Vegetable Oils in Food Technology

Composition, Properties and Uses

Second Edition

Edited by

Frank D. Gunstone

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Preface to the First Edition

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 by-products (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 are followed by chapters on 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 D. Gunstone

Preface to the Second Edition

It is nine years since the first edition of this book was published. The success of this led to the idea that we should produce a second, updated and extended edition. Each revised chapter has new information that has been published since 2002 and the final chapter has been extended to cover the more important minor seed oils. As in the first edition, there is an emphasis on data for both the major and minor components present in each oil.

Significant changes in the last nine years have been the development of seeds producing oils with a different fatty acid composition based on current nutritional views. For example, there are more high-oleic varieties of several oils. Current views on the nutritional properties of *trans* acids and the requirement in some countries to report these on food labels have had an influence on avoiding partial hydrogenation and finding alternative ways of producing oils and fats with the required nutritional and physical properties.

In the years between 2001/02 and 2008/09, production of the nine major vegetable oils rose 42% from 93 to 132 million tonnes. In this period there was an increased use for non-food purposes and consequent pressure on the supplies required to meet the food needs of a population growing in number and in disposable income.

While many of the chapters have been revised by the original authors, new authors were found for three of the chapters. I am indebted to all the authors for their efforts and for their patience with the editor. I also acknowledge the assistance provided by David McDade and his colleagues at Wiley-Blackwell.

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List of Abbreviations

ABTS	2,2′-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid)
ALA	alpha-linolenic acid (18:3n-3, all *cis*)
AMF	anhydrous milk fat
AOCS	American Oil Chemists' Society
AOM	active oxygen method
AP	ascorbyl palmitate
B	behenic acid
BCO	blackcurrant oil
BF	butterfat
BfR	Federal Institute for Risk Assessment
BHA	butylated hydroxyanisole
BHT	butylated hydroxytoluene
BNO	Brazil nut oil
BO	borage oil
CAE	caffeic acid equivalent
CAN	canola oil
cp	Centipoise
CB	cocoa butter
CBE	cocoa butter equivalent
CBI	cocoa butter improver
CBR	coca butter replacement
CHD	cardiovascular heart disease or coronary heart disease
CLA	conjugated linoleic acid
CLnA	conjugated linolenic acid (18:3)
CO	coconut oil
CPKO	crude palm kernel oil
CPO	crude palm oil
CVD	cardiovascular disease
DAF	days after flowering
DAG	diacylglycerol(s)
DGDG	digalactosyl diglyceride
DHA	docosahexenoic acid
DMPS	dimethylpolysiloxane
DNA	deoxyribonucleic acid
DOBI	deterioration of bleachability index
DPPH	1,1-diphenyl-2-picrylhydrazyl
DSC	differential scanning calorimetery
EDTA	ethylenediaminetetraacetic acid

EPA	eicosapentaenoic acid; or Environmental Protection Agency
EPO	evening primrose oil
EU	European Union
EU-27	27 countries of the European Union
FA	fatty acid
FAC	fatty acid composition
FAO	Food and Agriculture Organisation
FAS	Foreign Agricultural Service
FDA	Food and Drug Administration (US)
FFA	free fatty acids
FFB	fresh fruit bunch
FHSBO	fully hydrogenated soybean oil
GC	gas chromatography
GE	glycidol fatty acid esters
GG	galactosyl glycerol
GHG	greenhouse gas(es)
GLA	gamma-linolenic acid (18:3n-6, all *cis*)
GLC	gas liquid chromatography
GLCO	gamma linolenic canola oil
GM	genetically modified or genetic modification
HDL	high-density lipoprotein(s)
HEAR	high-erucic rapeseed oil
HLaCO	high-lauric canola oil
HNO	hazelnut oil
HO	high-oleic oil
HOCO	high-oleic canola oil
HOLLCO	high-oleic low-linolenic canola oil
HOLLSOY	high-oleic low-linolenic soybean oil
HOSO	high-oleic sunflower oil
HOSUN	high oleic sunflower oil
HP HL	high-palmitic/high-linoleic sunflower oil
HP HO	high-palmitic/high-oleic sunflower oil
HPKS	hydrogenated palm kernel stearin
HPLC	high-performance liquid chromatography
HPO	hydrogenated palm oil
HPOo	hydrogenated palm olein
HS HL	high-stearic/high-linoleic sunflower oil
HS HO	high-stearic/high-oleic sunflower oil
HS HP	high-stearic/high-palmitic sunflower oil
HSCO	high-stearic canola oil
HYDCO	hydrogenated canola oil
HYDSOY	hydrogenated soybean oil
ICCA	Interstate Cottonseed Crushers Association
IEPO	interesterified palm oil
IOOC	International Olive Oil Council
ISO	International Standard Organisation
IV	iodine value
L	linoleic acid

LCA	life-cycle analysis
LCPUFA	long-chain polyunsaturated fatty acids
LDL	low-density lipoprotein
LEAR	low-erucic rapeseed oil
LFRA	Leatherhead Food Research Association (UK)
LLCO	low-linolenic canola oil
Ln	linolenic acid
LPC	lysophosphatidylcholines
LPE	lysophosphatidylethanolamines
M&I	moisture and impurities
MAG	monoacylglycerol(s)
MCF-7	human breast cancer cell line
MCFA	medium-chain fatty acid
MCPD	3-monochloro-1,2-propanediol
MEOMA	Malayan Edible Oil Manufacturers' Association
MGDG	monogalactosyl diglycerol
MNO	macadamia nut oil
MO	mid-oleic oil
MOSUN	medium-oleic sunflower oil
MPOB	Malaysian Palm Oil Board
MPP	dipalmitoyl myristoyl glycerol
MT	metric ton (tonne, 1000 Kg)
mt	million tonnes
MUFA	monounsaturated fatty acids
NCPA	National Cottonseed Products Association
NCVT	National Cotton Variety Trials
NESHAP	National Emission Standards for Hazardous Air Pollutants
NSA	National Sunflower Association (US)
NMR	nuclear magnetic resonance
ND	non detectable
nr	not recorded
O	oleic acid
O/L	ratio of oleic acid to linoleic acid
OOO	oleic-oleic-oleic triacylglycerol (triolein)
OSI	oxidative stability index
P	palmitic
PA	phosphatidic acids
PBSY	prime bleachable summer yellow (grade of cottonseed oil)
PC	phosphatidylcholines
PCR	polymerase chain reaction
PDG	palm diacylglycerols
PDI	protein dispersibility index
PDO	Protected Designations of Origin
PE	phosphatidylethanolamines
PET	polyethylene terephthalate
PFAD	palm fatty acid distillate
PG	phosphatidylglycerols; or propyl gallate
PHSBO	partially hydrogenated soybean oil

PI	phosphatidylinositols
PKO	palm kernel oil
PKOo	palm kernel olein
PKS	palm kernel stearin
PL	phospholipids
PMF	palm mid-fraction
PO	palm oil
POME	palm oil mill effluent
POO	dioleo palmitoyl glycerol (includes OPO isomer)
POo	palm olein
POP	dipalmitoyl oleoyl glycerol (includes PPO isomer)
POs	palm stearin
ppm	parts per million (mg/kg)
PPP	tripalmitoyl glycerol (triplamitin)
PPSt	dipalmitoyl stearoyl glycerol
PS	phosphatidylserines
PV	peroxide value
RBD	refined, bleached and deodorised
RI	refractive index
RNAi	RNA interference (genetic technique used to interrupt the normal translation of mRNA molecules)
RSO	rapeseed oil
S	stearic; or saturated (type of fatty acid)
SBDD	soybean deodorizer distillate
SBO	soybean oil
SCPA	Society of Cotton Products Analysts
SDA	stearidonic acid (18:4n-3, all-*cis*)
SEP	sequential extraction process
SFI	solid fat index
SfMF	soft milkfat fraction
SFO	sunflower oil
SG	esterified phytosterol glycoside; or specific gravity
SMP	slip melting point
sn-	stereospecific or regiospecific numbering
sn-1, sn-2 and sn-3	positions of the glycerol backbone
SOO	stearic-oleic-oleic triacylglycerol
SOS	stearic-oleic-stearic triacylglycerol
SPC	soy protein concentrates
SPI	soy protein isolate
SSS	trisaturated acyglycerols or trisaturates
St	stearic acid
StOO	stearic-oleic-oleic triacylglycerol
StOSt	stearic-oleic-stearic triacylglycerol
SUS	disaturated monounsaturated acylglycerols
SUU	diunsaturated monosaturated acylglycerols
SV	saponification value
TAG	triacylglycerol(s)
TBARS	thiobarbituric acid-reactive substances

TBHQ	tertiary-butylhydroquinone
TIU	trypsin inhibitor unit
TRF	tocotrienol rich fraction
tr	trace
U	unsaturated (type of fatty acid)
US	unsaponifiable matter
USDA	United States Department of Agriculture
USDA–NASS	United State Department of Agriculture – National Agricultural Statistics Service
VCO	virgin coconut oil
WHO	World Health Organisation
WNO	walnut oil
wt	weight

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: a fatty oil and a protein-rich meal. Seed extraction is achieved by pressing and/or by extraction with hexane. Oils such as palm and olive, on the other hand, are pressed out of the soft fruit (endosperm). Seeds give oils in differing proportions. Using USDA figures for 2008/09, world average oil yields are: soybean (18%), rapeseed (39%), sunflower (41%), groundnut (32%), cottonseed (14%), coconut (62%) and palmkernel (44%). In addition, yields from palm fruit (45–50%), olive (25–30%) and corn (about 5%) are as indicated. The relatively low yield of oil from soybeans is compensated for by the value of the high-quality protein meal (79%) accompanying the oil.

Some oils, such as virgin olive oil, are used without further treatment other than filtering, 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, sulphur compounds and pollutants), but may also remove valuable minor components, including antioxidants and vitamins such as carotenes and tocopherols. The refining processes must therefore be designed to maximise the removal of undesirable components and minimise the removal of the valuable minor components. Some of the latter are recovered from side streams of the refining process to give commercial products such as phospholipids, free acids, tocopherols, carotenes, sterols and squalene. Because of changes that occur during refining, it is important to know whether compositional data refer to crude or refined oil. Details of the levels of these in the various seed oils are given in appropriate chapters in this volume. Extraction processes have been described by Fils (2000), De Greyt and Kellens (2000) and, more recently, Dijkstra and Segers (2007). Hamm (2001) has discussed the major differences in extraction and refining procedures in 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 on their own these are sometimes inadequate to meet the physical, chemical and nutritional properties required for use in food products. Over a century or more, lipid technologists have designed procedures for overcoming the limitation of having only a restricted range of natural products. In particular, they have sought to modify fatty acid and

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Table 1.1 Methods of changing fatty acid and triacylglycerol composition to modify physical, chemical and nutritional properties.

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

Source: Gunstone (2006).

triacylglycerol composition, knowing that such changes influence the important properties of food fats. These have been classified (Gunstone 2006) into technological and biological procedures such as those listed in Table 1.1.

The procedures most relevant to this book are fractionation, hydrogenation and modification of fatty acid composition by conventional seed breeding or genetic engineering. Details are given in some of the following chapters. As an example, the usefulness of palm oil and palmkernel oil is greatly extended by fractionation. Hydrogenation may be applied in three ways. A very light hydrogenation (brush hydrogenation) applied to soybean oil or rapeseed oil will halve the level of linolenic acid and thereby increase oxidative stability (shelf-life). More extensive, but still partial, hydrogenation is applied to unsaturated liquid oils to produce semi-solid fats that can be used as margarines and spreads. Through this process the levels of polyunsaturated fatty acids are markedly reduced, saturated acid content rises slightly, and there is a large rise in the levels of monounsaturated acids, much of it with *trans* configuration. The *trans* acids have higher melting points than their *cis* isomers, thereby contributing to the desired increase in solid acids. However, *trans* acids are now accepted as having undesirable nutritional properties and the food industry has revised procedures to limit their level. In some countries the level of *trans* acids has to be reported on the packaging and this increases the pressure to minimise the levels of these acids (Wilson 2009). Complete hydrogenation gives a product with virtually no unsaturated acids and therefore no *trans* acids. This is hardstock that can be blended with unsaturated oil, often before interesterification.

In the following chapters examples are cited of 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), high-oleic sunflower oil and low-linolenic soybean oil, but attempts to develop oils with modified fatty acid composition and/or a changed composition of minor products such as tocopherols are being pursued actively in many countries. Some of these have been described (Gunstone 2007b; Watkins 2009) and others are cited in the following chapters of this book. Perhaps the most exciting of these are the attempts to produce long-chain polyunsaturated fatty acids such as eicosapentaenoic acid (20:5) and docosahexaenoic acid (22:6) in a field crop (Napier 2006).

Following their introduction into commercial agriculture in 1996, genetically modified (GM) crops are now grown in many countries. Nevertheless, opposition to such crops remains in Europe and elsewhere and GM-free products are in demand (Section 1.3.8). This restriction also applies to minor products and it has sometimes been difficult to obtain GM-free lecithin (phospholipid), which comes mainly from soybean oil (Gunstone 2008c).

1.2 VEGETABLE OILS: PRODUCTION, CONSUMPTION AND TRADE

1.2.1 Nine vegetable oils

Oils and fats are produced from animal and vegetable sources, with the former group declining in market share though not in production tonnage. Tallow, lard and butter still occupy the fifth, sixth and seventh positions after the four dominant vegetable oils (palm, soybean, rapeseed and sunflower seed). During the twentieth century the contribution of animal fats fell from 50% to 20% and in 2009 it was less than 16%, showing that vegetable fats have become increasingly dominant (Table 1.2).

Statistical information about production, consumption and trade in oils and fats comes from two major sources. Oil World ISTA Mielke of Hamburg, Germany, is a market analyst producing weekly, monthly, annual and occasional reports on 10 oilseeds, 17 oils and fats (13 vegetable and 4 animal) and 10 oil meals. This valuable information has to be purchased. In contrast, information from the USDA is available free online and is updated each month (search for ‘USDA-FAS oilseeds’ in Google or any other search engine). However, this latter source does not include animal fats and covers only seven oilseeds (copra, which is the source of coconut oil, cottonseed, palmkernel, groundnut, rapeseed, soybean and sunflower seed), nine oils (from these seven oilseeds and from palm and olive) and eight oilmeals (from the seven oilseeds and from fish). The four additional vegetable oils covered by Oil World are corn, sesame, linseed and castor oils. These two sources of information show good but not perfect agreement. It is not easy for those who produce these reports to collect all the necessary data and figures continue to be subject to revision over several years. Figures in this chapter will come primarily from the USDA source and only occasionally from Oil World. This makes it easier for readers to consult the website themselves for up-to-date information.

The nine vegetable oils can be classified in several ways. One categorisation recognises four major oils (palm, soybean, rapeseed and sunflower), two lauric oils (coconut and palmkernel, with a very different fatty acid composition from the other commodity oils) and the remaining oils (cottonseed, groundnut and olive).

It is also useful to distinguish between oils and fats obtained from tree crops (coconut, palm and olive) and those from annual seed/bean crops, and also to recognise those that are

Table 1.2 Average annual production of total oils and fats and of animal fats (million tonnes and % of total) during the twentieth century.

Years	1909/13	1936/39	1958/62	1976/80	1986/90	1996/2000
Oils and fats (17)	13.1	20.2	29.8	52.6	75.7	105.1
Animal fats (mt)	6.5	8.5	11.8	17.2	19.8	21.3
Animal fats (%)	50	42	40	33	26	20

Source: Based on Mielke (2002) for 17 commodity oils and Hatje (1989).

by-products. These are important factors in understanding the dynamics of production and trade. Trees have to be planted and mature, usually for many years, before they produce an economic crop. Yields from tree crops are influenced by climatic changes from season to season and by inputs such as fertiliser, pesticides, herbicides and irrigation, although crops will continue for many years (25–35 years for palm, around 100 years for olive). Annual crops (soybean, rapeseed, sunflower etc.), on the other hand, depend on planting decisions that farmers make each year based on agricultural and economic factors. These decisions result in changes in supply from year to year. For vegetable oils that are by-products, decisions on annual production depend on factors other than oil production. For example, cotton is grown according to the demand for fibre and not for cottonseed oil. Corn is not grown primarily for its oil and peanuts are grown as much for consumption as nuts as for oil production. It is also worthy of note that crushing soybeans produces two components – soybean oil (18%) and soybean meal (79%) – both of which are valuable commercial products. At different times the oil or the meal is in greater demand.

Annual crops are produced at harvest time, which comes late in the calendar year in the northern hemisphere and early in the calendar year in the southern hemisphere. However, equatorial tree crops such as palm and coconut are harvested throughout the year, though there is some seasonal variation in quantity. Production data are often reported in harvest years such as 2008/09. These relate to 2008 harvests in the northern hemisphere and 2009 harvests in the southern hemisphere.

Table 1.3 Population (millions), production, exports, imports and total consumption (million tonnes) of seven oilseeds and nine vegetable oils in selected countries in 2008/09.

	Pop	Oilseeds*			Oils§			
		Prod	Exp†	Imp	Prod	Exp†	Imp	Consump
World**	6829	395.3	94.4	92.9	131.8	55.1	54.3	129.3
China	1323	57.8	1.2	44.1	16.0		9.8	24.6
EU-27	497			17.8	15.4		8.7	22.6
India	1198	33.7			6.8		8.8	14.7
USA	315	89.2	35.8		9.6	1.5	3.2	11.2
Indonesia	230			1.4	22.7	16.6		6.0
Brazil	194	59.5	30.1			2.0		5.1
Malaysia	27				19.4	16.8	1.3	4.6
Pakistan	181						2.2	3.4
Russia	141							3.0
Japan	127			5.8				2.1
Mexico	110			4.9				2.0
Argentina	40	35.7	6.3		7.7	5.8		1.8
Turkey	75			1.7			0.8	1.7
Egypt	83			1.2			1.5	1.6

Source: USDA, December 2009.
Notes:
* Oilseeds are copra, cottonseed, palmkernel, peanut (groundnut), rapeseed, soybean and sunflowerseed. Oils also include palm and olive.
** The countries selected are the largest consumers of vegetable oils.
§ These figures cover oil extracted from both indigenous and imported seeds.
† Canada (population 34 million) exported 10.0 million tonnes of seed and 1.6 million tonnes of oil. Ukraine (population 46 million) exported 3.7 million tonnes of seed and 2.2 million tonnes of oil.

In discussing trade in oilseeds and oils in geographical terms, it is useful to recognise four types of countries/regions. These are discussed below and illustrated in Table 1.3. Population figures are in millions and relate to 2009.

- Countries with small populations that produce large amounts of oilseeds/oils and are large exporters of these commodities. Examples are Australia (population 21 million), Malaysia (27 million), Canada (34 million), Argentina (40 million) and Ukraine (46 million).
- Countries with large populations that produce large amounts of oilseeds/oils and fats to feed their own populations but are still significant exporters. Examples are the USA (315 million), Indonesia (230 million) and Brazil (194 million).
- Countries with very large populations that are major importers despite local production. China (1323 million), India (1198 million) and other highly populated countries in Asia belong to this category. The Indian subcontinent of India, Pakistan (181 million), Bangladesh (162 million) and Sri Lanka (20 million) is a very large importer of vegetable oils.
- Finally there are countries/regions that are essentially traders. They produce, consume, import and export these commodities. The 27 countries of the European Union (EU-27) form the biggest example, but Hong Kong and Singapore are also significant traders by virtue of their geographical closeness to the world's largest importer (China) and exporters (Indonesia and Malaysia).

Tables 1.4 and 1.5 show the annual production of nine vegetable oils between 1995/96 and 2008/09 (14 years). Total production of the nine oils rose from 71 to 133 million tonnes

Table 1.4 Production (million tonnes) of nine vegetable oils during the period 1995/96 to 2008/09.

	9 oils	Palm	Soya	Rape	Sun	5 oils*
1995/96	71.2	16.2	20.3	11.1	9.1	14.5
1996/97	73.8	17.6	20.4	10.5	8.6	16.7
1997/98	75.2	16.9	22.4	11.4	8.5	16.0
1998/99	80.3	19.2	24.4	11.8	9.3	15.6
1999/2000	86.0	21.8	24.5	14.0	9.3	16.4
2000/01	89.8	24.3	26.7	13.3	8.2	17.3
2001/02	92.7	25.3	28.9	13.1	7.4	18.0
2002/03	96.1	27.6	30.6	12.2	8.1	17.6
2003/04	102.8	30.0	30.2	14.1	9.2	19.3
2004/05	111.7	33.5	32.6	15.7	9.2	20.7
2005/06	118.7	35.8	34.6	17.3	10.6	20.4
2006/07	121.5	37.2	36.4	17.0	10.6	20.3
2007/08	127.8	40.9	37.5	18.3	9.7	21.4
2008/09	131.8	42.4	35.7	20.4	11.8	21.5
Increase 1995/96 to 2001/02	21.5	9.1	8.6	2.0	–1.7	3.5
Increase 2002/03 to 2008/09	35.7	14.8	5.1	8.2	3.7	3.9

Source: USDA, December 2009.
Note:
* Coconut, cottonseed, olive, palmkernel and peanut (groundnut) oils.

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