Bhattacharyya *et al*. 1986). The refined oil is washed with water to remove traces of soaps and dried, prior to bleaching for removal of colour pigments and other undesirable components. Depending upon the characteristics of the neutral oil and acid activity of the bleaching earth employed, the bleaching doses may range from 2–4% under standard conditions. The oil is then deodorised by steam stripping (220–250°C, 2–5 mm of Hg) to remove objectionable flavours/odours and any residual undesirable contaminants.

Physical refining, also called steam refining, may be an option for better edible oil yield from high FFA crude rice-bran oil. However, the oil must be dewaxed, degummed/acid pre-treated, and bleached before the steam refining step. The presence of even small amounts of lecithin (phospholipids) will irrevocably darken the oil being steam-refined at standard physical refining temperatures. Therefore, in many cases, high FFA rice-bran oil is partially neutralised with caustic and washed prior to steam refining to obtain lighter colour, high-grade, edible rice-bran oil. The fully refined rice-bran oil thus produced may become frequently cloudy/turbid below 15°C, due to the presence of saturated and high melting triacylglycerols remaining in the oil. The oil requires winterisation to satisfy a cold test of 5.0 h if the oil is to be sold in bottles. Typically, rice-bran oil winterisation involves cooling from 30–35°C to 15°C at a uniform rate over a period of 12 h with slow agitation. The oil is then further cooled to 4–5°C without agitation, followed by a holding period of 24–28 h. This allows the higher melting components to crystallise as large stable crystals, which are separated using appropriate filter aids. Winterisation is normally performed prior to deodorisation. Recently, the effect of the various refining steps on the retention of oryzanol in fully refined rice-bran oil has been reported (Gopala Krishna *et al*. 2001). Steam refining of crude rice-bran oil did not affect the content of oryzanol appreciably (total loss, 8%) but 83–95% of the original oryzanol content (1.9–2.1%) was lost during alkali refining.

The byproducts of rice-bran oil refining include waxes, lecithin, soap-stock (containing high-value oryzanol), and deodoriser distillate containing sterols, tocopherols, tocotrienols and squalene. The characteristics and physical properties of purified rice wax are similar to carnauba wax (Sayre and Saunders

1990). Rice-bran wax (2–4% level in crude oil) consists of long chain fatty acids (C_{16}–C_{26}) and fatty alcohols (C_{22}–C_{30}). Crude rice wax is usually purified by washing with acetone or ethanol. In many countries, purified rice wax has been approved as a releasing agent for plastic packaging material intended for food contact, and is employed as a coating for fruits and vegetables to prevent moisture loss. Also, it is being used for several applications in the cosmetics industry. Standard water degumming techniques are used to obtain food grade rice lecithin. Degumming temperatures above 80°C are employed to keep waxes from crystallising and being removed with gums, thereby avoiding concentration of waxes in the lecithin fraction. The lecithin produced from rice-bran oil is very similar in composition and function to that obtained from soybean oil (Orthoefer 1996a). Caustic refining of rice oil removes, along with the soap-stock, substantial quantities of oryzanol, present in the oil at a level of 1.5–2.9%. The soap-stock residue contains 5–10% oryzanol and is excellent feedstock for industrial production of oryzanol (Nishihara and Shibuya,1968; Seetharamaiah and Prabhakar, 1986). After acidification of the soap-stock, oryzanol may be recovered by ether extraction at pH 9.5 and further purified by chromatographic and crystallisation techniques. A simulated moving bed chromatography separator has been examined for recovery of oryzanol from degummed and dewaxed rice-bran oil (Saska and Rossiter 1998). The crude product containing 12–15% oryzanol was purified by crystallisation from heptane to produce 90–95% pure oryzanol. Rice-bran oil deodoriser distillate contains substantial quantities of tocopherols, tocotrienols, squalene and free sterols. The fatty acid distillates from steam refining may also contain small amounts of oryzanol. These valuable components may be concentrated by molecular distillation at very low pressure and low temperature. Other procedures such as distillation of esters, chromatography, and solvent crystallisation are being employed commercially to recover these valuable nutrients in a purity state.

11.3.3 Oil composition and food uses

Crude rice-bran oil may contain 14–17% of non-triacylglycerol components and 4–5% of unsaponifiable material (Table 11.7). The minor constituents of the oil consist of phospholipids, glycolipids, waxes, sterols, ferulic esters of sterols (oryzanol), tocopherols, tocotrienols, colour pigments, hydrocarbons and squalene. The predominant phospholipid components are phosphatidylcholine, phosphatidylethanolamine and phosphatidylinositol. The glycolipids are mainly galactose and glucose derivatives. Rice waxes have been classified into hard wax melting at 79.5°C and soft wax melting at 74°C (Orthoefer 1996a). Refining of crude oil removes almost all of glycolipids, phospholipids and waxes, colour pigments, and (partly) other minor components depending upon the conditions used. Table 11.8 lists some important characteristics and fatty acid composition

Table 11.8 Physical and chemical characteristics and fatty acid composition of refined rice-bran oil

Parameter	Typical	Range
Specific gravity (20°C)	0.916	0.916–0.922
Refractive index (20°C)	1.470	1.470–1.474
Free fatty acid (as % oleic)	0.05	0.05–0.12
Iodine value	95	90–110
Saponification value	193	180–195
Smoke point (°C)	213	–
Colour Lovibond (5.25 inch)	2.5R, 27Y	2.5–3.5R, 25–35Y
Fatty acid composition (% wt)		
14:0	0.4	0.2–0.7
16:0	19.8	12–28
16:1	0.2	0.1–0.5
18:0	1.9	2–4
18:1	42.3	35–50
18:2	31.9	29–45
18:3	1.2	0.5–1.8
20:0	0.9	0.5–1.2
20:1	0.5	0.3–1.0
22:0	0.3	0.1–1.0
Others	0.6	1.0 max

Source: Sayre and Saunders 1990; Orthoefer 1996a; Firestone 1999; Gopala Krishna 2000.

of refined rice-bran oil. Depending upon the winterisation conditions and the intended application, the cloud point of the refined rice oil may vary from below 0–17°C. Palmitic, oleic and linoleic fatty acids constitute 93–95% of the fatty acid portion of the glycerol esters. The major triacylglycerol molecular species of rice-bran oil comprises PLO, PLL and OOO (i.e. all glycerol esters containing the acyl groups indicated).

Most of the unsaponifiable material in rice-bran oil consists of sterols, present as free sterols, sterol esters, sterol glycosides and acylsterol glycosides. Sterol glycosides are effectively removed during degumming and refined rice-bran oil is virtually free from these components. Refined rice-bran oil contains considerable quantities of Δ^5-avenasterol and related sterols containing an ethylidene group (185–355 mg/100 g). Table 11.9 lists the content and percentage composition in rice-bran oil of 4-desmethyl sterols, 4-monomethyl sterols, and dimethyl sterols. As with common vegetable oils, β-sitosterol is the major sterol (49–55%) in rice oil. More than 75% of the sterols of rice-bran oil are esterified and are collectively called oryzanol (as previously mentioned, a group of ferulic acid esters of triterpene alcohols and plant sterols). These sterol esters of ferulic acid show antioxidant activity as well as physiological/biological effects. The major oryzanol components are cycloartenyl ferulate, 24-methylene

Table 11.9 Sterols content and their percentage composition in rice-bran oil

Desmethyl sterols (%)

Oil sample	Campesterol	Stigmasterol	β-Sitosterol	Δ^5-Avenasterol	Δ^7-Stigmastenol	Δ^7-Avenasterol
Crude* (3,225 mg/100 g)	658	252	1745	355	71	142
Refined* (1,055 mg/100 g)	215	82	571	116	23	46
Range (%)	20–28	7–15	49–55	5–11	1–3	2–5

Monomethyl sterols (%)

Oil sample	Obtusifoliol	Cycloeucalenol	Citrostadienol	Others
Crude (total = 420 mg/100 g)	7	39	31	23

Dimethyl sterols (triterpene alcohols) (%)

Sample	Cycloartanol	Cycloartenol	24-Methylene cycloartanol	Others
Crude (total = 1176 mg/100 g)	9	41	42	8

*Others: 2 mg/100 g.

Source: Firestone 1999; Kochhar 1983; Weihrauch and Gardner 1978.

Table 11.10 Content of tocopherols and tocotrienols (mg/kg) in commercially refined rice-bran oil

	Typical	Mean*	Range
α-Tocopherol	347	292	nd–454
β-Tocopherol	nd	1	nd–10
γ-Tocopherol	89	144	16–358
δ-Tocopherol	42	15	nd–42
α-Tocotrienol	126	71	nd–174
γ-Tocotrienol	301	319	62–975
δ-Tocotrienol	10	18	nd–104
Total	915	860	88–1609

*Mean of 22 refined oils from various producers; nd = not detected.
Source: Rogers *et al*. 1993; Kochhar 2001.

cycloartanyl ferulate, campesteryl ferulate, β-sitosteryl ferulate and cycloartanyl ferulate. The total content of oryzanol in five refined rice oils from different processors were reported to be 115–787 mg/100 g, and the individual components: cycloartenyl ferulate, 24-methylene cycloartanyl ferulate, campesteryl ferulate, β-sitosteryl ferulate plus cycloartanyl ferulate were 35–232, 30–314, 39–342, 0–84 mg/100 g respectively (Rogers *et al*. 1993). The large variation in the concentration of these oryzanol components is probably due to the different rice varieties used as well as potential losses during processing. Recently, the effect of different processing steps during refining on retention of oryzanol in refined rice-bran oils and on the oryzanol content (1.63–2.72%) of 18 Indian paddy cultivars have been reported (Gopala Krishna *et al.* 2001). Rice-bran oil contains relatively high amounts of tocopherols and tocotrienols. The major types present are α-tocopherol, γ-tocopherol, α-tocotrienol and γ-tocotrienol (Table 11.10). The tocotrienols (α, γ, δ) comprises 48–80% of the total tocols. The antioxidant properties of tocotrienols are similar to that of tocopherols but they also have a variety of physiological functions (Eitenmiller 1997; Nesaretnam *et al*.1998).

Rice-bran oil is being used for edible purposes in Japan, Thailand, Korea and India. The oil exhibits excellent frying stability and contributes a pleasant flavour to the fried food. The oxidative stability of rice-bran oil was found to be equivalent to peanut oil when tested in simulated deep frying conditions (Orthoefer 1996b). The stability of rice-bran oil is probably due to the combined protective effects of oryzanol, phytosterols, squalene, tocopherols and tocotrienols. These make the oil a premium choice for frying high quality products with delicate flavours, ranging from potato chips (crisps) to other snack products and convenience foods. For the same reason, rice-bran oil is rapidly gaining popularity in stir-frying of a variety of oriental dishes both in the US and European countries.

Winterised rice-bran oil is an excellent salad oil and is very suitable for producing mayonnaise and salad dressings. The stearin fraction separated during

winterisation process can be used for margarine and shortening applications. In addition to its pleasant flavour, several factors contribute to the remarkable performance of rice-bran oil as a component in margarine and spreads. Its natural tendency to form a stable β′ crystals and its palmitic acid glycerol esters result in a good balance between plasticity, creaminess, and spreading properties. Specially produced rice-bran oil, retaining high levels of potent antioxidants, can be used as coating/spray oil for a wide range of products, such as crackers, nuts, and other similar snacks, to extend their shelf life. Alternatively, as mentioned earlier with sesame oil, the blend of specially refined rice-bran oil and 'dedicated' sesame oil may be used to fortify less-stable soft oils such as rapeseed oil, sunflower oil and soybean oil. This small addition (4–6%) of the oil blend will improve not only frying oil stability but also enhance the shelf life and flavour quality of the fried product. The functional and nutraceutical properties of rice-bran oil provide several applications in the health food industry (McCaskill and Zhang 1999). In other words, the unique properties of rice-bran oil make it an attractive food ingredient that can provide health benefits to a wide range of food products.

11.3.4 Biological effects and future trends

Rice-bran oil has a fatty acid composition similar to that of peanut (groundnut) oil. As mentioned earlier, rice-bran oil contains oryzanol which is a mixture of at least five sterol esters of ferulic acid. Moreover the oil is rich in phytosterols and tocopherols and tocotrienols. Rice-bran oil has many health benefits such as lowering plasma cholesterol levels (Nicolosi *et al*. 1991; Rukmini and Raghuram 1991; Sharma and Rukmini 1987; Yoshino *et al*. 1989). It is also reported to decrease early atherosclerosis (Rong *et al*. 1997), inhibit platelet aggregation (Seetharamiah *et al.* 1990), decrease hepatic cholesterol biosynthesis (Nakamura 1966), increase faecal bile acid excretion (Nakamura 1966), and decrease cholesterol absorption and aortic fatty streaks formation (Ni *et al*. 1997). The biological effects of oryzanol and rice-bran oil also include anti-ageing activities (Noboru and Yusho 1970) and anti-dandruff and anti-itching properties (Shugo 1979). Rice-bran oil contains significant levels of tocotrienols (400–1000 mg/kg) which display protective benefits in reducing LDL cholesterol. Their anti-carcinogenic effects have also been reported in several studies (Gould *et al*. 1991; Qureshi *et al.* 1991; Kato *et al*. 1985; Ngah *et al*. 1991). Elson and Yu (1994) suggested that isoprenoid constituents of the diet suppress tumour growth by depriving the cells of mevalonate-derived products. This hypothesis links suppression of HMGR (3-hydroxy-3-methylglutaryl co-enzyme A reductase) with the anti-carcinogenic properties of various isoprenoids, including tocotrienols present in rice-bran oil.

The production of edible-grade rice-bran oil as a byproduct of rice milling will continue to grow in many countries, including India and the US. The

consumption of rice-bran oil is also expected to increase due to its potential health benefits. As consumer awareness of high value nutraceutical components such as oryzanol and the tocotrienols of rice-bran oil grows, more of this speciality oil will be used as a nutritional ingredient in a variety of food products.

11.4 Flaxseed (linseed and linola) oil

Flax crops have been grown for many centuries but originally for the fibres that can be used as linen textile. Linseed is an alternative name, 'twist title', for flax, which points towards the modern uses of the plant seed (Krawczyk 1999). Both linseed and flax are cultivars of *Linum usitatissimum.* Linseed varieties have shorter (60–80 cm high) and thicker stems with more branches compared with flax (80–120 cm). A flax crop produces fewer capsules and smaller seeds than linseed. Crops grown for seed are termed linseed in India and in the UK, flax seed in Canada, and oil flax or seed flax in many European countries. The crops grown for both seed and flax are generally called dual-purpose flax, or flax grown for fibre flaxseed. The oil content of commonly grown linseed varieties may vary from 40–44%. The content of linolenic acid (18:3), usually above 50%, makes linseed oil an excellent drying oil. This is used principally for non-edible purposes such as in the manufacture of paints, varnishes, linoleum and printing inks. As discussed below, among the unique features of flaxseed is that it is a rich source of ω-3 α-linolenic acid, plant lignans and dietary soluble fibre. The whole flaxseed/linseed is edible and is used in baking and confectionery industries. Moreover, edible flaxseed or linseed oil is sold at health food stores where its health benefits are recognised.

11.4.1 Flax production and oil composition

Flax is a sub-tropical or cool-to-warm temperature annual crop grown mainly in Canada, Argentina, India, the US, China, some European countries, and the former USSR. More than 60 years ago the world production of flaxseed was around 3.4 million tonnes (Krawczyk 1999) which was more than sunflower oil at 2.5 million tonnes. Since then, however, world production of flaxseed has remained between 2 and 3 million tonnes, while the production of other oilseeds has increased considerably. In 2000–2001, world production of flaxseed was 2.34 million tonnes, with Canada the largest producer and largest exporter. Figures for the production, disappearance and exports/imports of linseed oil are given in Chapter 1.

Most flax is now grown to make linseed oil. The seeds are usually pressed and extracted by solvent to yield crude linseed oil which is brown/dark amber in colour. The colour can be reduced by caustic refining and bleaching. Such processing also removes 'gums' or phospholipids present in the oil. Table 11.11 lists some characteristics and fatty acid composition of linseed oil from high

Table 11.11 Characteristics and fatty acid composition of linseed oil (high linolenic acid varieties)

Parameter		
Specific gravity (20°C)	0.927–0.932	
Refractive index (20°C)	1.478–1.482	
Iodine value	170–203	
Saponification value	188–196	
Unsaponifiable matter (%)	1.5 max	
Fatty acid composition (% wt)	**Typical**	**Range**
14:0	tr	tr
16:0	6.0	5–7
16:1	0.1	tr–0.2
18:0	2.5	2–6
18:1	19.0	14–40
18:2	24.1	14–19
18:3	47.4	35–60
20:0	0.5	0.1–0.7
Others	0.4	1.0 max
Tocopherols (mg/kg)		
α-Tocopherol	5–10	
γ-Tocopherol	430–575	
δ-Tocopherol	4–8	
Total	440–588	

Source: Turner 1987; Gunstone *et al*. 1984; Firestone 1999.

linolenic acid varieties of *L. usitatissium*. Seed variety and climatic conditions during maturation both affect the linolenic acid content of the oil. Linseed oil contains 0.42% of the usual sterols. The predominant sterols, namely β-sitosterol, campesterol, Δ^5-avenasterol, and stigmasterol, have been reported to be 46%, 29%, 13% and 9% respectively (Gunstone *et al*. 1994). Linseed oil contains 440–588 mg/kg of tocopherol, γ-tocopherol being most predominant (Firestone 1999). The high levels of α-linolenic acid (18:3 *n*-3) make the oil oxidise quickly. When the oil is used for food purposes a 'paint-like' flavour is imparted to food products in a very short time. Therefore, edible flaxseed oil must be stored under cold, oxygen-free, light-free conditions and be protected by an addition of suitable antioxidant formulation containing metal chelators and oxygen quenchers. Recently Nag (2000) showed that incorporation of oil-soluble capsicum extract slowed considerably the rate of oxidation of the oil. The colour of the stabilised oil was bright red but the product flavour was acceptable when used as a salad oil. Traditionally, the oil for human consumption is extracted by a 'cold-press' technique. Depending upon the applications, the oil is then mildly refined and perhaps deodorised at low temperature for encapsulation and blending with other healthful oils.

11.4.2 Edible uses of flaxseed and its oil

Edible flaxseed oil is not generally used as a food oil due to its very low oxidative stability. However, ground or whole flaxseed is edible and is used in many bakery and confectionery products to enhancing nutritional value by supplying a good source of ω3 essential fatty acid, α-linolenic acid. Flaxseed contains about 25% fibre, of which 20–40% is soluble fibre (Vaisey-Genser 1994) that may play an important role in lowering plasma cholesterol. Flaxseed is also a rich source of plant lignans thought to be protective against hormone related cancers of the breast, prostrate and colon. Flaxseed and its oil is sold at many health food stores because of these benefits. Carter (1993) reviewed usage and health aspects of flaxseed and flaxseed oil with special emphasis on their high fibre and *n*-3 fatty acid contents, and their potential use in baked goods and other foods. Cunnane and Thompson (1995) have discussed various nutritional characteristics and health benefits of flaxseed and its oil. After oil extraction, flax cake or meal is usually sold for cattle feed. Krawczyk (1999) reported that whole flaxseed can be used as a dairy feed to promote the production of conjugated linoleic acid in milk (Dhiman *et al*. 2000) and in milk fat (Chouinard *et al*. 2001). Flaxseed can also be used in chicken feed to produce eggs high in ω3 fatty acids (Suzuki *et al*. 1994; Stroh *et al*. 1997). The egg protects against oxidative deterioration of α-linolenic acid during its shelf life and ω3 enriched eggs fetch a premium at the grocery store.

Most flaxseed destined for human consumption is sold in health food stores or in capsule form as a dietary supplement. The volume of 'organically' grown flax is increasing to meet the demands of the typical health food consumer. The edible use of linseed and its oil containing health beneficial components is expected to rise in the future.

11.4.3 Linola oil

The low oxidative stability of linseed oil renders it unsuitable for use as an edible oil. Through traditional plant breeding procedures, a joint venture between CSIRO (Commonwealth Scientific and Industrial Research Organisation, Australia) and United Grain Growers Ltd of Winnipeg, Canada has led to the development of edible linseed oil. The fatty acid composition of the new oilseed crop, named 'Linola' (a registered trademark of CSIRO) has been changed and the level of linolenic acid substantially reduced from 50% to 2%. This greatly increases the oxidative stability of the oil, which is a polyunsaturated oil almost identical to sunflower oil, safflower oil, or corn oil in fatty acid composition (Table 11.12). The colour of linola seed is also changed to a pale yellow colour, which allows it to be distinguished from (brownish) traditional flaxseed. The generic common name is 'Solin'. Development work on solin (linola brand) is

Table 11.12 Fatty acid comparison of linola, traditional flaxseed and other oils

	Fatty acid (%)					
Oilseed	16:0	18:0	18:1	18:2	18:3	P/S ratio
Linola	6	4	16	72	2	7.4
Safflower	7	2	12	79	–	8.8
Sunflower	7	4	16	73	–	6.6
Corn	11	2	27	59	1	4.6
Soybean	12	4	25	51	8	3.7
Canola	5	2	66	19	8	3.9
Flax	7	4	20	17	52	6.3

Source: Haumann 1990; Green and Paul Dribnenki 1994.

Table 11.13 Analytical data for crude and pilot-plant refined, bleached and deodorised (RBD) linola oil

Parameter	Crude oil	RBD oil
Refractive index (46°C)	1.4657	1.4665
Specific gravity	0.921	0.920
Viscosity (cp)	46.8	46.4
Phosphorus (mg/kg)	325	<0.5
Chlorophyll (mg/kg)	0.4	0.0
Colour	5R, 70Y	0.9R, 4.7Y
Free fatty acid (as % oleic)	0.3	<0.02
Iodine value	142	144
Fatty acid composition (% wt)		
16:0	5.6	5.6
18:0	4.0	4.0
18:1	15.9	15.9
18:2	71.8	71.9
18:3	2.0	2.0
Others	0.7	0.6
Sterols (mg/kg)		
Brassicasterol	30	17
Campesterol	801	530
Stigmasterol	164	96
β-Sitosterol	1608	1251
Δ^5-Avenasterol	492	430
Total	3095	2324
Tocopherols (mg/kg)		
α-Tocopherol	20	tr
γ-Tocopherol	471	172
δ-Tocopherol	16	nd
Total	507	172

Source: Green and Paul Dribnenki 1994.

continuing to reduce saturated fatty acid, increase linoleic acid content above 70% consistently, and improve the feeding quality of the meal.

The new oilseed crop, developed in Australia, can be grown wherever flax and linseed varieties are currently cultivated (Haumann 1990; Weiss 1993). The climate in northern Europe is highly suitable for production of linola, where sunflower and corn/maize can not be produced. Linola seed can be processed in existing crushing plants using standard procedures, and linola meal can also be used in ruminant feed in the same way as linseed meal. Refining of crude linola oil by conventional steps (degumming, alkali refining, bleaching, winterisation and deodorisation) produces a pale coloured bland oil with good oxidative stability (Green and Paul Dribnenki 1994). Analytical data of crude and RBD linola oils are given in Table 11.13. The flavour quality and oxidative stability of pilot-plant deodorised linola oil were found to be comparable with that of rapeseed (canola) oil. The Food and Drug Administration (FDA) has given GRAS approval to solin oil (linola) for use as a general-purpose cooking, frying and salad oil, and as an ingredient in margarine, shortenings, and other food products (INFORM 1998). Currently, because of several beneficial dietary effects, there is a growing interest in the use of linola seeds in many bakery and confectionery applications. Moreover, the golden-yellow colour of linola seed make it an attractive and appealing topping on bakery goods. Both linola oil and the seed of the new oilseed crop appear to have a promising future.

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Abbreviations

AEDA	aroma extract dilution analysis
AOCS	American Oil Chemists' Society
AOM	active oxygen method
BHT	butylated hydroxy toluene
CBE	cocoa butter equivalent
CBS	cocoa butter substitutes
CIE	Commission Internationale de l'Eclairage
CLA	conjugated linoleic acid
CNO	coconut oil
COPA	Canadian Oilseed Processors Association
CS	commodity soybean oil
CV	Crismer value
DAG	diacylglycerol(s)
DSC	differential scanning calorimetry
ECN	equivalent chain number
E-E	extruded expeller
EU-15	European Union (15 countries)
FDA	Food and Drug Administration (US)
FFA	free fatty acid
FFB	fresh fruit bunch
FHSBO	fully hydrogenated soybean oil
GC-MS	gas chromatography-mass spectrometry
GLC	gas liquid chromatography
GRAS	generally recognised as safe
HCNO	hardened coconut oil
HEAR	high-erucic acid rapeseed
HO	high-oleic acid soybean oil
HPKO	hardened palmkernel oil
HPKOo	hardened palmkernel oil olein
HPKOs	hardened palmkernel oil stearin
HPLC	high performance liquid chromatography
HPO	hydrogenated palm oil
HPOo	hydrogenated palm olein
IEPO	interesterified palm oil
IV	iodine value
KER	kernel extraction rate
LEAR	low-erucic acid rapeseed
LFRA	Leatherhead Food Research Association (UK)
LLL	low-linolenic acid soybean oil
LOX	lipoxygenase-free soybean oil
LS	low-saturated fatty acid soybean oil
M&I	moisture and impurities
MAFF	(UK) Ministry of Agriculture, Fisheries, and Food (now DEFRA)
MAG	monoacylglycerol(s)
MCT	medium chain triglyceride
MEOMA	Malaysian Edible Oil Manufacturers' Association
mp	melting point
MPOB	Malaysian Palm Oil Board
NHP	non-hydratable phospholipids
NMR	nuclear magnetic resonance (spectroscopy)
NOPA	National Oilseed Processors Association
NSA	National Sunflower Association
o/w	oil-in-water emulsion
OAV	odour activity value
OER	oil extraction rate
OSI	oxidative stability index
PHSBO	partially hydrogenated soyabean oil
PKM	palmkernel meal
PKO (pko)	palmkernel oil
PKOo	palm kernel oil olein
PKOs	palmkernel oil stearin
PLs	phospholipids
PMF	palm mid-fraction
PO	palm oil
POo	palm olein
PORIM	Palm Oil Research Institute of Malaysia (now MPOB)
POs	palm stearin
PUFA	polyunsaturated fatty acid
PV	peroxide value
RBD	refined, bleached and deodorised
RI	refractive index
RSO	rapeseed oil
SBDD	soybean deodoriser distillate

SBO	soybean oil
SCI	solid content index
SD	standard deviation
SFC	solid fat content
SFI	solid fat index
SfMF	soft milkfat fraction
SFO	sunflower oil
SG	specific gravity
SMP	slip melting point
sn	stereospecifically numbered
SV	saponification value
TAG	triacylglycerol(s)
TBHQ	tertiarybutylhydroquinone
US	unsaponifiable matter
w/o	water-in-oil emulsion

Websites

The following websites may provide information about the oils which have been described in this book. Search engines such as www.google.com and vivisimo.com can be used to find other relevant websites. It is not generally necessary to preface the address with the symbols http://

General
www.codexalimentarius.net
www.fosfa.org
www.ncaur.usda.gov/currentres.html
www.usda.gov/nass
www.margarine.org
www.nal.usda.gov/fnic
www.oilworld.de
www.gafta.com

Soybean
www.unitedsoybean.org
www.asa-europe.org
www.soyatech.com

Palm and palmkernel
www.mpob.gov.my
www.palmolis.mpob.gov.my
www.palms.org
www.mpopc.org.my
www.kpu.gov.my
www.isphg.com
www.acidchem-international.com
www.agroindonesia.com

Rapeseed
www.canola-council.org
www.cgc.ca/

Sunflower
www.sunflowernsa.com

Coconut (see also under palm/palmkernel)
www.cocofed.org.ph
www.coconutboard.nic.in
www.apcc.org.sg

Cottonseed
www.cottonseed.com/csopage.htm-

Groundnut
www.fas.usda.gov

Olive
http://europa.eu.int/comm/agriculture/index_el.htm
http://europa.eu.int/comm/agriculture/prom/olive/medinfo
http://sadoun.com/OliveOil.htm (books related to olive oil)

Corn
www.corn.org

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