Animal and Vegetable Fats, Oils, and Waxes

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Edmund W. Lusas, Mohammad S. Alam,
Richard C. Clough, and Mian N. Riaz

Biotechnology in Agriculture and Processing

Human Survival Is Biotechnology

Biotechnology has been defined by various groups and broadly includes technologies that utilize living organisms or parts of biological systems. The nurture of man and animals, and provision of replenishable industrial materials, typically includes: (1) growing selected species or their genetic modifications; (2) harvest, preprocess storage, conversion into useful products, and protection until use; and (3) utilization or disposal of byproducts and wastes in the most beneficial or least-cost manner. Specific actions may be taken to suppress residual enzymes and contaminating microorganisms that could degrade product value. Also, *remediation* (restoration) of air and water used in processing to near-pristine condition often is mandated today.

The first *transgenic* (across genera) oilseed crops were planted in the United States and Canada in 1996 and were followed by rapid acreage expansion. Transgenic oilseeds generally do not require special processing unless they contain higher melting oils. In this chapter, the reader is first introduced to modern biology principles, and industry terms are presented throughout.

Human understanding of life processes, and competition between genera, continually broadens. Many biological reactions are catabolic and split large compounds into smaller units to obtain energy (carried by ATP, adenosine triphosphate) for heat, work, or reinvestment in syntheses and chemical structures for making required compounds. Plants are the original source of nutrients for man and animals. Microscopic plants, plankton, and larger members synthesize proteins, carbohydrates, lipids, and other compounds from inorganic elements and water, using ATP obtained from the sun by photosynthesis. In the process, carbon dioxide also is reduced to oxygen. Some products are used to build the plant's structures and maintain its functions, and others are stored in the seed as enzymes, proteins, and energy reserves (starches and lipids) for reproduction as new plants, or as sugars or starches in roots of perennials for later growth cycles. Humans rely on plants and animals, which consume plants (herbivores), or carnivores which eat other animals, for their food. Animals vary in their abilities to synthesize intermediate chemical structures needed for their development and life; generally, those lower in the food chain are more self-sufficient. As examples, amino acids are the building blocks of proteins and 11 are *dietary essential* (must be obtained from food) by humans; approximately 12–14 are dietary essential for economic animals (grown for meat or other food products), the exact needs varying with species, age, and physiological state. Carnivorous fish obtain long-chain highly unsaturated fatty acids in the wild by feeding on plankton eaters and often lose the ability to synthesize them directly. When grown in captivity, as in salmon farming, oils of plankton-eating fish are added to their feed. Diunsaturated linoleic acid and triunsaturated linolenic acid are considered dietary essential for humans. Also, longer-chain higher-unsaturated fish oils sometimes are prescribed for people with lipid metabolism deficiencies.

All organically made compounds, fossilized or not, were once synthesized by specific enzymes and pathways. They must remain degradable by enzymes of the same organism to perpetuate its life and by enzymes of other species for their nutrition and for biodegradation and carbon recycling. Life processes come to a halt if the laws of biochemistry and physical chemistry aren't satisfied. This chapter is limited to

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E.W. Lusas (✉)
Ed Lusas, Consultant, 3604 Old Oaks Drive, Bryan, TX 77802, USA

M.S. Alam • R.C. Clough • M.N. Riaz
Food Protein Research and Development Center, Texas A&M University, 2476 TAMU, College Station, TX 77843-2476, USA
e-mail: mnriaz@tamu.edu

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lipids, but business and policy decisions about food, feed, and replenishable industrial raw materials also require holistic information about protein and carbohydrate technologies, about needs and preferences of biological users, and about human enterprises throughout the world.

Biotechnology has been implemented in two phases. Macro-biotechnology examples are commonplace and include agriculture, baking, and various fermentations. Implementation began about 10,000 years ago, even before written history, when humans initiated symbiotic relations with selected wild animals and plants to ensure a more reliable food supply than possible by hunting/fishing and gathering. Animals were refashioned through selection, protection, crossbreeding, and increase, to meet man's food, transportation, security, and compatibility needs. Higher-yielding seeds, which also were easier to dehull and process into food, were replanted for succeeding harvests. In time, the face of the earth's habitable lands was changed. Except in remote areas or designated refuges, humans: (1) eliminated wild animals dangerous to them and their protected crops and animals; (2) cleared lands and jungles for firewood, building materials, and growing additional crops, as the population increased; but (3) sometimes also destroyed arable land by over-grazing and erosion of uncovered top soil.

Biotechnology currently emphasizes microscale aspects that were not visible or envisioned until about 150 years ago, including: (1) microbes; (2) stereochemistry of reactions, molecular biology including transcription of genetic codes and translation for protein production, and cell multiplication; and (3) enzymes as catalysts. Humans came to only partially understand the nature of systems (animals, plants, insects, and soil) they handled in agriculture. Modern biotechnology must address needs of these systems, as well as those of people. Animals and plants must be healthy and adequately nourished, the pests (weeds and insects) controllable, the soil kept productive, and all must function in acceptable harmony if the quality of human life is to be sustained or improved as the population increases.

Histories of biotechnology progress in agriculture, genetics, medicine, pharmacy, industrial fermentations, food processing, and nutrition are reported in many books and on the Internet. Archeologists tell us the Babylonians brewed beer in 6000 BC, Egyptians baked yeast-leavened bread in 4000 BC, and other early cultures made wine and vinegar by fermentation and preserved cheeses by salt and acid. Sophisticated herbal medicines were developed. But, without scientific knowledge of why certain practices were successful, early progress through trial and error was earned slowly. Some of the less-mentioned milestones relevant to food production and utilization are described next.

Development of the microscope by Anton van Leeuwenhoek (1673) and others enabled man to see a new world of "microcreatures," including bacteria, yeasts, molds, blood cells, and spermatozoa, and microstructures such as muscle fibers and plant and seed tissues. This added credibility to later claims by Louis Pasteur and Robert Koch that microorganisms can spoil foods and cause disease at a time when many influential learned men still clung to theories of spontaneous generation of life.

Louis Pasteur (1863) invented a process to pasteurize wine by heating to inactivate microbes and prevent its turning sour from fermentation to acid. Nicolas Appert had already won a 12,000-franc prize from Napoleon I in 1809 by inventing a process for "canning" foods (actually packing precooked foods in glass bottles, sealing, and heating in boiling water). But, spoilage occurred frequently because few understood the roles of acidity or osmotic pressure in restricting microbial growth, problems of recontamination, or heating inactivation requirements for different bacteria, especially spore formers. The roles of bacteria and yeast in fermentations had been accepted when Eduard Buchner (1897) demonstrated that filtered extracts also could catalyze fermentation in the absence of intact yeast cells [1]. This led to modern enzymology where more efficient enzymes are extracted and purified from a variety of nontraditional sources, and more recently from "engineered" microorganisms that carry gene sequences from relatively unrelated species.

Genetic Messages

Gregor Mendel, an Austrian botanist and monk working with sweet pea plants, proposed that "factors" (units of information responsible for observable traits) are passed from one generation to the next (1866). But, his work essentially went unnoticed until rediscovered by several scientists in the early 1900s. Walther Flemming reported the discovery of chromosomes and mitosis in 1882. William Sutton (1902) announced that chromosomes are paired and may be the carriers of heredity. He named Mendel's factors "genes" and suggested they occur on chromosomes.

After observing meiosis, he developed the Chromosomal Theory of Heredity that gametes (egg and sperm cells) are haploid and carry only one of each pair of chromosomes from each parent in forming the new being (a diploid zygote) which then holds on to life as it best can. Details of genetics continued to develop. Alfred Hershey and Marsha Chase showed that deoxyribonucleic acid (DNA) is the genetic code carrier rather than proteins as was thought by some (1952). James Watson and Francis Crick proposed the double-stranded, complementary, antiparallel structure model for DNA (1953) [1].

Development of recombinant DNA techniques to produce engineered, genetically engineered (GE), or genetically modified organism (GMO) products is among the boldest achievements of cellular biologists. Paul Berg (1972) first

demonstrated use of a selected enzyme to cut DNA strands into sections and reattach them to produce recombinant DNA molecules. In 1973, Stanley Cohen, Annie Chang, and Herbert Boyer announced splicing a viral DNA section with a bacterial DNA section to form a recombinant DNA molecule, which then was spliced into the DNA of a bacteria to produce the first *transgenic* (across genera) recombinant DNA organism. Herbert Boyer and Robert Swanson founded Gene tech, Incorporated, a biotechnology company dedicated to developing and marketing products based on recombinant DNA technology in 1976. It was the first company to receive US Food and Drug Administration (FDA) approval for marketing a genetically engineered drug (a form of human insulin produced by bacteria) in 1982, and since has developed many other products [1].

Research in genetic and protein structures created tremendous amounts of data. Fortunately, means to handle it also were being developed on another front. Norbert Wiener, a mathematician at the Massachusetts Institute of Technology and a founder of the science of cybernetics, published his book *Cybernetics; or, Control and Communication in the Animal and the Machine* in 1948 [2]. In this volume and its 1961 edition [3], Wiener, a specialist in communications and later in artificial intelligence [4], knew that messages degrade and can be fouled in retransmission and suggested that aging and diseases are analogous degradations of the genetic code. Realizing that a revolution in information handling was occurring, Wiener became concerned that cybernetics and automation not degrade the quality of life and published *Human Use of Human Beings: Cybernetics and Society* in 1954 [5]. It also was reissued posthumously in 1967 [6]. Cybernetics, and especially digital computing, have made the massive record keeping, data summarization, inventory handling, sequencing, scheduling, and control systems of today's business, government, and science possible. Complete amino acid sequences of proteins have been mapped, as well as genomes of microorganisms, plants, animals, and man. As medical research workers become interested in specific genetic traits or problems, or desire to investigate modified-protein drugs, they will more readily know where to locate the corresponding genes and structures.

Cell culture techniques, developed during research leading to transgenic DNA organisms, greatly assisted in the development of many nontransgenic *cultivars* (uniform subvarieties of a recognized genus and species) by selective cross-breeding of closely related germplasms.

Fatty acids in plants and animals typically are elongated during synthesis to chain lengths of 18 carbons by successive additions of two carbon units. The resulting product, stearic acid, is fully saturated, but has a melting point too high for most physiological reactions. Nature remedies this situation by also providing *desaturase* systems that enable organisms to introduce 1, 2, or 3 unsaturated bonds in the 18-carbon chain, thus lowering melting point of fatty acids and triglycerides. Melting points differ between fat deposit locations in animals, change seasonally in animal bodies, and vary with seed maturation temperatures of the same cultivar.

Stability of fatty acids against oxidation decreases as unsaturation increases, a prime example being tri-unsaturated 18-carbon linolenic acid in soybean oil. Biotechnologists developing soybean with greater oil stability have sought to do so by seeking germplasms with reduced desaturation for selective crossing, and by altering or suppressing expression of desaturation [7], to produce oils with reduced linolenic acid and increased oleic or stearic acid contents.

Water Activity

W.J. Scott, an Australian microbiologist, published a classic food science chapter "Water Relations of Food Spoilage Microorganisms" in 1957 [8]. He recognized that microorganisms compete with other solutes in mixed systems for water required for their metabolism and summarized ranges within which most bacteria, yeasts, and molds grow. However, water was not expressed as percent of system mass, but rather as *water activity* ($a_W = p/p_o$), where p is the vapor pressure of the solution (or product), and p_o is the vapor pressure of the pure solvent (water). Some prefer to use the term relative vapor pressure (RVP), which can be determined by measuring percent relative humidity in the headspace above a product that has equilibrated within its container and the relationship RVP = (percent ERH)/100. Water activity, osmotic pressure, lowering of freezing point, and rising of boiling point are colligative properties of solutions that follow Raoult's Law.

The guides indicated that relatively few bacteria grow at a_W below 0.91, few yeasts below 0.87, and few molds below 0.75–0.65 a_W and helped explain why many foods do not spoil even though they are not sterile. Microbial growth ability can be further reduced by increasing osmotic pressure by addition of soluble salts and sugars, lowering pH, use of microbial inhibitors, and reducing product temperatures. Exceptions to the guides exist, for example, halophilic bacteria tolerate high salt concentrations and osmophilic yeasts can grow on high sugar content products.

Food-induced diseases are mainly of two types: *food poisoning,* the effect of toxins produced during growth of a microorganism in the food before ingestion, and *infection,* resulting from food-borne microorganisms taking up residence in the body before doing their damage. Low a_W has been reported to inhibit production of toxins by various food-poisoning bacteria, even though the live organisms are present. However, some low a_W processed meats have

been implicated as carriers of viable food infection bacteria, which apparently resume growth when a_W and temperature increase. Water activity can be controlled by: product formulation; drying fruits, vegetables, and meat; and by storing products like meats and fish in salt brines and fruit preserves in sugar syrups.

Over time, diagrams were developed relating water activity with: enzyme activity, dormancy of stored seed, loss of dry product crispness by moisture absorption, pigments and vitamins degradation, nonenzymatic browning, and fat oxidation. Response curves generally are not linear, and readers working with food or feed formulations are referred to the technical literature about their products.

Herbicide- and Insect-Resistant Oilseed Crops

Crop producers and processors were provided with powerful tools during the last four decades of biotechnology evolution. Seed producers can develop new cultivars by crossing two selected parents, or by *hybridization* (crossing two genetically diverse genotypes to obtain additional vigor). Generally, transgenic crops also are hybrids. The world's current major biotech oilseed crops are herbicide-tolerant (HT) soybean, corn, cotton, and canola (a type of rapeseed), and insect-resistant corn (maize) and cotton.

United States and European pharmaceutical and chemical companies have taken the lead in biotechnology, frequently by purchasing plant breeders and growers of planting seeds. Various producers offer transgenic crop seeds resistant to several herbicides. The Monsanto Company (St. Louis, MO) has often been among the first to get its products to the marketplace and is used as an example here. Roundup Ready® Soybean (planting seed) was introduced in the United States, and Roundup Ready Canola in Canada, in 1996. These transgenic crops are resistant to Roundup,® Monsanto's brand of glyphosate, a *nonselective* (broad-spectrum) herbicide for killing *weeds* (unwanted plants). A grower of a Roundup Ready crop needs to make fewer spray passes across the field, often with one herbicide, to control a season's weeds. Roundup Ready Cotton was commercialized in 1997 and Roundup Ready Corn in 1998. Monsanto introduced Bollgard® Cotton in 1996, and YieldGard® Corn in 1998. The Bollgard and YieldGard seeds included a gene sequence from the soil bacterium *Bacillus thurigiensis* var. kurstaki ("Btk") which enables the plant to make *systemic pesticides* toxic to larvae of specific insects. These compounds are known as plant-incorporated protectants (PIP) and formerly were called "plant pesticides"; the crops categorically are called "B.t."

By 2005, the Monsanto Company marketed: Roundup Ready Soybeans, Roundup Ready Canola, Roundup Ready Cotton, Roundup Ready Corn, and Roundup Ready Corn 2. Additional gene sequences from "Btk," which produce other PIP specific for other insect larvae, had been inserted into seeds, and Monsanto also offered: Bollgard Cotton for controlling tobacco budworm and pink bollworm, and high suppression of cotton bollworm; and Bollgard II® for control of tobacco budworm, pink bollworm, cotton bollworm, fall armyworm, cabbage and soybean loopers, and other secondary leaf- or fruit-feeding caterpillar pests in cotton. (It is ironic that none of the commercial B.t. cotton seeds control the cotton boll weevil, a long-time nemesis, but concurrent boll weevil eradication programs have made good progress toward this objective.) Monsanto's B.t. Corn line included: YieldGard Corn Borer®, effective against European corn borer, southwest corn borer, sugarcane borer, southern cornstalk borer, corn earworm, fall armyworm, and stalk borer; and YieldGard Rootworm®, effective against western, northern, and Mexican corn rootworm. In addition, YieldGard Plus® offered the protective properties of both YieldGard Corn Borer and YieldGard Rootworm®. The inclusion of two or more transgenic properties in a seed is known as "stacking." Other seeds offered include: YieldGard Corn Borer with Roundup Ready Corn; YieldGard Corn Borer with Roundup Ready Corn 2; YieldGard Rootworm with Roundup Ready Corn 2; YieldGard Plus® with Roundup Ready Corn 2; and Bollgard II with Roundup Ready Cotton. The Monsanto Company also licenses the use of Roundup Ready traits to other seed producers who offer their Roundup Ready lines in the marketplace. The growing of transgenic crops is approved variety-by-variety and state-by-state. The Monsanto Company sees its relation with growers as licensor-licensees of its technologies, rather than as traditional seller-buyers, and establishes licensor-monitoring rights before selling seed.

The *2005 Technology Use Guide*, downloaded from the Monsanto Company Web site, states that growers are required to sign a Monsanto Technology Stewardship Agreement to: (1) comply with all EPA (US Environmental Protection Agency) mandated Insect Resistance Management (IRM) requirements; (2) use all purchased seed with biotech traits for planting a single crop; and (3) sell harvested corn with biotech traits not yet approved by the European Union only to grain handlers who confirm their acceptance, or use that grain as on-farm feed. Finding an initial crop buyer is the grower's responsibility, and prior discussions with grain elevators and Monsanto seed dealers are encouraged.

Refuges (20% minimum to 50% of the total crop acreage) planted to the same crop (corn or cotton) with non-B.t. seed are required by the EPA as part of the IRM effort to slow development of B.t.-resistant insects. The concept is to provide an area for presumably B.t.-resistant insects escaping the B.t. crop area to mate with non-B.t.-resistant

insects in an area where other insect control practices are used, and thus slow development of B.t.-resistant insects that survive to the following year. Options for refuge patterns and location are described, and growers must agree that Monsanto personnel or its agents will have access to monitor the transgenic crop and refuge areas.

Growers may use glyphosate herbicides, other than those designated by Monsanto, but only if they have been approved for use over Roundup Ready crops, and have been labeled for this use by all required governmental agencies.

If Monsanto suspects a grower may have planted saved seed containing a Monsanto genetic trait, it may request invoices or otherwise confirm that newly purchased seed has been planted. If information is not provided within 30 days, Monsanto may inspect and test all the grower's fields to determine if saved seed has been planted. Inspections are to be scheduled in advance at a reasonable time so the grower can be present if desired.

The US Department of Agriculture (USDA) has estimated that herbicide-tolerant (HT) soybeans reached 85% of total US soybean acreage and HT cotton reached 60% of total in 2004, whereas the HT share of corn reached 18% [9]. The ISAAA (International Service for the Acquisition of Agri-Biotech Applications) has reported that world cultivation of biotech crops increased 47-fold, from 1.7 million hectares (4.2 million acres) to 81.0 million hectares (1 ha = 2.47 acres) in the 9-year period 1996–2004, and was up by 20% from 2003. The number of countries growing 50,000 ha (123,500 acres) or more annually increased from the original United States and Canada to 14 in 2004, with the US still planting the most land (59% of global GMO plantings), followed by Argentina (20%), Canada (6%), Brazil (6%), China (5%), Paraguay (2%), India (1%), South Africa (1%), and Uruguay, Australia, Romania, Mexico, Spain, and The Philippines each planting less than 1%. Approximately 34% of the global biotech crop area in 2004 was in developing countries, with use in Southern Hemisphere developing countries increasing about three times more rapidly than northern industrial countries [10]. Growth in the five principal developing countries (China, India, Argentina, Brazil, and South Africa) portends significant changes in world food/feed trade patterns, which already are unfolding.

Concerns About Transgenic Crops

Benefits of biotech crops have not always materialized as expected. Introductions of many glyphosate-resistant transgenic crops have been met with complaints of "yield drag" in the initial years, with as much as 6–10% yield reduction for soybean compared to nontransgenic hybrids in test plots reported. Damage to root inoculants or nitrogen-fixing nodules by glyphosate and incomplete cleaning of mixed herbicide residues from weed sprayer tanks have been proposed as causes. However, problems seem to lessen in succeeding years, with no yield drag observed in glyphosate-resistant corn, and ~3% yield drag reported in more recent soybean tests. Yield is determined by genes other than those for glyphosate resistance and by adaptability of cultivars to specific soil conditions. It takes longer to optimize crops as the number of desired traits increases, and improved nontransgenic hybrids may be brought to market in shorter time. Soils differ in fertility, drainage, compacting, and temperature, and some growers chose several seed varieties for different soil conditions on the same farm. Reduced costs of tillage, including opportunities for drilling seed into no-tilled fields (nonplowed stubble of previous crops) and fewer trips across fields for herbicide application, are offset by higher seed costs in calculating overall costs of producing a crop. Economical justification of herbicide-tolerant crops seems confirmed by rapid increases in acres planted in the United States in recent years. Insect larvae carry fungi that produce mycotoxins in corn and cottonseed that can cause illness and death in economic animals and cancer in humans. Elimination of such problems also is welcomed, in addition to increased yields of B.t. crops protected against insect invasion.

Experience showed that some early visions of one-pass herbicide treatment of HT crops per season were overly optimistic. Various practices for controlling weeds are needed across the country, including an herbicide "burn down" of sprouted weeds before crop drilling, dealing with weeds that emerge at different times during the year and well into the growth of cotton, and control of perennial weeds and those resistant to glyphosate. Weed control practices must be tailored to local conditions, even though fewer applications may be required when planting glyphosate-resistant crops.

Many early skeptics predicted development of weed resistance to glyphosate and other herbicides used with HT crops, and insect resistance to PIP insecticides. But, resistance occurs as a natural adaptation for survival and has continuously led to the need for more powerful pest control methods in agriculture. Very strong weed resistance was experienced in growing HT canola in parts of Canada, also suggesting triple stacking of genetic resistance from exposures to previous sequences of herbicides. Canola itself, volunteering from previous plantings, could be a resistant super-weed if a locality switched to growing other crops. Various antibiotech concerns, and activist groups and their causes, can be found on the Internet. Glyphosate has been registered as an herbicide for nearly 30 years and is claimed to have attracted less resistance than other herbicides.

In early days of transgenic crop research, various scientific groups passed resolutions that extreme care should

be taken to avoid biotech materials escaping into the environment. But, handling transgenic seeds in open fields by uninstructed personnel is far different than aseptic microbe transfers between test tubes in laboratories by trained technicians. Broad contamination of seed supplies and germplasm resources by transgenic sequences has become major concerns. Although unplanted borders around experimental and seed increase plots are recommended to reduce cross-contamination by wind-blown pollen, occasional winds may be stronger and pollinating insects may fly farther than expected. Floods can carry seed to other fields. Bulk seed can spill from trucks, sprout along roadways and fencerows, and the resulting plants pollinate related plants and later plantings. Inadequate cleaning of seed handling, storage, and transporting equipment can contaminate other crops (even at low levels of $<0.5\%$) and spread transgenic seeds that eventually germinate and pollinate their own kind or wild relatives.

Protecting gene pools at *centers of diversity* (locales where a wild plant was first domesticated) from contamination by transgenic sequences has become a major concern among plant scientists. Farmers growing soybean for the organic foods market have difficulty finding planting seed uncontaminated by transgenic sequences and keeping the crop genetically uncontaminated during growth [11].

Concerns exist about potential gene flow problems arising from producing nonfood products such as industrial chemicals and pharmaceuticals in transgenic plants grown in open fields. The inability of current practices to keep such materials out of the food supply was demonstrated by the StarLink® corn incident. The EPA approved sale of StarLink, a B.t.-type corn developed by Aventis CropScience for animal consumption and industrial production of ethanol, in 1998. However, it was not approved for human consumption because of potential allergenic effects. In 2000, a coalition of environmentalists sent a collection of corn food products to a private laboratory and paid for its testing. In September, newspapers reported that StarLink corn was detected in taco shells sold in grocery stores, and Aventis suspended sales soon after. Although only about 0.4% of the United States corn crop had been planted to StarLink in the most popular of its 2-year cultivation, and much of the crop remained in feed channels, it had broadly contaminated the United States food corn supply and some export lots. Many corn-based foods were recalled because of concerns about contamination, and considerable unrest occurred throughout the food processing and exporting industries. Costs to Aventis for numerous analytical bills experienced by processors and traders holding corn in storage, and buying back the remaining StarLink corn and recalled products, reportedly, were approximately $100 million. No evidence was found that StarLink had produced an allergy reaction in any person. The EPA stopped granting split registrations for genetically engineered crops [12]. The concern is that far greater damages might occur if a more noxious chemical entered the food or feed supply through misplaced shipments of a common-looking transgenic crop.

The feasibility of producing plant made pharmaceuticals (PMPs) has been demonstrated with common crops such as corn in a practice sometimes called *biopharming* or simply *pharming*. Production of vaccines, pharmaceuticals, or their precursors in plants, rather than by animal cell culture or transgenic animals, has the advantage of avoiding potential transfer of bacterial or viral diseases. The need for greatly increased oversight in this emerging industry was demonstrated by the Prodigene incident in 2001. The company planted corn, genetically modified to produce pharmaceutical components, at various field sites. The following year, conventional soybean was grown at one of the sites. Seed from the previous year's experimental crop germinated as volunteers, and the corn plants were harvested with the soybean. Pieces of the transgenic corn plants were found with the soybean in elevators, and USDA inspectors quarantined 500,000 bushels of soybean [12]. The pharmaceuticals were in the corn plant trash and not in the soybean seed. It is difficult to predict what may have happened if commercial practices had run their course. If the soybean was extracted for oil, it may have been cleaned and the trash (including corn stalk pieces and any corn seed) sold for feed use. Depending on digestibility, the active compound may have entered the milk or meat supply. A public health disaster did not occur, but some feel the potential for misdirection of intended drugs has been demonstrated.

Over 85% of domestic foods are estimated to contain biotech crops. Whether, or how, to label GMO-containing foods has been an issue since their initial introduction. The EPA, which rules on safety and use of herbicides and pesticides, and the FDA, have adopted the *substantial equivalence* principle when granting approvals and look for closeness of similarities of genetically modified crops or foods with existing products based on chemical analyses. Acute toxicity and suspected allergenicity tests are run in initial screenings. European and some US scientists prefer multigeneration animal testing, reminiscent of earlier food additives approval practices, before release.

Attempts to tag EPA/FDA-registered GMO foods by product labeling have consistently been denied by the government and courts, apparently on the principle they cannot be identified as different from traditional crops because they already have been declared equivalent. Attempts to limit growing of GMO crops in specific areas also have failed, with state programs overruled as interfering with interstate commerce. The alternative of labeling nontransgenic products as "non-GMO" also has been denied on the principle they cannot be implied to be better.

Additionally, formulated non-GMO foods would have to carry the burden of ensuring that all ingredients were non-GMO, including cheeses, ice cream, and other products, which may contain dried nonfat milk solids from cows treated with recombinant bovine somatotropin (rBST). It would be extremely hard to track such products from originating farms to the point of formulation. Currently in the United States, organic foods, produced under certification programs, appear the most reliable non-GMO option (with non-GMO labeling not allowed). GMO products have been declared kosher for Jews and halal for Muslims, provided they do not contain genes from non-kosher or non-halal sources (e.g., pigs).

In Europe and other countries, contents of GMO ingredients are limited, or labeling may be required under the principle that the "right to know" what is in food is a citizen's right. Domestic consumer activist groups initially strongly supported GMO labeling. The issue has become less vocal with the passing of years without recognized major health problems, but continues to be challenged as in current marketing of "natural hormone-free milk" and "organic" milk.

Still, diseases do not follow governmental decrees. The United States does not have mechanisms in place for specifically following food ingredients or additives approved by the FDA after they enter the marketplace as occurs with drugs. If chronic negative effects from long-term consumption of transgenic crops occurred across the broad population, they might not be attributed to the cause for years because hardly anyone is watching. The National Research Council has recognized needs for in-market follow-up of certain types of new foods [13] and has suggested legislation.

Drivers and Tools for the Future

The basic driver for the biotechnology evolution is rapid growth of the population and its needs. World population doubled (from 3 to 6 billion persons) between 1960 and 1999. In theory, this meant learning to grow as much food in 39 years as was learned during the first 10,000 years of agriculture. In practice, much more was accomplished, including increased life expectancy and improved health and living standards. A slowdown in population growth is expected. Currently, few forecasts venture beyond a world population of nine billion in 2043, still a sizeable increase. Significant quantities of easily accessed fossil energy (petroleum, gas, and coal) and minerals already have been exhausted. With high population densities, solutions to disposal of wastes can no longer be dilution in air, water, or landfills. But, waste disposal and air and water reclamation, by known means, are energy-intensive and place additional loads on resources. There seems to be little choice but to more completely harness recurring energy sources such as sunshine, wind, falling water, and possibly ocean tides and to produce more recyclable food, textiles, building materials, coatings, plastics, and moldable materials through applied biotechnology. Whereas in the past, chemical processing options often were chosen because they are faster, enzymatic routes are more likely in the future because they require less energy. But we must become better applied biophysical chemists to implement such changes.

Our tools include the already discussed abilities to tailor transgenic plants, animals, microorganisms, enzymes, and pharmaceuticals to our needs. We live at a time when communications and transportation are developing rapidly, and the most promising insurance for peace appears to be an international trade so interdependent that rational nations would hesitate before upsetting the balance and linkages by wars. Confidence in the rapidly globalized trade requires reliable trading standards, uniform analytical methods and quality control practices such as ISO 9001–2000 14001–2004, and appropriate enforcement by exporting nations.

The digital computer age has brought us sophisticated analytical instruments and computation abilities to delve even deeper into basic sciences. It also has enabled close monitoring and feedback control of processes, even in remote inhospitable atmospheres, to ensure that operations, and materials and products storage, are continuing as intended.

Government policies do not always turn out as expected. It long was common practice in some countries to direct uneducated workers to production agriculture and to hand operations in food processing. But modern crop and animal production facilities are capital-intensive and require skilled operators and knowledgeable supervisors. The same is true in crop, animal, and seafood processing, where machines and sorters never tire and prove more effective than hand laborers. Where sanitation is critical, quality usually improves as fewer hands touch the product. Whereas some governments in developing nations have sought to create manual jobs in processing foods for local consumption, traders, available alternate suppliers, and eventually consumers will decide what will be carried to the international marketplace.

Many industries have adopted integrated planning. It is a management by objective (MBO)-type technique, often without a name. Integrated pest management (IPM) has been one of the most successful examples. The term was introduced in 1967 by R.F. Smith and R. van den Bosch and formalized by the US National Academy of Sciences in1969 [14]. The initial objective was to find ways to reduce amounts of insecticides used on cotton. As it developed,

implementation included: (1) an exhaustive review of the factors leading to application of insecticides, and opportunities for using other options; (2) removal of refuges such as crop stubbles, which protect insects during winter, and host plants in fencerows; (3) consideration of life cycles of beneficial insects, which prey on the species to be controlled by the insecticide; and (4) realization that major crop damage occurs only after several generations of insect build-up, and relatively little is accomplished by spraying early, except killing beneficial insects that would help in control. The solution is closely monitoring numbers of undesirable insects on the crop and delaying spraying until costs are warranted by benefits. Significant reductions occurred in amounts and costs of insecticides used in applying these simple concepts. The principle has caught on quickly. Today, IPM systems are also used to control insects in schools, libraries, museums of natural history, and operations. But the main principles, (1) review the holistic system and interactions between alternative options and (2) continue to monitor the problem closely, but take remedial action only when benefits warrant the costs, are applicable to other management situations. Such approaches have led to energy savings, reduction of waste disposal costs, improvement of oil yield and stability, and increased profits in the edible fats and oils industry.

Biotechnology Practices in Soybean Production and Processing

A brief summary of biotechnology practices in modern production of soybean and oil follows. Farmers select planting seeds, which have been produced by breeding, hybridization, or transgenic means already described. Most varieties grown are "daylight determinant," and flower and produce seed only when day lengths shorten to their optimum photoperiod. The United States has been divided into ten parallel regions for soybean, each about 100–150 miles wide in latitude. Local dealers stock seed of the maturity group appropriate for their region [15]. The soil is prepared by plowing-harrowing, or disk harrowing, for planting. In "no-till" planting, the seed is drilled into the stubble of the previous year's crop, but an herbicide "burn-down" is applied first if weeds are obvious before planting. Farmers typically inoculate the seed with commercial rhizobia inoculum (*Rhizobium* and *Bradyrhizobium* genera) if soybean has not been grown recently or to refresh inoculation. These bacteria establish a symbiotic relationship and create root nodules on the legume which convert atmospheric nitrogen to ammonia usable by the plant. Efforts to induce nitrogen-fixing nodulation in the grasses (specifically corn) have been unsuccessful, but inoculation has been extended to other legume crops.

Farmers also may deposit fertilizer near the seed when planting, or drill it in the previous fall. Depths of topsoil and moisture levels vary in fields in slightly rolling country. The effects often can be seen by aerial and infrared photography. Programs for mapping fertility levels within fields by global positioning systems (GPS), and adjusting rates of fertilizer application as planting–fertilizing equipment moves through the field, have become available. GPS is also used for variable-rate application of other chemicals [16] and for autoguidance of tractors across fields with four-inch precision in strip tilling and planting of close rows [17].

Plant nutrition, seasonal temperatures, and moisture availability affect final composition of soybean and yield/acre. Plants typically create the protein systems in their seed first and add energy reserves (oil in the case of soybean) later before maturing and dying. If the plant is lightly frosted before maturing of the oilseed, it may reinitiate growth and deposit additional chlorophyll in the seed. This compound is oil-soluble and a very strong light-catalyzed prooxidant, which reduces shelf life of bottled oil. Additional efforts must be made to remove chlorophyll by absorption with bleaching clays and silica gels during oil refining. During the summer, the farmer may decide to speculate on the soybean futures market and commit some of the expected crop at a guaranteed price to ensure recovery of at least critical expenses.

Harvest (combining) of soybean continues in some localities even after light snowfall, although quality (as monitored by free fatty acids increases) and market value decrease. Price is also discounted for water-mottled soybean. Whenever soybean is harvested, drying to the 0.65–0.75 a_W range puts it into a dormant state and maximizes the remaining storage life. Drying can occur at the farm, at elevators, or at a processor's holding facilities. Seeds continue to respire in the dormant state and must be aerated, the amount dependent on storage temperature.

By law, organic foods should not be made from transgenic seed. Organic growers cannot use chemical fertilizers, herbicides, or insecticides, but "organic pesticides" are available. Standards may exist about acceptable previous crops on the same soil. Precautions must be taken to ensure the crop is not contaminated with transgenic seed and is identity-preserved (IP) during trading and shipping. The Agricultural Marketing Service of USDA supervises organic foods as a marketing alternative and regulates the National Organic Program.

Although soybean is the world's major oil currently, it is the secondary product after feed meals and food proteins in percent of weight yield and value per bushel processed. Oil extraction processes should not degrade the more valuable protein fractions, which usually is not a problem with soybean processed to make feed protein meals. Enzymatic degradations during extraction and processing of oils can

include: (1) a variety of lipases, which can cleave free fatty acids from triglycerides and reduce yield of saleable neutral oil; (2) phospholipases, which can render the phosphatides (lecithins) water-insoluble, difficult to remove when refining, and shorten oil frying life; and (3) two lipoxygenases which can cause off-flavors in refined oils. Maintaining the seed at low water activity, equivalent to about 10–11% during processing, is helpful in slowing enzyme activity. The ideal approach would be to inactivate the enzymes very early in soybean processing, and effectiveness of such processing already has been demonstrated in small extraction plants.

Enzymes have been used to assist oil extraction and in *degumming* (phosphatides removal), splitting fatty acids from trigly-cerides, *interesterification* (rearranging fatty acids on triglyceride molecules), and preparation of specialty oils. These processes are described later in this chapter.

Introduction to Lipids

Fats and oils predominantly *are triesters* (triglycerides, triacylglycerols, TAG) of glycerol and aliphatic fatty acids containing up to 22 carbon atoms. *Waxes are esters of long-chain fatty acids,* usually containing 24–28 carbon atoms, with long-chain primary alcohols (16–36 carbon atoms) or with alcohols of the steroid group [18].

Fats and oils are members of a broader group of chemical substances called *lipids*, which has been classified by the National Research Council into: (1) nonpolar lipids, including esters of fatty acids (triacylglycerols and cholesteryl esters) that are virtually insoluble in water, but soluble in most organic solvents and enter metabolic pathways only after hydrolysis; and (2) polar or amphipathic lipids, including fatty acids, cholesterol, sphingolipids, and glycerolphospholipids (mainly lecithins). The term phospholipids (phosphatides) includes lecithins and sphingomyelins [19]. Other minor natural compounds, also extracted by low-polarity organic solvents, include fat-soluble vitamins, colors, and flavors.

Fats and oils have major roles in human nutrition. They are concentrated dietary sources of energy, providing approximately 9 kcal/g when metabolized compared with 4 kcal/g for carbohydrates and proteins, and account for about 36% of domestic caloric intake per capita [19]. Dietary lipids also can provide essential molecular structures that are synthesized by the body into compounds required for selective functioning of cell membranes and regulation of life processes.

Fats and oils modify product texture in preparation of foods, serve as heat transfer media in food frying, carry flavors, colors, and oil-soluble vitamins, improve mouthfeel, provide a sensation of product richness, and induce satiety. They are used as energy sources in feeds for domesticated animals, and as components of many industrial products, including soaps and detergents, lubricants, plastics and protective coatings, and printing inks, and as carriers of pesticides for aerial spraying, for controlling grain dust, and as feedstocks for manufacturing chemicals. Considerable public interest has developed in the last two decades in replenishable biodegradable carbon sources and in liquid fuels such as biodiesel.

Recent Fats and Oils Industry Changes

Although many chemistry and processing principles have long been established, the industry has undergone major changes in the last three decades, with many starting in the mid-1980s. Rising costs of energy have led to more efficient equipment designs and to the installation of heat recapture systems throughout modern extraction plants and refineries. In the United States, Occupational Safety and Health Protection Agency (OSHA) regulations to prevent injuries and protect the health of workers have led to increased use of safety guards, dust collection systems with shrouding of equipment and improved ventilation, oversight of workers entering dangerous areas such as bins, and periodic checks for hearing loss. Redesigning and retrofitting the equipment was expensive. Process control computers became available concurrently in the early 1990s, and many companies chose instead to install robots in health- and safety-risk areas and to automate processes for operation from control rooms. The few people now seen on extraction plant and refinery floors are mainly repair and cleaning personnel, with hardly any "operators." With computers making process adjustments, product quality, defined as "uniformity," typically has improved.

Environmental Protection Agency (EPA) air emissions regulations have led to increased dust controls and to reduced solvent losses in extraction plants. Regulations on the discharge of polluting process streams into public waterways have led to containment and treatment where required of rain runoff from grain storage and processing properties and even from employee parking lots. Silica gel adsorption (modified caustic refining) processes have been developed to avoid production of waste waters in refining oils and problems associated with their disposal. Similar changes are being adopted at various rates throughout the world.

The effects of economic development loans and private investments in developing countries in the 1960–1990 era have matured and are changing the global fats and oils industry. World production of soybean has increased 7.5 times since 1960, with approximately 44% of the world's crop now entering global trade as soybean, meal, and oil [20].

The growth of palm oil production has been even more spectacular. Hardly known as a crop after World War II, palm oil production increased nearly 21 times since 1960. World production of palm oil has surpassed that of soybean oil. Currently, the total world production of soybean oil is 42.00 million metric tons, whereas palm oil is 47.47 million metric tons (2010/2011). This has brought equatorial countries such as Malaysia and Indonesia into the group of leading edible oil producing and exporting nations. Establishment of trading rules, product definitions and standards, and analytical procedures for the erupting world market also has been part of the technical progress.

Strong competition in the world's oilseeds market, and concerns about the environment, have refocused interest in the United States on *nonfood-nonfeed uses* of crops, including biodegradable applications, renewable hydrocarbon sources, including liquid fuels, and *chemurgy,* the use of agricultural crops as chemicals feed stocks [21]. Nor is the United States alone in the current movement. Germany, Hungary, France, and other European countries, whose climates are too cold for raising soybean or oil palm but can raise rapeseed, recently have installed biodiesel production facilities.

AOCS, an Information Source

This chapter cannot summarize advances in all related technologies and concentrates on current major fats and oils extraction, refining, and utilization practices. The reader may need to browse the Internet for commercial information and computer-based technical abstract services for research reports. Much of the world's research on fats and oils processing and utilization is reported in the *Journal of the American Oil Chemists' Society* (*JAOCS*) published by the AOCS Press, an activity of AOCS (An International Society for the Science and Technology of Fats, Oils and Related Materials), Champaign, Illinois. The AOCS Press also publishes proceedings of selected Society conferences, a broad variety of related books, and the following journals: *INFORM*, a monthly business, news, and scientific publication addressed to professionals interested in the science and technology of fats and oils, surfactants, detergents, proteins, oleochemicals, and related substances; *Oil Mill Gazetteer,* a monthly news magazine for oil extraction and refining plants; *Lipids,* a monthly journal on basic chemistry and nutrition of lipids; *Journal of Surfactants and Detergents* (*JDS*), a quarterly science and news journal on the practical and theoretical aspects of oleochemical and petrochemical surfactants, soaps, and detergents.

The Technical Services function of AOCS establishes, revises, and annually updates "AOCS Methods," the *Official Methods and Recommended Practices of the American Oil Chemists Society* [22] for fats, oils, and soap technology; *Spanish AOCS Methods,* a Spanish translation of the more commonly used AOCS Methods; and *Physical and Chemical Characteristics of Oils, Fats and Waxes*. Leaders of the methods development committees coordinate closely with AOAC International (formerly the Association of Official Analytical Chemists). AOCS Methods are recognized as "Official Methods" in US FDA activities and when litigation becomes necessary in industry trade. Additionally, the Technical Services function operates a Laboratory Proficiency Program (formerly the *Smalley Check Sample Program*) and oversees distribution and statistical analysis of 30 different series of basic laboratory quality assurance/quality control test samples. Certification as AOCS Approved Chemists, or as AOCS Certified Laboratories, and successful participation in the Laboratory Proficiency Program, is expected for industry arbitrators and referees.

Nutrition and Health Implications

Comments on fats and oils in nutrition and human and animal health are limited in this chapter, primarily because of frequent changes in advice given, but regulations are summarized. Three classes of foods exist: generally recognized as safe (GRAS) foods and ingredients, food additives, and food supplements. All are monitored by the FDA, but at different levels of review; meat products are monitored by the Federal Safety Inspection Service (FSIS) of the USDA. Within the FDA, foods are under the jurisdiction of the Center for Food Safety and Applied Nutrition (CFSAN), and animal feeds under the Center for Veterinary Medicine (CVM). Readers are referred to other authorities [23, 24], and FDA and USDA Web-sites, for more details about US food and feed regulatory systems.

The US government does not guarantee the safety of foods; it is the responsibility of respective manufacturers, and ultimately is enforced by torts litigation. USFDA-CFSAN decides whether a food or ingredient is listed as GRAS (useable without restriction), or as a food additive (useable in limited applications and amounts), on the basis of thorough review of applications and may request additional tests for proposed additives. *Food supplements* (vitamins, minerals, botanicals, plant extracts, etc.) may be marketed directly by the manufacturer, but the FDA has the power to check on underlying safety data and to remove unsafe products from the market. Food supplements also include *nutraceuticals, functional foods,* and *designer foods*—groups of products consumed for expected health benefits aside from nutrition and medication. These products became a major growth market in the last decade, but at times have been launched with limited documentation, and possibly

knowledge about effectiveness. The FDA earlier held that food and drugs were separate classifications and did not allow health claims to be made for food products until the 1990s. Congressional legislation, including the Nutrition Labeling and Education Act of 1990, Dietary Supplement Health and Education Act of 1994, and the Food and Drug Administration Modernization Act of 1997, led to today's practices of allowing health claims, provided specific requirements are met [25].

A basic problem when considering food safety is the wide range of genetics, physiological ages, and individual health status in the United States population of nearly 300 million. Almost any product may prove adverse for an unpredictable portion of the population, especially if consumed in large quantities.

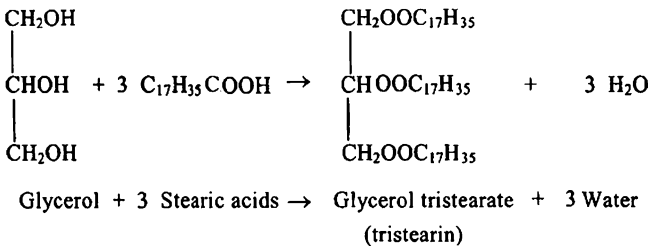
Many of the extraction, concentration, and purification techniques and equipment used in preparation of nutraceuticals originated in the vegetable oils and proteins processing industries. Byproduct streams often are further purified for this market.

Nomenclature and Molecular Structures

General

The choice of the term "oil" or "fat" usually is based on tradition and the physical state of the material. Generally, *oils* are liquid at ambient temperatures, and *fats* are semi-solid mixtures of crystals in oil. *Fats* often are of animal origin (beef tallow, pork lard, and butter fat) or *hardened* (hydrogenated, interesterified, or thermally fractionated) vegetable oils, whereas oils are extracted from plant seeds or tissues or fish. In English-speaking countries outside the United States, oils liquid at room temperature sometimes are called *soft oils,* and those hard or pasty are called *hard oils*. Nutritionists generally use "fats" for solids or liquids.

Over 95% of the weight of most extracted/separated food fats are TAG (triacylglycerols or triglycerides) formed by the enzymatic combination of glycerol (a trihydric alcohol) with three fatty acids also yielding one molecule of water for each ester linkage:



The reaction is reversible and favored by the presence of moisture and catalysts including lipases, alkalis, and alkaline metals. In the oleochemicals industry, TAG are split by high-pressure steam. Unassociated fatty acids are called free fatty acids or FFA.

Fatty Acids

Fatty acids are the building blocks of TAG. More than 90% of fatty acids have an even number of carbon atoms and are in aliphatic chains ranging from 4 to 22 carbons in length. The major fatty acid synthesis pathway is production of stearic acid (18 carbons) after which separate desaturase systems introduce 1, 2, or 3 unsaturated (double) bonds. Additional enzymes become active in elongating the chain as needed. Shorter fatty acids also are produced. Trace amounts of odd-number carbon fatty acids are found in most fats and also have been synthesized for research purposes. Microorganisms frequently produce odd-number carbon fatty acids, with heptadecenoic (17 carbon) acid a major component of *Candida tropicalis* yeast fat. Up to 8% C_{17} fatty acids have been found in milk and meat fats of ruminants (cattle, sheep, goats) and are of rumen microbe origin.

The names of common fatty acids under several conventions, carbon numbers, and selected properties are shown in Table 34.1. The common (trivial) names of some fatty acids are of long standing and often indicate the initial source studied. As examples: butyric acid is a major component of butter flavor; the 6, 8, and 10 saturated fatty acids have been called the *goaty acids* because they impart the characteristic flavors of goat and sheep milks and their cheeses. The terms *olein* and *stearin* were applied to the liquid and solid fractions, respectively, of tallow separated by pressing in early manufacture of oleomargarine and compounded shortenings. The iodine value (IV) is an indicator of the unsaturation of a fatty acid or fat/oil. It is determined by AOCS Method Tg 1a-64 or Cd 1–25, respectively: the higher the IV, the more unsaturated the fat and the lower the melting point.

Fatty acids sometimes are designated by the number of carbon atoms in the chain, followed by a colon with additional numbers indicating the number of double bonds. In the 18-carbon series, C18:0, C18:1, C18:2, and C18:3 represent *stearic, oleic, linoleic*, and *linolenic* acids, respectively. One- or two-letter abbreviations sometimes are used, with these acids designated as St, O, L, and Ln, respectively.

Under the most common convention, fatty acids are named on the basis of the number of carbon atoms, starting with the terminal carboxyl (-COOH) carbon as number "1."

Table 34.1 Names and characteristics of some important fatty acids

Carbon atoms and abbreviations	Common name	Symbol	Systematic name	Melting point (°C)	Iodine value	Common sources
Saturated fatty acids						
3:0	Propionic	–	Propanoic	−20.8	–	Bacterial fermentation
4:0	Butyric	B	Butanoic	−7.9	–	Milk fats
5:0	Valeric	–	Pentanoic	−33.8	–	Bacterial fermentation
5:0	Isovaleric	–	3-Methylbutanoic	−51.0	–	Dolphin and porpoise fats
6:0	Caproic	H	Hexanoic	−3.4	–	Milk fats, some seed oils
8:0	Caprylic	OC	Octanoic	16.7	–	Milk fats, *Palmae* seed oils
10:0	Capric	D	Decanoic	31.6	–	Sheep and goat milk, palm seed oils, sperm head oil
12:0	Lauric	La	Dodecanoic	44.2	–	Coconut oil
14:0	Myristic	M	Tetradecanoic	54.4	–	Palm and coconut oils
16:0	Palmitic	P	Hexadecanoic	62.9	–	Palm oil, most oilseeds and animal fats
18:0	Stearic	St	Octadecanoic	69.6	–	Animal fats
19:0	Tuberculostearic	–	10-Methylstearic	11.0	–	Tubercle bacillus lipids
20:0	Arachidic	Ad	Eicosanoic	75.4	–	Some animal fats
22:0	Behenic	–	Docosanoic	81.0	–	Peanut and various other seed oils
24:0	Lignoceric	–	Tetracosanoic	84.2	–	Minor amounts in some seed oils
26:0	Cerotic	–	Hexacosanoic	87.8	–	Plant waxes
28:0	Montanic	–	Octacosanoic	90.9	–	Beeswax and other waxes
30:0	Mellisic	–	Triacontanoic	93.6	–	Beeswax and other waxes
Unsaturated fatty acids						
10:1	Caproleic	–	9-Decenoic	–	149.1	Milk fats
10:2	Stillingic	–	2,4-Decadienoic	–	–	*Stillingia* oil
12:1	Lauroleic	–	2-Dodecenoic	–	128.0	Butterfat
14:1	Myristoleic	–	9-Tetradecenoic	18.5	112.1	Some feed fats, milk fats
16:1 (*n*–7)	Palmitoleic	–	9-Hexadecenoic	0.5	99.8	Many fats and marine oils
16:3	Hiragonic	–	6,10,14-Hexadecatrienoic	–	–	Sardine oil
17:1	–	–	9-Heptadecenoic	14.0	–	*Candida tropicallis* yeast
18:1 (t-oleic)	Elaidic	–	9-Octadecenoic	43.7	–	Butterfat
18:1 (*n*–9)	Oleic		9-Octadecenoic	16.3	89.9	Almost all fats and oils
18:1	Petroselinic	–	6-Octadecenoic	30–33	–	Parsley seed oil
18:1 (*n*–7)	Vaccenic	–	11-Octadecenoic	44.0	–	Butterfat, seed oils
18:2 (*n*–6)	Linoleic	Lo	9,12-Octadecadienoic	−6.5	181.0	Most vegetable oils
18:3 (*n*–6)	(gamma) Linolenic	–	6,9,12-Octadecatrienoic	–	–	(Omega-6); Evening primrose, borage, vegetable oils
18:3(*t*)	Eleostearic	–	9,11,13-Octadecatrienoic	–	–	Tung oil
18:3 (*n*-3)	(alpha)Linolenic	Ln	9,12,15-Octadecatrienoic	−12.8	273.5	(Omega-3); Linseed, soybean, canola, other vegetable oils
20:1	Gadoleic	–	11-Eicosenoic	23–24	81.8	Some fish oils
20:3 (*n*–9)	Eicosatrienoic		5,8,11-Eicosatrienoic	–	–	Brain phospholipids
20:3 (*n*–6)	Dihomo-γ linolenic		8,11,14-Eicosatrienoic	–	–	Shark liver oil
20:5 (*n*–3)	EPA		5,8,11,14,17-Eicosapentanoic	−33.5	75.0	Fish, plants
22:1	Erucic	E	13-Docosenoic	34	–	Rapeseed oil
22:2			13,16-Docosadienoic	–	–	
22:5 (*n*–3)	DPA		7,10,13,16,19-Docosapentaneoic	–	–	Fish oils
22:6 (*n*–3)	DHA		4,7,10,13,16,19-Docosahexaenoic	–	–	Cooler climate fish oils
Fatty acids of more unusual structure						
18	Chaulmoogric	–	13,(2-Cyclopentenyl) tridecanoic	68.5	90.5	*Chaulmoogra* oil
18	Malvalic	–	8,9-Methylene-8-heptadecenoic	–	–	*Malvaceae* seeds, cottonseed
18	Ricinoleic	–	12-Hydroxy-9-octadecenoic	5.5	86.0	Castor oil
18	Vernolic	–	12,13-Epoxy-9-octadecenoic	30–31	–	Some *Compositae* seeds
19	Sterculic	–	9,10-Methylene-9-octadecenoic	–	–	*Sterculiaceae* seeds, cottonseed

(continued)

Table 34.1 (continued)

Carbon atoms and abbreviations	Common name	Symbol	Systematic name	Melting point (°C)	Iodine value	Common sources
20	Arachidonic	–	5,8,11,14-Eicosatetraenoic	−49.5	333.5	Lard
20	–	–	5,8,11,14,17-Eicosapentaenoic	–	–	Some fish oil
20	Lesquerolic	–	14-Hydroxy-11-Eicosenoic	–	–	*Lesquerella* seed oil
22	–	–	4,7,10,13,16,19-Docosahexaenoic	–	–	Some fish oil

The terminal letter *e* of the respective alkane hydrocarbon is replaced with *oic* to indicate an acid; thus:

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Octane

8 7 6 5 4 3 2 1

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH$

Octanoic acid

The suffix *dioic is* used if the acid contains two carboxyl groups.

Occasionally in the literature, the carboxyl unit is regarded as a group substituted for hydrogen. In this case, the number 1 location is moved one position away from the reactive end, and the suffix *carboxylic* acid is added:

5 4 3 2 1

$CH_3CH_2CH_2CH_2CH_2COOH$

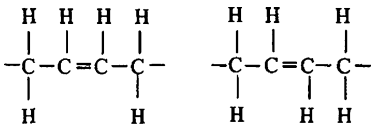
1 - Pentanecarboxylic acid

(hexanoic acid)

(caproic acid)

A double bond between two carbon atoms indicates the site, and possibly type, of hydrogen unsaturation. When double bonds are present, the suffix *anoic* is changed to *enoic, dienoic*, or *trienoic* to indicate the number of bonds. The location of the first carbon in the double bond is indicated by a number preceding the systemic name. Under International Union of Pure and Applied Chemistry (IUPAC) convention, stearic, oleic, linoleic, and linolenic acids are called octadecanoic, 9-octadecenoic, 9,12-octadecadienoic, and 9,12,15-octadecatrienoic acids, respectively.

The 3D geometric configuration of hydrogens at double bonds is indicated on paper by the Latin prefixes *cis* (both hydrogens on one side) and *trans* (hydrogens across from each other). Linoleic acid, with the *cis* configuration in both double bonds, is called *cis*-9, *cis*-12-octadecadienoic acid. Most fatty acids occur in nature in the *cis* form. Oleic acid is in the *cis* configuration and the corresponding *trans* form is called elaidic acid.



cis *trans*

Increasing the number of double bonds lowers the melting point of the fatty acid from its fully or partially saturated form. Double bonds also are the sites of oxidation initiation on free fatty acids and within triacylglycerols. Creating a *trans* bond by hydrogenation increases the melting point, but not as much as full saturation.

Locations of the double bonds, and especially the last double bond in long-chain polyunsaturated fatty acids, are of special interest. Whereas chemists traditionally count with the carboxyl carbon (-COOH) assigned number "1," biochemists and nutritionists assign number "1" to the methyl carbon (CH_3^-). Thus, linoleic acid (9,12-octadecadienoic acid), known as C18:2 to a chemist, carries the same trivial name for biochemists but is known as C 18:2 ω-6 or C 18:2 *n*-6 with *omega* or *n* signifying "count from the methyl carbon." From a nutrition viewpoint, four families of fatty acids (*n*-7, *n*-9, *n*-6, and *n*-3) exist. Members of the *n*-7 and *n*-9 families generally are synthesized by each species as needed, but members of the *n*-6 and *n*-3 families may be dietary essential either because the species is unable to synthesize the fatty acid, or metabolic mechanisms are impaired in specific individuals. Plants, including plankton, are the ultimate source of dietary essential fatty acids (EFAs). Humans and most animals are considered to require linoleic and linolenic acids (C 18:2*n*-6 and C 18:3*n*-3, respectively). Fish vary by species, with carnivorous members like the salmonoids (salmon and trout) requiring EPA (C20:5*n*-3;5,8,11,14,17-eicosapentaenoic acid) and DHA (C22:6*n*-3;4,7,10,13,16,19-docosahexaenoic acid) when raised in captivity [26].

Contents of individual fatty acids in the fat of a species can vary by over 100%. Table 34.2 summarizes general fatty acids contents of the major edible fats and oils, and Table 34.3 does likewise for industrial fats and oils.

On a global basis for all species, oils produced in the tropics are more completely saturated and have the highest

Table 34.2 Fatty acid composition of some edible oils and fats[a]

Source	<14:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1	22:0	22:1	24:0	24:1
Almond oil	–	0.0	6.5	0.6	1.7	69.4	17.4	–	–	–	–	–	–	–
Avocado oil	–	–	11.0	3.4	0.7	71.5	12.0	1.5	–	–	–	–	–	–
Barley bran oil	–	0.5	10.8	0.2	1.0	17.8	55.3	4.4	–	–	–	–	–	–
Borage oil	–	–	11.3	–	3.7	16.3	38.1	23.0	0.2	3.9	–	2.4	–	1.4
Buffalo gourd seed oil	–	–	11.8	–	3.5	21.9	60.6	0.0	0.0	–	–	–	–	–
Butter fat	23.8	8.2	21.3	1.8	9.8	20.4	1.8	1.2	–	–	–	–	–	–
Canola oil[b]	–	–	4.8	0.5	1.6	53.8	22.1	11.1	1.1	1.5	0.3	0.1	0.1	–
Cherry pit oil	–	–	7.8	0.4	2.4	43.9	44.8	0.5	0.7	–	–	–	–	–
Cocoa butter	–	0.1	25.4	0.2	33.2	32.6	2.8	0.1	–	0.0	–	–	–	–
Coconut oil	58.7	16.8	8.2	–	2.8	5.8	1.8	–	–	–	–	–	–	–
Corn oil	0.0	0.0	10.9	–	1.8	24.2	58.0	0.7	–	–	–	–	–	–
Cottonseed oil	–	0.8	22.7	0.8	2.3	17.0	51.5	0.2	–	–	–	–	–	–
Evening primrose oil	–	–	8.5	–	2.5	8.5	72.5	11.0	–	–	–	–	–	–
Fish (manhaden) oil	–	9.6	20.5	12.6	3.3	11.0	0.7	1.6	0.3	–	–	0.8	–	–
Grapeseed oil	–	0.1	6.7	0.3	2.7	15.8	69.6	0.1	–	–	–	–	–	–
Illipe butter	–	–	23.7	–	19.3	43.3	13.7	–	–	–	–	–	–	–
Lard	0.5	1.3	23.8	2.7	13.5	41.2	10.2	1.0	–	1.0	–	–	–	–
Lupine oil	–	–	8.3	–	2.5	55.0	17.7	9.3	–	–	–	–	–	–
Macademia nut oil	–	0.6	8.5	21.7	3.7	56.0	1.7	–	–	1.4	–	–	–	–
Mango kernel oil	–	–	7.6	–	36.0	49.4	5.0	0.5	1.4	–	–	–	–	–
Mustard seed oil	–	0.1	1.9	0.3	0.1	17.7	9.1	0.5	0.6	3.91	1.8	55.1	0.2	1.9
Okra seed oil	–	0.2	33.7	0.6	3.3	17.9	42.2	0.2	0.1	–	0.2	–	–	–
Olive oil	–	0.0	11.0	0.8	2.2	72.5	7.9	0.6	–	–	–	–	–	–
Palm oil	0.1	1.0	43.5	0.3	4.3	36.6	9.1	0.2	–	0.1	–	–	–	–
Palm kernel oil	54.2	16.4	8.1	–	2.8	11.4	1.6	–	–	–	–	–	–	–
Peanut oil	–	0.1	9.5	0.1	2.2	44.8	32.0	–	–	1.3	–	–	1.8	–
Rapeseed oil[c]	–	–	1.7	–	0.9	12.3	12.7	7.6	1.2	5.8	0.9	59.4	0.5	1.6
Rice bran oil	–	0.7	16.9	0.2	1.6	39.1	33.4	1.6	–	–	–	–	–	–
Safflower oil	–	0.1	6.2	0.4	2.2	11.7	74.1	0.4	–	–	–	–	–	–
Safflower oil[d]	–	–	4.8	–	1.3	75.3	14.2	–	–	–	–	–	–	–
Sal seed oil	–	–	5.3	–	34.0	49.1	3.8	3.3	4.0	–	–	–	–	–
Sesame oil	–	–	8.9	0.2	4.8	39.3	41.3	0.3	–	0.2	–	–	–	–
Shea butter	1.7	0.1	4.4	0.1	38.8	43.5	4.9	0.3	–	0.0	–	–	–	–
Soybean oil	–	0.1	10.3	0.2	3.8	22.3	51.0	6.8	–	–	–	–	–	–
Sunflower oil[e]	–	–	7.0		5.0	19.0	68.0	1.0	–	–	–	–	–	–
Sunflower oil[f]	–		4.0	–	5.0	65.0	26.0	–	–	–	–	–	–	–
Tallow	0.9	3.7	24.9	4.2	18.9	36.0	3.1	0.6	–	0.3	–	–	–	–
Teaseed oil	0.1	0.1	17.5	0.5	3.1	49.9	22.2	0.7	–	1.0	–	–	–	–
Tomato seed oil	–	0.2	15.0	0.5	4.4	21.9	50.8	2.3	–	–	–	–	–	–
Walnut oil	–	–	7.0	0.1	2.0	22.2	0.4	52.9	10.4	–	–	–	–	–
Wild cucurbit oil	–	–	19.0	–	–	34.0	47.0	15.0	–	–	–	–	–	–

[a]These are average values from recent years' crops
[b]Low-erucic-acid variety rapeseed
[c]High-erucic-acid variety
[d]High-oleic variety
[e]Maturing in coller climates
[f]Mid-oleic sunflower seed

melting points, with melting points decreasing with distance from the equator (in north and south latitudes). Many dietary fatty acids are transposed from plant or plankton feed sources to body tissues, and fish oils from the Arctic and Antarctic species generally melt at lower temperatures than those from the tropics. Many oilseed species are *daylight determinate;* that is, they require a specific number of hours of sunlight to blossom and produce seed. Thus, a plant

Table 34.3 Fatty acid composition of some industrial oils and fats[a]

Source	<14:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1	22:0	22:1	22:2	24:1
Caster oil[b]	–	–	1.1	0.2	1.0	3.3	3.6	0.32	0.4	–	–	–	–	–
Chinese tallow	1.3	2.1	65.0	–	4.4	22.5	0.8	–	–	–	–	–	–	–
Crambe oil	–	–	2.0	0.4	0.4	16.9	8.6	6.4	0.5	3.2	2.0	57.2	–	1.4
Crepsis foetida oil[c]	–	0.1	4.8	–	2.9	4.3	27.8	–	–	0.3	–	–	–	–
Croton oil	2.5	5.4	6.2	0.2	3.2	15.8	49.4	3.0	2.9	8.9	0.2	0.6	–	–
Cuphea oil	–	76.4	7.8	2.4	–	0.7	5.9	6.9	0.1	–	–	–	–	–
Jojoba oil	–	–	1.0	–	–	9.0	–	–	–	70.7	–	16.3	–	3.0
Lesquerella seed oil	–	1.4	1.4	2.0	17.6	7.9	13.2	–	52.5	–	–	–	2.7	–
Linseed oil	–	–	5.3	–	4.1	20.2	12.7	53.3	–	–	–	–	–	–
Meadowfoam oil	–	–	–	–	–	–	–	–	–	64.5	–	18.5	13.5	–
Neatsfoot oil	–	0.7	16.9	–	2.7	64.4	2.3	0.7	0.1	–	–	–	–	–
Oitica oil[d]	–	–	7.0	–	5.0	6.0	–	–	–	–	–	–	–	–
Rapeseed[e]	–	0.1	2.6	0.3	0.9	11.2	12.8	8.6	–	7.5	–	48.1	–	–
Rubber seed oil	–	0.2	19.1	–	17.8	24.5	30.5	2.4	–	0.1	0.9	0.4	–	–
Stokes aster oil[f]	–	–	2.8	–	0.9	7.0	16.5	–	–	–	–	–	–	–
Tall oil	–	–	–	–	–	50.0	7.0	41.0	–	–	–	–	–	–
Tung oil	–	–	3.1	–	2.1	11.2	14.6	69.0	–	–	–	–	–	–
Veronia seed oil[g]	–	–	2.7	–	1.3	2.0	8.8	0.4	–	–	–	–	–	–
Whale oil	–	3.3	8.1	26.9	1.1	33.3	–	–	–	10.9	–	2.2	–	–

[a]These are average values from recent years' crops
[b]Contains 89.2% ricinoleic and 1.4% dihydroxystearic acids
[c]Contains 59.8% crepenynic acid
[d]Contains 78.0% licanic acid and 4.0% hydroxy acids
[e]High-erucic-acid variety
[f]Contains 71.3% vernolic acid
[g]Contains 78.5% vernolic acid and 5.8% hydroxy fatty acids

grown from seed adapted to another latitude may sprout and produce much foliage, but not flower and produce seed. Earlier soybean and sesame varieties were mainly light determinate, but indeterminate varieties also exist now.

Each oil has its unique properties and history, as demonstrated by sunflower seed. Sunflowers generally are indeterminate, with the same seed productive in the prairie provinces of Canada and in Mexico. When polyunsaturated oils were promoted in the 1960s and 1970s, United States processors of table oils (for salads and light cooking) purchased only sunflower seed grown north of the 39th parallel in the United States and Canada to maximize the polyunsaturated fatty acids (PUFA) content of their products. Fall seed maturation temperatures in the Northern climates are lower, resulting in higher PUFA and lower monounsaturates (oleic) contents than sunflower seed maturing at the same time in Texas. However, the higher oleic acid oil of Texas seed is less susceptible to oxidation and produces deep-fried foods and snacks with longer shelf lives. If growers in areas of Texas, capable of raising two crops annually, want to produce high-polyunsaturated oil, they merely have to time their second planting for seed to mature in the cooler winter months [27, 28].

Several important changes occurred in the early 1980s. First, oil processors realized that a significant market existed for high-stability oils and began seeking higher oleic acid content oils. Second, the medical community and nutritionists realized that, although PUFA do not cause cancer, they might promote growth of existing cancer cells more than monounsaturated fatty acid (oleic). Emphasis was changed from encouraging consumption of polyunsaturated vegetable oils to reducing fat intake in general, with recommendations that no more than 30% of dietary calories come from fats, of which no more than 10% are saturated (animal, tropical, or hydrogenated) fats [19], with some nutritionists believing that PUFA also be no more than 10%, essentially leaving at least 10% for monounsaturated fat.

The world's traditional monounsaturated fat is olive oil (~70% oleic acid), historically consumed in countries surrounding the Mediterranean Sea, thus the term *Mediterranean Diet*. However, olive oil is expensive and too limited in supply to satisfy the growing popularity of high-oleic acid oils. Thus, US table oil processors turned to importing high-oleic acid content canola oil from Canada. A mid-oleic sunflower seed oil (~65% oleic acid), grown in the northern states, was introduced to the fried foods industry in 2000. High oleic acid varieties of safflower and peanut have been introduced, and a transgenic high-oleic acid soybean was patented in late 2001. Two nontransgenic lines of high-oleic

acid sunflowers, containing 80–82 and 90–92% oleic acid, were developed in the early 1980s, and their oils were marketed as feedstock for oleochemicals production. The venture was not commercially successful. Interest in nontraditional fats/oils sources, including newly domesticated crops, forest oilseeds, bacteria, yeasts, molds, and algae, has increased in recent years. The reader may consult the references and later publications for unusual fatty acids and their occurrence in various sources [29, 30].

Triacylglycerols

Glycerol esterified with one, two, or three fatty acids is found in nature and can be made commercially. The designations monoacylgly-cerol, diacylglycerol, and triacylglycerol (TAG), respectively, now are encouraged in the scientific literature, but the older mono-, di-, and triglyceride terminology is used in commerce. As the number of fatty esters on the glycerin "backbone" decreases, the compound becomes more polar and functionally effective as a surfactant. Mono- and diacylglycerols are further described throughout this chapter.

Triacylglycerols are named in various ways. For example, unsaturated fatty acids sometimes are indicated as U and the saturated as S. If glycerol is completely esterified with stearic acid, the resulting monoacid TAG may be designated as SSS, or, more descriptively as StStSt, tristearin, tristearoylglycerol, or glycerol tristearate.

If more than one species of fatty acid is present, its relative location on the glycerol may be important to its functionality, enzyme susceptibility, and oxidation stability of the fat/oil. Several conventions have been developed to specify arrangements of fatty acids on the glycerol molecule (if known). To avoid confusion from inversion of the 1 and 3 carbon positions, hierarchies have been established to designate the number 1 carbon under the R/S (*rectus-sinisturs*) system [31] and the *sn* (stereospecific numbering) system [32]. In the R/S system, the longest chain fatty acid is assigned to the 1 position, the second longest to 2, and the shortest to 3.

If the positions of fatty acids on the TAG molecule are known, the *sn* system is preferred for identifying their locations: *sn* immediately before the word glycerol, as in 1-stearoyl-2-oleoyl-3-myristoyl-*sn*-glycerol, identifies the respective fatty acids in the 1, 2, and 3 positions; the term *rac* (racemic mixture), as in *rac*-StOM, identifies the middle acid in the 2-glycerol position and the remaining fatty acids are equally divided between the *sn*-1 and *sn*-3 positions; and the term β, as in β-StOM, identifies the middle acid in the 2-glycerol position, but distribution of the other two acids is unknown [33]. Despite international efforts to standardize chemical terminology and abbreviations, a variety is still used, especially in *cis* and *trans* notations.

Table 34.4 Relative rates of oxidation and hydrogenation of fatty acid chains ([a]Modified from Beckman [34])

Fatty acid	Iodine value	Relative oxidation rate	Relative hydrogenation rate
Stearic (18:0)	0	1	0
Oleic (9*cis*-18:1)	90	10	1
Linoleic (9*cis*, 12*cis*-19:2)	181	100	20
Linolenic (9*cis*, 12*cis*, 15*cis*-18:3)	274	150	40

Oxidation

As shown in Table 34.4, oxidation and hydrogenation reactivity of a fatty acid, in free form or as part of a TAG, increases with the number of double bonds [34]. Oxidation of fatty acids and TAG (aldehyde formation, breakdown into shorter chains, and crosslinking to form polymers) is initiated at double-bond sites. However, linoleic acid, C18:2 *n*-6, does not decompose into a mixture of C9, C3, and C6 compounds. Instead, as the molecule starts degrading, positions of the double bonds migrate and provide many opportunities for splitting. Over 250 different breakdown compounds have been found [33, 35–38]. Part of the confusion about oxidation reactions is related to the type present, with light-induced photosensitized singlet oxygen oxidation the fastest [39]. For this reason, removal of photo-sensitizers such as chlorophylls and porphyrins during refining and use of oil is extremely important.

The extent of prior oxidative activity in a fat sample may be estimated by the following tests: Peroxide Value (PV), a titrametric method (AOCS Method Cd 8–53); thiobarbituric acid test (TBA), which measures the presence of malonaldehyde; Anisidine Value-Totox; Kreis test; oxirane test; total and volatile carbonyl compounds content; chromatographic analysis; ultraviolet spectroscopy; fluorescence; and especially organoleptic evaluation. However, the resulting peroxides are unstable and decompose. Peroxide values are not cumulative and, alone, are not always indicative of the extent of earlier oxidation. An oil sample may be starting to degrade or may already have passed through a serious oxidation cycle; thus, age and history of the sample should be considered in forming a conclusion.

Predisposition (susceptibility) to oxidation can be estimated for oils and fats by the Active Oxygen Method (AOM) and Oil Stability Index (OSI) for oils and fats and by the Schall oven test or the oxygen bomb method for fat-containing products. The stability of triglycerides formerly was determined by the AOM (AOCS Method, Cd 12–93), in which heated air was bubbled through a heated liquid sample of the oil or fat, and the number of hours for the sample to reach 100 milliequivalents (meq) of peroxide was recorded. The AOM procedure was put in *surplus status* (still legal but

not preferred) in 1997 and the focus then shifted to the Oil Stability Index (OSI) (AOCS Method, Cd 12b-92). However, AOM is still used in product and purchase specifications and in reports. In the OSI procedure, heated air is bubbled through heated liquid triglycerides and is scrubbed on exiting in a bath of deionized water, whose conductivity is continuously monitored spectrophotometrically. Absorption of polar degradation products is noticed immediately. Whereas the AOM method determines the time for the triglyceride to reach a specific level of oxidation (100 meq peroxide value), OSI determines the *induction period* (time required to exhaust the antioxidant properties), but not oxidation progress in the oil. OSI values always are lower (less time) than AOM values.

Biohydrogenation and Conjugated Linoleic Acids

Rumen microorganisms, in cattle, sheep, and other ruminants, hydrolyze exposed TAG in feeds and metabolize the glycerol. The unsaturated FFA are especially toxic to microorganisms and are *biohydrogenated* by enzymes in microbial cell walls to prevent permeation into their cells, possibly by raising their melting points above rumen temperature. Although polyunsaturated fatty acids can be reduced to stearic acid, rumen hydrogenation often is incomplete. It yields products such as monounsaturated vaccenic acid (*trans*-11-octadecenoic acid; *trans*-11 C18:1) and conjugated linoleic acids (CLA) in which the methylene carbon in the C9 through C13 (—C═C—**C**—C═C—) sequence of linoleic acid is eliminated to form a *conjugated sequence* of double bonds (—C═C—C═C—). The conjugated sequence can appear in many positional isomers along the 18-carbon chain, usually between carbons C6 and C14, resulting in a variety of CLA. Two of the CLA, 9 *cis*-11 *trans*-18:2 (rumenic acid), and 10 *trans*-12 *cis*-octadecadienoic acid have shown physiological activity: the 9,11-*ct* CLA isomer displaying antimutagenic properties, and the 10,12-*tc* CLA isomer displaying antifat deposit and cholesterol-modulating properties [40, 41].

Although more research is needed to document consistent modes of action, capsules containing CLA produced by microbial fermentation are sold as food supplements. CLA in ruminant products are considered natural, and levels of up to 1.5% of the fat in beef and 6% of the fat in cheeses made from spring pasture milk have been reported.

Vaccenic acid and CLA conjugation were once thought not to exist in plant oils, but with improved analytical instruments and methods, are increasingly reported, especially in spices. Conjugation also is an early step in chemical hydrogenation and in initiation of oxidative degradation of fats and oils. Recent research further supports that the majority (78%) of c9,t1 1-CLA in cow's milk is produced exogenously from body fat vaccenic acid in the mammary gland by *delta*-9 desaturase [42].

Recently, in 2008, the United States Food and Drug Administration (FDA) approved CLA containing conjugated *cis* and *trans* double bonds as a food ingredient. The announcement states that CLA is generally regarded as safe for use in foods. This clears the way for CLA, to be used as an ingredient in foods and beverages sold in the United States.

Fatty Acid and Triacylglycerol Melting Characteristics

Body temperatures are approximately 37°C/98.6°F for humans; 38.5–39.5°C/101–103°F for domestic animals; and 40.5–41.5°C/105–107°F for poultry. As shown in Table 34.1, the longest saturated fatty acid that is fluid at these temperatures is caproic (C10:0). All longer saturated fatty acids must be accompanied by lower melting unsaturated fatty acids as in a TAG structure to be fluid. The C18 oleic acid (*c*-9-octadecenoic acid) has a melting point of 16.3°C, the *trans* isomer elaidic acid (*t*-9-octadecenoic acid) melts at 43.7°C, and the biohydrogenated product *trans*-vaccenic acid (*t*-11-octacedenoic acid) melts at 44°C [40].

Fat digestion and absorption in mammals occur in the small intestine and mainly consist of emulsification of TAG by bile salts, lecithin, and agitation, followed by pancreatic lipase cleavage at the 1,3 positions to produce free fatty acids and 2-monoglycerides. These are carried by the bile to surfaces of the microvilli, where they are absorbed through the membranes into the intestinal lymph. While passing through the intestinal epithelial cells, the fatty acids and monoglycerides are resynthesized into new TAG that are transported, mainly in lymph chylomicrons, through the thoracic lymph duct which empties into the circulatory blood [43]. (Although the free fatty acids may be rearranged onto new TAG, fatty acids in the 2-position remain as before.) Animals have various mechanisms for ferrying fatty acids during absorption at the small intestine, and moving fatty acids and triglycerides through their circulatory systems. Readers interested in details are referred to books on medical physiology.

The positioning of fatty acids on the triglyceride chain follows several patterns. If unsaturated fatty acids are limited in availability, nature tends to place them in the number 2 position to obtain the lowest melting point for a plant's triglycerides. If more plentiful, the preferred positions will be 2 and 1 or 3 or both [44]. In contrast, saturated fatty acids are more likely to be in the 2 position in fats of warm-blooded animals, with palmitic acid in the 2 position in (pork) lard as an example.

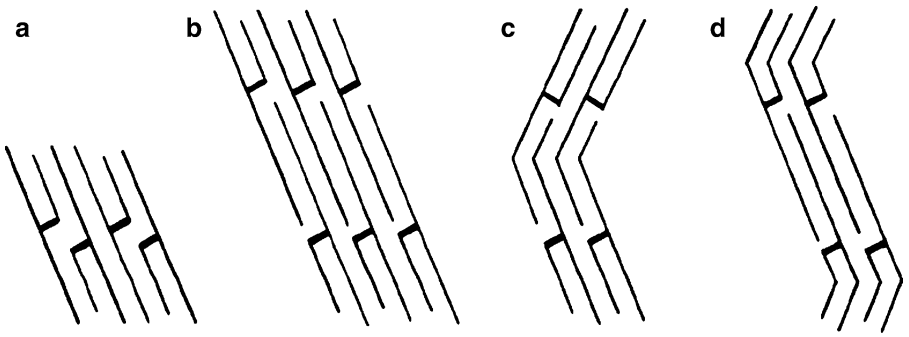


Fig. 34.1 Drawings of two- and three-chain triacylglycerol layers: (**a**) saturated monoacid SSS-type; (**b**) saturated symmetrical PSP-type where 2 chain differs from 1 and 3 chains in length; (**c**) symmetrical POP-type where 2 chain is unsaturated; and (**d**) symmetrical OPO-type where 1 and 3 chains are unsaturated. Crystals grow in bilayer units

Factors affecting the melting points of specific fat samples include: the types of fatty acids present (lengths of the fatty acids chains, number and location of *cis* and *trans* double bonds in the chains), location of specific fatty acids on the glycerol, compatibility of the different TAG in the mixture, and types of crystals present. Melting points increase with chain length. *Trans* fatty acids always have higher melting points than their *cis* counterparts for any chain length. Where only one double bond exists in a fatty acid, as in C18:1, the melting point is lower if it is located after an odd-number carbon than an even-number carbon, and also if the double bond is located near the middle of the chain as compared with a location at either end [45]. Compatibility of mixed fats from different sources can be a factor. For example, the melting points of multifatty acid TAG, consisting primarily of 16–18 carbon fatty acids, generally rise smoothly with increased content of higher melting fats. However, when TAG with 12–16 carbon fatty acid fats (from coconut and palm kernel oils) are added, concentration-related eutectic points and incompatibility (miscibility gaps) may occur [46–48]. Chemical interesterification of natural fat usually raises its melting point.

Polymorphism and Crystal Types

Polymorphism means "many bodies." Having determined the melting point of tristearin in 1849, Heintz continued to heat the capillary and witnessed: resolidification, a second melting point at a higher temperature, and resolidification and a third melting point for the same sample. Duffy confirmed the principle and reported three melting points, at approximately 52, 64, and 70°C in 1853. Later, five and even seven crystal forms were reported for some fatty acids and mono- and mixed-acid TAG, depending on the heating and cooling history of the sample [49].

As fatty acids or TAG cool, Gibbs free energy ($G = H - TS$) decreases by reduction of both enthalpy (H) and entropy (S, the degree of disorder). At decreased S, fatty acid chains assume pole-like structures that are less co-repulsive and pack more tightly into crystal lattices. It is widely accepted that, to participate in a crystal structure, TAG assume an "h" configuration (also called two-legged chair or tuning fork). This can be envisioned in our gravity-oriented world by assuming that each ester linkage acts as a hinge. If the glycerol number 2 carbon chain is held upright at the methyl end, the number 3 carbon chain hangs directly beneath it forming the back and one leg of the chair, and the number 1 carbon chain juts out at a right angle and curves downward to form the second leg [48, 50–54]. In order to save space, half of the chairs are packed upside down to form a palisade-like structure. A stack of two such structures forms a bilayer whose outer surfaces, consisting of methyl groups, display low inter-attraction. This helps explain why TAG crystals are relatively flat, grow rapidly in length and less rapidly in width by adding parallel chair structures, and grow slowly in thickness by adding additional bilayers.

Within each layer, the chair backs and legs can be further envisioned to act as a vertical loose palisade of knobby-surfaced posts. (Although the hydrocarbon chains have stiffened into pole shape, the carbon atoms are not positioned as beads on a tight string, but rather in sawtooth-like fashion with carbon–carbon bonds of 112°.) The poles can slide behind each other to obtain tighter packing with lowered free energy and can be tilted in two directions to allow the sawtooth-configured carbon atoms on adjacent chains to slip by each other and pack even more tightly. Furthermore, all the vertical units in one layer can be tilted at an opposing angle to the units in the other layer.

As shown in Fig. 34.1, if the three fatty acids in the TAG are saturated and approximately of the same length, each of the layers in the fat bilayer will be approximately two fatty acid chains in height. If the fatty acid on the number 2 glycerol carbon is appreciably shorter than those on the 1 and 3 carbons, each of the layers will be three chains thick. If the TAG is symmetrical, with the 2 position glycerol carbon or both the 1 and 3 carbons unsaturated, the layer will be three chains long but with a zigzag configuration to accommodate the *cis* configuration.

On rapid chilling, a glass (vitreous, γ) form occurs, which can change into a α or β' form as activation energy becomes available. The form showing the least amount of crystalline

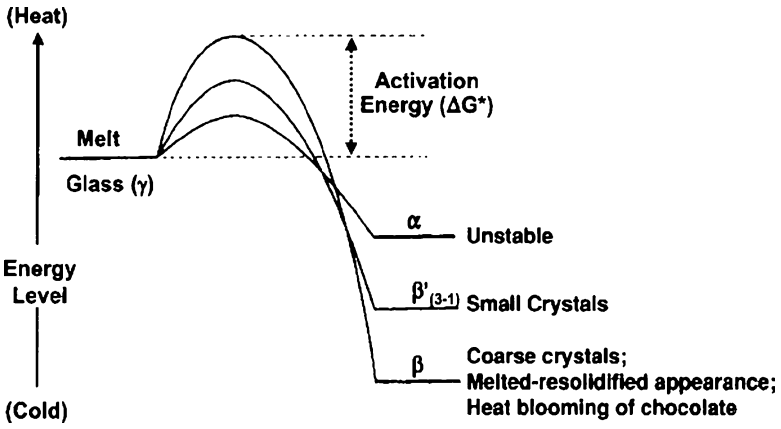


Fig. 34.2 Gibbs energy relationships of polymorphs of a triglyceride. (Modified from Sato [53] pp. 227–263)

order for a TAG, as determined by X-ray diffraction and infrared spectroscopy, is called the *alpha* (α) form. The most compact crystalline form, with the lowest free energy and the highest melting point, is called the *beta* (β) form. One or more intermediate *beta* prime (β') forms also may exist and are indicated as β'_3, β'_2, and β'_1 as the crystal progresses to tighter packing, a lower free energy state, and an increased melting point. When a TAG is cooled very slowly and without mixing, it preferentially assumes the β crystal form. But the tight packing of crystals requires time for alignment and may be thwarted by increased viscosity as the fat/oil mixture cools.

The free energy relationships between the different crystal forms are depicted in Fig. 34.2. Although the β crystal form has the lowest free energy G, induction of its formation requires the highest activation energy ΔG. Differential scanning calorimetry (DSC) often is used to follow free energy changes as fats melt and change between their polymorphic forms. Left to itself, a fat will seek its lowest thermodynamic free energy crystal state.

The formation of β crystals may intentionally be encouraged or hindered, depending on the processing application. The α crystals are relatively unstable, and commercial interest is primarily placed on the differences between the β' and β forms. Generally, β' crystals are smaller (about 0.5–2.0 μm diameter in shortening, and 5–10 μm in margarine [55]), whereas β crystals can grow as large as 20–30 μm. When the objective is to thermally fractionate fats by crystallization, production of the β form is encouraged by carefully controlling temperatures (to not shock the fat into a semi-stable β' form), gentle stirring, and nuclei seeding. The smaller β' crystals have smoother mouthfeel, minimize oiling from margarine, and entrap more air in creaming cake batters. Their production is intentionally encouraged by formulating mixtures of natural or preprocessed fats, by the inclusion of emulsifiers to interfere with crystal growth, and by rapid agitation during plasticizing of the margarine or shortening.

Figure 34.2 also helps explain the mechanisms of defects appearing in fatty products. If a fat that has been conditioned into a stable β' fine crystal form is suddenly exposed to thermal shock and then left unattended, the energy may activate it to settle into the lower energy, coarse β crystal form. Thus, chocolate bars, left to melt and cool several times in an automobile during the summer, turn coarse in texture and mousy in color.

An awareness of crystal packing characteristics and polymorphism helps one to understand incompatibility problems of different fats. Crystal formation has specific demands, and individual crystals in mixed systems each consists of only one species of TAG. However, surfactants and other molecules can act as impurities and interrupt crystal growth. Different TAG are considered compatible when they co-crystallize as separate crystals under the same conditions without the formation of a eutectic.

Other Lipids

Many minor lipids are extracted by nonpolar solvents along with FFA and TAG. Although present in small quantities, they must be removed in refining and sometimes are isolated and purified for medicinal and other uses.

Waxes

Waxes are fatty acid esters of alcohols and are formed by the general reaction:

$$\underset{\text{Alcohol}}{CH_3(CH_2)_nCH_2OH} + \underset{\text{Fatty acid}}{CH_3(CH_2)_nCOOH} \rightarrow$$

$$\underset{\text{Wax ester}}{CH_3(CH_2)_nCH_2COOCH_2(CH_2)CH_3} + \underset{\text{Water}}{H_2O}$$

Table 34.5 Sources and compositions of natural waxes

Type	Melting point (°C)	Main components
Animal waxes		
Beeswax	64	Myricyl palmitate
Chinese	82–84	Isoheptacosyl isoheptacosanoate, ceryl lignocerate
Shellac	81–82	Ceryl lignocerate, ceryl cerotate
Spermaceti	–	Cetyl palmitate
Wool (anhydrous lanolin)	36–42	Cholesteryl estolidic esters, alcohol esters of iso- and anteiso acids
Mineral waxes		
Montan	86	Tricontanyl esters of $C_{28–30}$ acids
Petroleum waxes		
Microcrystalline	71–88	Hydrocarbons (490–800 molecular weights)
Paraffin	54–57	Hydrocarbons (350–420 molecular weights)
Vegetable waxes		
Bayberry	43–48	Trimyristin, tristearin
Candelilla	70–80	$C_{29–33}$ hydrocarbons, simple esters and lactones
Carnauba	80–85	Esters of $C_{26–30}$ alcohols and $C_{26–30}$ ω-hydroxy acids
Esparto	69–81	Hydrocarbons, esters of $C_{26–32}$ acids and alcohols
Japan	51–62	Tripalmitin
Jojoba (a liquid wax)	11–12	Docosenyl eicosanoate
Ouricury	79–85	Myricyl cerotate and hydroxycerotate
Sugarcane	79–81	Myricyl palmitate stigmasteryl palmitate

A major role of waxes in nature is the protection of plant tissues. Examples include coating upper surfaces of leaves to reduce dehydration by the sun and protecting seeds against moisture loss during storage. Minor quantities of waxes are always present in oils extracted by solvents. Waxes extracted from seed hulls cause cloudiness in refrigerated sunflower seed oil and failure of the 5.5-h cold test at 0°C. Sunflower seed oil may be dewaxed by first degumming or miscella refining to remove the natural emulsifier lecithin, which limits the growth of wax crystals, and then winterizing (chilling and filtering) the oil or its *miscella* (oil in its extraction solvent) [56, 57]. With the improvement of dehulling equipment, some sunflower seed processors remove the hulls before extraction. Extracted rice bran, a relatively recent development in the United States, contains waxes with potential commercial promise. Methyl and ethyl fatty acids esters, used as liquid fuels, solvents, and in other applications, also are "waxes" of short-chain alcohols; these are described later.

Waxes are common forms of high-energy storage, in the oils of fish and other marine animals. The major lipids of commercial whale oil consist of approximately 65% waxes and 35% TAG. The lipids of Australian orange roughy (*Hoplostethus atlanticus*) and dory fish oils are 97.1 and 90.9% wax esters, respectively [58]. Essentially all the oil in jojoba (*Simmondsia chiensis*) seed is in wax form. Whale and jojoba oils have been valued for stability in cosmetics and heavy-duty lubrication applications.

Extraction processes for waxes vary in sophistication, from: boiling crushed leaves and berries and skimming the oil (as in the regulated production of Candelilla wax a substitute for hard carnauba wax from *Euphorbia antisyphilitica* in the Big Bend area of Texas and Mexico); to screw pressing seeds such as jojoba; to direct solvent extraction. Cold-pressed jojoba oil is preferred for cosmetics because of concern about other lipids that might be extracted in solvent processes. Oil remaining in the meal has been recovered by secondary hexane extraction for industrial uses. Waxes are susceptible to hydrolysis by nonspecific lipases and are at least partially digestible. They may be hydrogenated or sulfurized into solid forms. The compositions of significant commercial waxes from natural sources are given in Table 34.5.

Terpenes

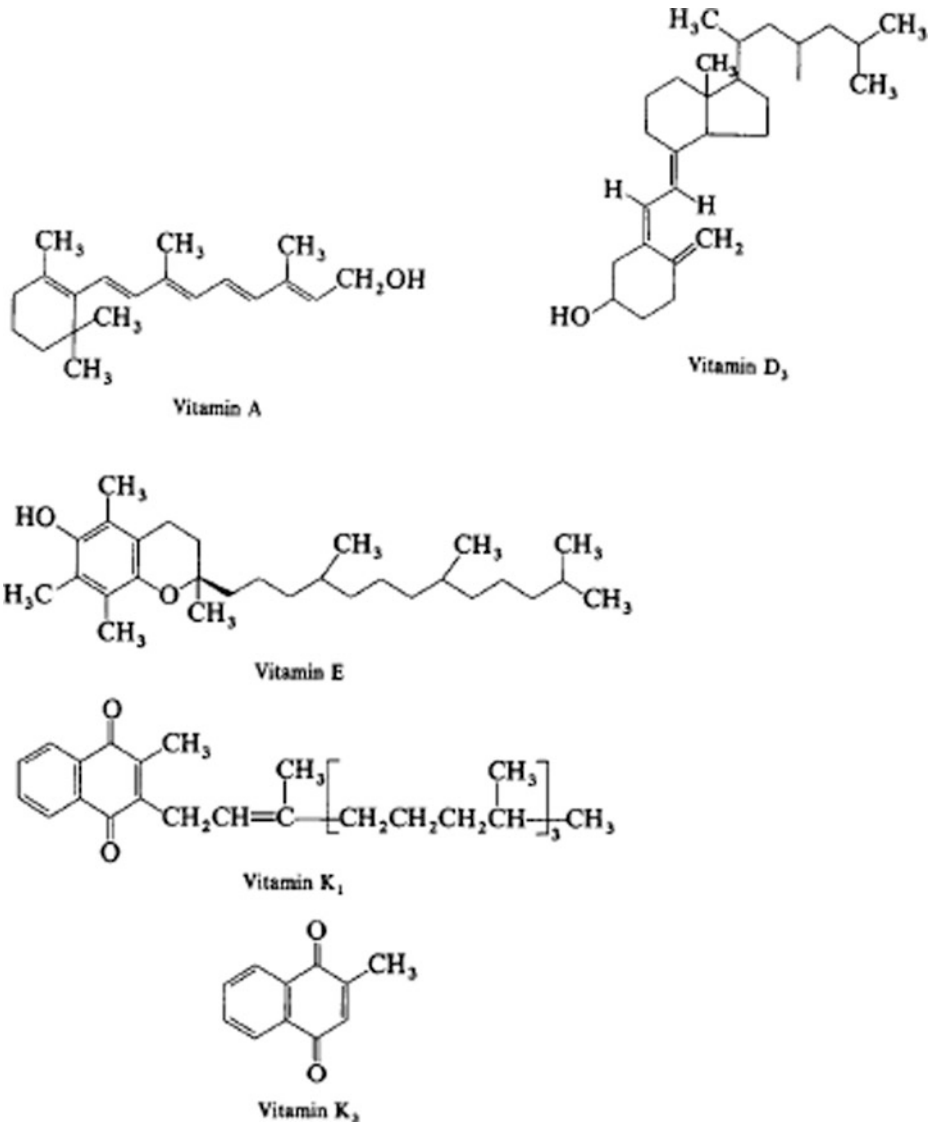
Terpenes are condensation products of the five-carbon *isoprene* (2-methyl-1,3-butadiene) and are extractable by nonpolar solvents. They are classified according to the number of isoprene units: two units, *monoterpenes*; three units, *sesquiterpenes*; four units, diterpenes; six units, triterpenes; eight units, tetraterpenes; and *polyterpenes*. Terpenes may be linear or cyclic. Taken together, this class of compounds includes major essential oils (used in perfume and flavorings), fat-soluble colors, fat-soluble vitamins, and steroids. A saw-toothlike shorthand form often is used to depict the longer chains.

Examples of monoterpenes include the linear aldehyde citral, which is found in many essential oils, and the (*cis*) alcohol *geraniol,* a major component of oil of geranium. Cyclic monoterpenes include limonene, menthol, pinene, camphor, and carvone, major components of lemon oil, mint oil, turpentine, camphor oil, and caraway oil,

respectively. Sesquiterpenes include farnesol, a component of rose oil, and bisabolene, a component of Bisabol myrrh. The diterpenes include phytol, a component of chlorophyll, and vitamin A, which is one half of the tetraterpene β-carotene. The triterpenes include squalene, a precursor of cholesterol. Examples of tetraterpenes are the oil-soluble: carotenoid plant pigments; xanthophylls, including the yellow pigments lutein in plant leaves and *zeaxanthin in* corn (*Zea mays*); capsanthin, the red pigment in red peppers (*Capsicum annuum*); lycopene, the red coloring of tomatoes (*Lycopersicum esculentum*); and β-carotene, a yellow-orange pigment that is the precursor of vitamin A. Bixin, from the seedpods of *Bixa orellana*, is the yellow-orange pigment in annatto food color. It is considered to be a form of carotene oxidized to remove both six-membered end rings. Polyterpenes include gutta, natural water repellant and electrical insulating material from *Palaquium gutta*, and natural rubbers with molecular weights of up to 1.2 million daltons obtained from the latex of the *Hevea brasiliensis* tree and from rubber-filled cells in the branches and roots of the guayule shrub (*Parthenium argentatum*).

Sterols

Structures of selected sterols are summarized in Fig. 34.3. Cholesterol is synthesized from lanosterol, which consists of six isoprene units. Cholesterol is a powerful emulsifier and intermediate for synthesizing other steroids and compounds in animals. It participates in multiple ways in fatty acids and



TGA transport and is monitored as a major index of arterial and general health. Other important (animal) zoösterols include ergosterol, a precursor of vitamin D required to avoid rickets in children. The ability of certain plant-origin phytosterols to reduce blood cholesterol levels, including low-density lipoproteins (LDL), was discovered in the 1950s and reconfirmed many times. Pine tree "tall" oil, a byproduct of papermaking, is a rich source for commercial preparations. In recent years, selected phytosterols have been approved as food additives and have been included in specialty margarines and spreads. Stanol homologues differ from sterols by saturation at the 5 position, to yield cholestanol instead of cholesterol, and sitostanol instead of *β*-sitosterol. Commercial phytosterol preparations are mixtures of *β*-sitosterol, sitostanol, campesterol, and campestanols. Free sterols have limited solubility in fat, and stanols are hardly soluble; thus, they are converted to fatty acid esters for use in formulated foods. Bennecol®, a table spread, developed by the Raisio Group in Finland and approved as GRAS by the FDA for the United States market in 1999, is an example of a plant sterol/stanol application. The FDA requires that a product provides at least 1.3 g/day of plant sterol esters or 3.4 g/day of plant stanol esters in use to qualify for a cholesterol-lowering health claim [59–61].

Frying studies have shown that phytosterols with double bonds at the 24–28 position in the ethylidene side chain (Δ^5-avenasterol, Δ^7-avenasterol, fucosterol, citrostadienol, and vernosterol) act as chemical antipolymerizers on the surface of frying oils and prolonged frying life. However, stigmasterol, *β*-sitosterol, spinasterol, lanosterol, ergosterol, and cholesterol are either ineffective or slightly increase polymerization [62–65].

Fat-Soluble Vitamins

The fat-soluble vitamins include: vitamin A (retinol), a colorless compound resulting from cleavage of *β*-carotene, vitamin D_3 (cholecalciferol), a steroid, and vitamins E and K (tocopherols and menadione and their derivatives, respectively), which consist of isoprene and phenolic-quinone components.

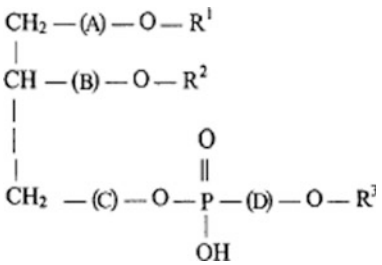
The carotenoids generally are highly susceptible to oxidation. Only selected members (xanthophylls, *β*-carotene, and bixin) are extracted for food coloring. They are used in products such as butter, margarine, and cheese, where exposure to oxygen and light is limited. The more stable yellow-orange pigments (lutein and xanthophylls) are extracted from alfalfa and marigold blossoms for use as poultry feed additives to increase the yellow color in egg yolks and in skins of broilers. Much of the world's *β*-carotene is produced synthetically and is increasingly obtained from (red) palm oil. There is current controversy whether lycopene, the red pigment of tomatoes, has antioxidant properties in the human body.

"Vitamin E" is a generic term for tocopherols and tocotrienols recovered from condensed deodorizer or physical refiner distillates. In earlier years, wheat germ oil was a major source. Structures of tocopherol and tocotrienol isomers are identical except for the presence of double bonds at positions 3′, 7′, and 11′ in the side chain of tocotrienols. The R_1, R_2, and R_3 positions are occupied by CH_3, CH_3, and CH_3, respectively, in the *alpha* (α) isomers; CH_3, H, and CH_3 in the *beta* (*β*) isomers; H, CH_3, CH_3 in the *gamma* (γ) isomers; and H, H, and CH_3 in the *delta* (δ) isomers. As shown in Table 34.6, tocopherols are the primary tocols in soybean, corn, olive, and sunflower seed oils, and tocotrienols are primary in wheat, rice bran, and palm oils. During chill fractionation, tocotrienols in palm oil concentrate in the olein (liquid) phase. The greatest vitamin E activity is shown by α-tocopherol—the commercial "vitamin E"—with lesser activities shown by other tocopherol and tocotrienol isomers. However, when used as antioxidants, the *gamma* and *delta* isomers often have proven more effective in protecting vegetable oils against oxidation. Intensive research continues on potentials of tocols for avoiding or curing various diseases, with considerable focus on diseases of aging.

Oils from the livers of cod and other fish species were early sources of vitamin D_3; also, ergosterol was irradiated by ultraviolet light to produce vitamin D_2. Currently, most of the commercial vitamin D is produced synthetically. Commercial vitamin E is recovered from deodorizer condensates from plants refining palm and other oils, including soybean.

Phosphatides

Phosphatides are natural emulsifiers with the following structures [66].

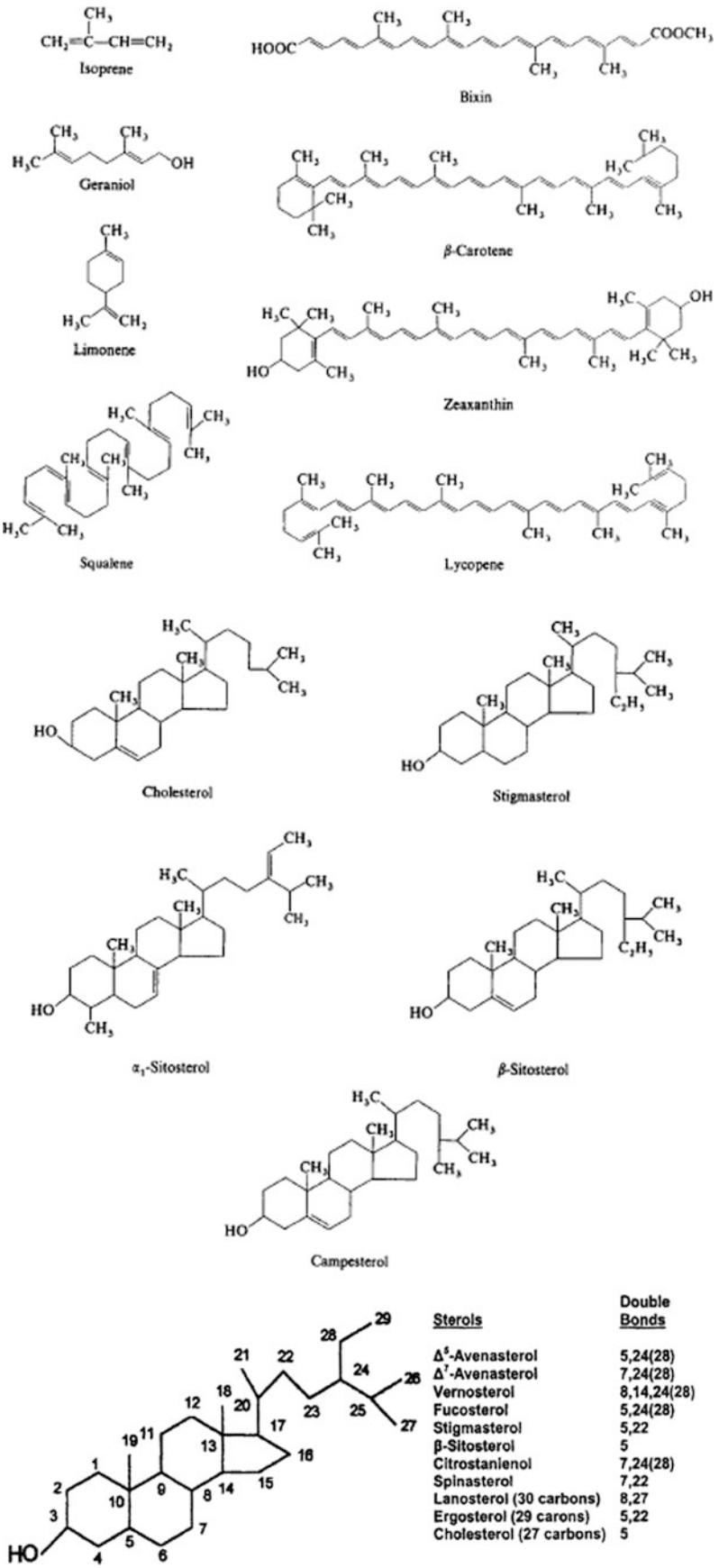


where

R^1 = fatty acid.

R^2 = fatty acid, or the phosphatidyl group in the 2 position.

When R^3 is one of the following, the phosphatide is named:



Sterols	Double Bonds
Δ^5-Avenasterol	5,24(28)
Δ^7-Avenasterol	7,24(28)
Vernosterol	8,14,24(28)
Fucosterol	5,24(28)
Stigmasterol	5,22
β-Sitosterol	5
Citrostanienol	7,24(28)
Spinasterol	7,22
Lanosterol (30 carbons)	8,27
Ergosterol (29 carons)	5,22
Cholesterol (27 carbons)	5

Fig. 34.3 Structures of selected sterols. Sources: animal—lanosterol, cholesterol, and ergosterol (also microbial); plant—all others. (From Warner [65], pp. 37–49, With permission)

Table 34.6 Tocopherol and tocotrienol contents (μ/g/g) of common refined edible oils (From: Sundram et al. [206], With permission)

Tocol isomers	Soybean oil	Corn oil	Olive oil	Sunflower oil	Milk fat (ghee)	Wheat germ oil	Rice bran oil	Palm oil	Palm olein	Palm stearin
α-Tocopherol	117.2	248.9	151.4	485.2	32.7	218.9	64.0	188.2	179.0	50.0
β-Tocopherol	19.8	10.1	13.3	3.0	n.d.	33.2	10.6	n.d.	n.d.	n.d.
γ-Tocopherol	560.7	464.1	10.9	51.0	n.d.	84.7	n.d.	n.d.	17.6	n.d.
δ-Tocopherol	178.2	58.2	n.d.	n.d.	33.8	n.d.	187.0	n.d.	n.d.	n.d.
α-Tocotrienol	n.d.b	n.d.	n.d.	n.d.	n.d.	n.d.	31.4	198.1	219.9	47.4
β-Tocotrienol	20.2	n.d.	n.d.	n.d.	n.d.	347.5	83.2	10.0	8.1	9.0
γ-Tocotrienol	6.2	n.d.	n.d.	n.d.	n.d.	n.d.	783.2	198.8	332.7	134.9
δ-Tocotrienol	n.d.	n.d.	n.d.	n.d.	n.d.	18.4	38.6	98.4	67.0	31.4
Total	902.2	781.4	175.6	547.5	66.5	702.7	1198.0	693.5	824.3	272.8

nd not detected

$R^3 = CH_2–CH_2–N^+(CH_3)_3$	diacylphosphatidyl choline
$R^3 = CH_2–CH_2–NH_3^+$	diacylphosphatidyl ethanolamine
$R^3 = CH_2–CH(NH_3^+)–CO_2H$	diacylphosphatidyl serine
$R^3 = C_6H_6–(OH)_6$	diacylphosphatidyl inositol
$R^3 = H$	diacylphosphatidic acid

and preceded by names of the two fatty acids if relevant.

In the pharmaceutical industry, the word *lecithin* is synonymous with phosphatidyl choline. However, the entire or modified mixture is sold as lecithin in food supplement capsules, and for food, feed, and industrial uses. Soybean oil phosphatides consist of 29–39% diacylphosphatidyl choline, 20–26% diacylphosphatidyl ethanolamine, 13–17% diacylphosphatidyl inositol, 5.9–6.3% diacylphosphatidyl serine, and 5–9% diacylphosphatidic acid [66].

The phosphatides have polar and nonpolar sites and generally act as water-in-oil emulsifiers. They are extracted by solvents with the oil, but preferentially will absorb available water, form gums, and precipitate. Commercial lecithin is produced by *water degumming* (precipitation from oil with ion exchange-treated water) as explained later.

Phosphatides precipitate on hydration during the storage of oils, foul bleaching earths, poison hydrogenation catalysts, and cause darkening of the oil during deodorization/physical refining and also if it is used in frying applications. Their removal is desirable, but requires close supervision to preserve oil yields. Four lipases are able to hydrolyze phosphatides. Phospholipase A cleaves fatty acids at the "A" position; phospholipase B (also called "A2") cleaves fatty acids at the "B" position; phospholipase C cleaves the phosphatidyl chain next to carbon "C;" and phospholipase D cleaves between the phosphate structure and choline, ethanolamine, serine, or inositol. Cleaving by phospholipase D and dissociation of the phosphorous group expose two negatively charged sites, which can complex with divalent cations (mainly calcium and magnesium, but also including iron, copper, and others) present in soybean tissue during solvent extraction. As a result, the phosphatide becomes nonhydratable.

The production of nonhydratable phosphatides (NHP) by phospholipase D can be minimized by heat inactivation of the enzyme by expanders/extruders while preparing seed for solvent extraction, by heating briefly to more than 112°C/235°F. However, some NHP are unavoidable, especially in wet fall seasons when high moisture seed may begin to sprout. Unless the NHP content is extremely high, they can be changed to the hydrated form by treating the crude oil with acidic chelating agents (*acid degumming*) to withdraw the divalent cations as described later. In the last two decades, several companies have introduced *enzyme degumming*. In these processes, usually a position 1 lipase is introduced to hydrolyze the R^1 fatty acid. This leaves the 1 position attractive to water and renders the phosphatide hydratable again.

The enzymatic degumming process is very robust and versatile. Using this process increases oil yields and reduces phosphorus content to a greater extent. The method is suitable for edible oil and biodiesel processing. Recently in 2010, Varenium has marketed their two Purifine PLC products for the degumming process.

Fats and Oils Sources and Consumption

Production

Global production and export estimates for fats and oils for 2003/2004 are shown in Table 34.7. Approximately 39% of the world's production of vegetable oils, and an additional 20% of oilseeds grown, enter international trade [20, 67]. Records of estimated production, imports, and exports are kept, country by country, by the Foreign Agriculture Service (FAS) of the US Department of Agriculture, and *Oilseeds World*, a publication in Hamburg, Germany.

The leading producers of the major oilseeds, in decreasing order, are *Soybean*: the United States, Brazil, Argentina, China, and Paraguay; *Rapeseed/Canola:* China, the

Table 34.7 Estimated production and exports of world's major edible-type vegetable oils (From: Foreign Agriculture Service Circular Series. Department of Agriculture, April 2010/2011)

	Seed/Copra		Meal		Oil	
Oil/Fat source	Production (MMT)	Exports (MMT)	Production (MMT)	Exports (MMT)	Production (MMT)	Exports (MMT)
Soybean	260.97	98.51	177.82	59.92	42.0	9.99
Palm	–	–	–	–	47.47	37.53
Canola/rapeseed	58.56	10.53	34.63	4.41	23.02	3.15
Sunflower seed	30.93	1.48	12.14	4.19	11.28	4.36
Peanut	34.71	2.49	5.93	0.11	4.89	0.17
Cottonseed	43.19	0.71	14.84	0.36	4.96	0.17
Copra/coconut	5.89	0.21	1.95	0.81	3.68	1.88
Palm kernel	12.73	0.02	6.70	5.03	5.65	3.27
Olive	–	–	–	–	3.01	0.65
Fish	–	–	4.97	2.87	–	–
Total	446.89	113.86	258.98	77.70	145.96	61.00

MMT million metric tons

European Union, Canada, India, and Eastern Europe; *Sunflower seed:* the former Soviet Union 12, Argentina, European Union, Eastern Europe, China, and the United States; *Peanut/Groundnut:* China, India, and the United States; and *Cottonseed:* China, the United States, India, Pakistan, the former Soviet Union 12, and Brazil.

Soybean oil is the world's largest supply of *visible* (separated) fats, accounting for approximately 29.8%. Palm, rapeseed/ canola, and sunflower seed follow it, and peanut oils in tonnages produced. The production of palm oil has been increasing and now accounts for 28.8% of the world's supply; added to the 3.4% palm kernel oil produced, the palm crop provides 32.2% of total oil supply. With oil palm plantings still to mature in various tropical countries, palm oil production alone is expected to bypass soybean oil within the next several years. However, palm oil generally is the lowest cost edible fat available and accounts for 54.7% of the world's exported oils. Thus, it is one of the more economical and easier acquired oils.

Currently, the United States is the world's leader in soybean production (35.2%), followed by Brazil (32.7%), Argentina (17.9%), and China (8%). Approximately 34% of the world's soybean meal (for animal feed), 29% of the oil (mainly in degummed form), and 34% of the world's soybean seed (mainly for overseas extraction) enter global trade. The United States exports 36% of its soybean crop in seed form, 12% of its processed meal, and 3% of its soybean oil. In contrast, Brazil exports 35, 65, and 48%, and Argentina exports 20, 98, and 98%, respectively. The latter two nations each surpass the United States in tonnage of meal and oil exports. This results partially from increasingly more of the domestic crop retained in the United States to supply the local population's needs. Also, larger tariffs were imposed on seed exports than on meal or oil in Brazil and Argentina in the 1970s and 1980s to encourage development of domestic oils extraction industries; these strategies appear to have been successful. Because of population growth, China now imports more soybean than is produced internally [20].

Rendered beef, pork, poultry, and other animal fats are not well reported internationally, and global statistics are unreliable. Total production of fats in the United States by the rendering industry for 2000 is estimated at 4.18 million metric tons [68]. Outputs of all rendering facilities captive to integrated broiler operations might not be included. Of the amount reported, 76% is inedible tallows and greases, 18% is edible beef or mutton tallows, and 6% is edible pork lard.

Fish oils are not well reported either, with annual estimates at about 1.3 million metric tons from sustainable (sea catch) fisheries. Production has ranged by as much as 50% between years, depending on availability of fish.

Changes in Sources

The maturing of nations as raw materials suppliers follows a sequence. Centuries ago, bands of marauders attacked villages to steal crops after harvest. Later, countries conquered neighboring lands for "a place in the sun" for their growing populations. With improvements in transportation and discovery of the New World, followed by Africa and Australia, it no longer was necessary to relocate large populations. Colonies could be established to supply the "mother country" with raw agricultural materials in addition to minerals and fossil fuels. As local education improved, colonies typically declared their independence, but the new countries needed something to trade for goods they were unable to produce themselves.

The oils of ancient times were olive and sesame oil in the Mediterranean basin, rapeseed and animal fats in Europe, and coconut (copra) oils in the tropics. Cottonseed was the world's first new oil of the Industrial Revolution age

Table 34.8 Gross composition of major undehulled oilseeds

Crop/Source	Moisture (%)	Protein (%)	Fat (EE) (%)	Crude fiber (%)	Ash (%)	Oil: co-products ratio
Soybean	8.5	36.5	19.5	5.8	4.9	1 : 4.1
Cottonseed	8.0	23.0	21.0	24.0	4.8	1 : 3.8
Peanut	6.5	25.7	49.2	4.9	2.3	1 : 1.0
Sunflower	6.0	21.1	42.0	17.4	3.3	1 : 1.4
Safflower	5.8	19.4	43.5	20.8	3.7	1 : 1.3
Coconut (copra)	4.0	7.5	67.3	5.0	1.9	1 : 0.5
Rapeseed/canola	8.0	22.0	41.2	11.5	5.1	1 : 1.4
Palm kernel	10.5	9.7	58.1	–	–	1 : 0.7
Sesame	8.0	24.2	47.6	11.2	6.1	1 : 10

EE ether extraction method.

(early 1800s) and became the dominant US oil after the Civil War (from the latter 1860s until the mid-1930s). But, cottonseed oil is a byproduct of growing cotton fiber, and edible oil and animal feed requirements of the world's growing populations soon exceeded supplies of this crop. Solvent extractors, invented in Germany in the early 1920s, maximized oil recovery and produced animal feed protein meals with less heat damage. As European demands grew for a closer and more reliable source of soybean than had been available from the Manchuria area of China since 1910, soybean export opportunities opened for the United States. Many of continental Europe's oil mills were demolished during World War II, placing the United States in the position of major soybean seed, oil, and meal supplier to the world. In 1960, the United States grew and traded about 60% of the world's soybean. China grew about 32% of the world soybean crop and supplied about 19% of the trade, but soon decreased as a world supplier because of its own population growth. The poultry broiler industry became global about 1960. Its large requirements for feed protein, best supplied by soybean meal, contributed to increasing world soybean production by 7.5 times in the succeeding 40 years.

Although slightly more than four tons of meal is produced for each ton of oil, the sheer volume of the meal business has co-produced enough soybean oil to keep it the world's major oil until now. Much of the production and processing technology was developed by the United States and European nations. In time, roads, canals, and port systems, crop production, and processing infrastructures in South America were funded as economic development programs by the World Bank, Regional Banks, and by private investors. The position of "lowest cost producer of soybean and soybean oil" has passed from the United States to South American countries. Brazil has opened its sub-Amazon basin to soybean growing, an area four to five times larger than available in the United States, and has developed varieties acclimated to the climate and day length. Its production of soybean is expected to surpass the United States in the near future. China also has developed salt-tolerant varieties that will grow in its coastal regions. At the same time, economic assistance and private investment in Southeast Asia and tropical countries have led to production of palm oils at prices lower than soybean oil.

The appearance of Asian soybean rust (*Phakopsora pachyrhizi)*, first of South America and in the United States in 2004, is a cause for concern. This fungus has potential for greatly reducing soybean yields per acre and could become a critical factor in world protein and oil supplies. No other crop is as capable of producing protein as soybean, essentially resulting in a monoculture. The Unites States has maintained a wheat rust response program for nearly half a century, continuously developing rust-resistant varieties for replacement as needed. Fortunately, biotechnology has provided even better tools for newer programs.

Many factors dictate which oilseed species will be grown and/or imported into a country. Climate and local demand for high-protein feed meals are leading factors. Cool weather and short growing seasons have essentially limited Canada, Northern Europe, and the former European Russian republics to growing rapeseed/canola or sunflower seed. Some European countries grow and export seed or oil of canola, but import soybean for their edible oil and animal feeding industries. Insect problems were important factors in selecting crops before modern insecticides and IPM systems became available. Devastation of the southeastern United States cotton crop by the boll weevil led to the introduction of large-scale peanut growing in the early 1900s.

As shown in Table 34.8, the oil content of row crop oilseeds varies from about 19% for soybean to 43% for sunflower seed, and 41–45% for rapeseed/canola. More feed co-products always are produced than oils, with a ratio 4:1 in the case of soybean. Soybean meal is the major feed protein source for production of poultry, currently the leading domestic and global meat source, and in the rapidly developing aquaculture industries.

The relative availability of fat- and oil-bearing byproducts of other current agri-businesses is an additional consideration in types and amounts of oilseeds grown. Because only about 12% of the return to cotton farmers comes from the seed, the domestic supply of cottonseed for

crushing is dictated by world demand and the price of cotton and is hardly affected by price of cottonseed oil. Corn oil has become the second major oil in the United States due to large quantities of corn germ provided by rapid growth of the domestic corn sweetener and ethanol industries. There is sufficient processing of rice in the United States now to warrant two rice bran oil extraction plants, with quantities of stabilized rice bran also shipped to Japan. Beef, pork, and poultry packing operations always produce fatty tissues for rendering into inedible tallow, lard, chicken fat, and meals used in animal feeds. Generally, fats/oils from co-products of other local processing industries must clear the market first, at whatever price they can get, before growing or importing of significant quantities of high-oil content crops becomes economically attractive.

Consumption

The world's current production of edible oils is estimated at about 101 million metric tons, and an increase of ~2.5 million metric tons is needed annually to meet the needs of the growing population. Average per capita consumption of fats/oils is difficult to determine from gross disappearance figures because these materials also are used in animal feeds and industrial applications. Generally, consumption is related to personal income and local availability, but once fats are introduced into the diet, their priority among food expenditures remains high. The annual consumption of oils is estimated at 10.4 kg per person for the world and ranges from 27.2, 42.9, and 29.3 kg for the United States, Belgium, and West Germany, respectively, to 13.1, 4.7, and 5.9 kg, respectively, for Egypt, China, and India.

About 60% of the total fat consumed domestically is "invisible," in meat, poultry, fish, dairy products, eggs, and prepared foods. The visible 40% is used primarily in the form of salad and in-home cooking oils, shortenings, and margarine. From 1965 to 1990, average domestic consumption of fat decreased from 50.7 to 32.5 kg per capita for men 19–50 years of age and 30.3 to 23.4 kg/year for women.

Since 1990, consumption increased to 36.9 kg/year for men and 23.7 for women in 1995 [69]. Approximately two thirds of visible fats available per capita in 1940 were from animal sources. The use of vegetable source fats has grown significantly, accounting for about two thirds of the visible fats consumed in 1965, and 90% in 1985 [70]. More recent data have shown that fat consumption per capita has not deceased in grams per day intake, but has decreased as a percentage of total diet with the average caloric intake increasing.

At times, the public acts indifferently regarding caloric intake. In the mid-1990s, various low-fat or nonfat snack foods were introduced, requiring different processing machinery, techniques, and flavoring technologies. Although promising at first, sales of these products showed a decline in 1997 [71]. The Procter & Gamble Company developed olestra (Olean™) during a 28-year period (1968–1996) before the FDA approved its use as a frying oil in *savory snacks* (salty chips, crackers, and tortilla chips) and spent several hundred million dollars in the process. Olean™ is a polyester of sucrose and 6 to 8 fatty acids, which is nondigestible by human lipases, and thus noncaloric. However, public interest shifted from snacks promoted as "healthy" to indulgence in salty, traditional-flavor, higher fat content products [72]. Many of the newer snack products were withdrawn from the marketplace. Digestive tract upsets also found in earlier evaluations of other nondigestable fats were again reported among Olean consumers.

Extraction of Fats and Oils

Basic Processes

By trial and error over the centuries, man has learned five basic skills in handling oilseeds:

1. *Preservation of seed by natural or artificial drying* and cooling to a dormant state before storage, with protection from insects and rodents. Generally among oilseeds, sprouting enzymes become active once seeds rise above 75% relative humidity (RH). Rise in free fatty acid (FFA) content signals need for early processing.
2. *Removal of trash and hulls*, by stamping, threshing, disk hullers, cracking rolls, and other devices, followed by winnowing, sieving, or aspiration to separate kernels ("meats") from hulls and chaff.
3. *Freeing the oil*, by pounding seed with rocks, mortar, and pestle-type grinders (which later became human, beast, water, or electric-driven ghanis); use of vertical stone/iron wheels known as "edge rollers" to crush the seed; cracking and flaking rolls; and, more recently, expanders/extruders.
4. *Heating the seed to increase oil recovery*. This was first interpreted as denaturation, making the protein matrix brittle to surrender the oil on pressing. Later, it was recognized that concurrent inactivation of enzymes also arrests development of various types of degradations.
5. *Separation of oil* from crushed seed by: draining; squeezing cooked mash in cloths by lever, wedge, or hydraulic presses; continuous screw presses, or by solvent extractors.

Initially, various societies used plant oils for medicinal and cosmetic purposes. Later, they were used for lighting and, as extraction and refining techniques improved, for food. Crude techniques are still used in remote areas.

Screw Press Operations

Continuous screw presses are used: (1) for extracting fats and oils in small operations where investment capital or supplies of raw materials are limited and installation of a solvent extraction plant is impractical; (2) to partially defat high-oil content seeds for easier handling in subsequent solvent extraction or hard pressing; and (3) for extraction of animal flesh and bones, fish, and fleshy-type oilseeds such as palm fruit, olives, and copra (dried coconut "meat") and oilseeds. These machines have been generically referred to as "expellers," but the Expeller® trademark belongs to Anderson International Corporation, Cleveland, OH, successor to the company founded by Valerius D. Anderson who patented the first continuous screw press in 1899.

The main principle in *hard pressing* is to preheat (cook and dry) prepared seed and animal materials to the point where cell walls become brittle and rupture readily on pressing. Generally, seed is dehulled, tempered, flaked, and cooked (dehydrated) to low moisture (3–4%) before hard pressing. Screw presses used for hard pressing row crop oilseeds (soybean, cottonseed, rapeseed/canola, sunflower seed, and peanut) typically include two stages: the second stage, operating at higher pressure, further extracts oil remaining after first stage pressing (Fig. 34.4). Approximately 4–5% oil is left in oilseed meals. Single-stage continuous screw presses typically are used in rendering operations and in pressing palm fruit and olives, which leave bone or hard seed pieces in the press cake. Approximately 9–12% fat is left in meat and bone, and fish, meals, and 5–6% oil in oilseed meals. High temperatures partially destroy the dietary essential amino acid lysine and reduce nutritional quality and economic value of protein feed meals. Milder *wet processing* techniques have been developed for meat and fish meals.

Generally, oils from press operations go to a settling tank. A layer of foam may be skimmed off; the *midfraction* (oil) is filtered and sent to refining, and the settled solids (*foots*) are spread over the stock going to the screwpress. Pressed oils benefit from cooling to less than 42°C/11°F as soon as possible to slow oxidation and setting of color.

The traditional practice in processing high-oil row crop oilseeds (containing over 25% oil, such as canola/rapeseed, sunflower, peanut, safflower, and corn germ) was to reduce the oil content to less than 18% using lighter duty *prepresses*, break up the press cake, and finish with solvent extraction. Such operations are called *prepress-solvent extraction*. Cottonseed also was prepressed in earlier years. Expanders with oil removal cages (Fig. 34.11, to be described in more detail later) are used to reduce oil content to less than 20% and are replacing prepresses in high-oil content seed extraction plants. Modified discharge heads are used on expanders to enhance hard pressing.

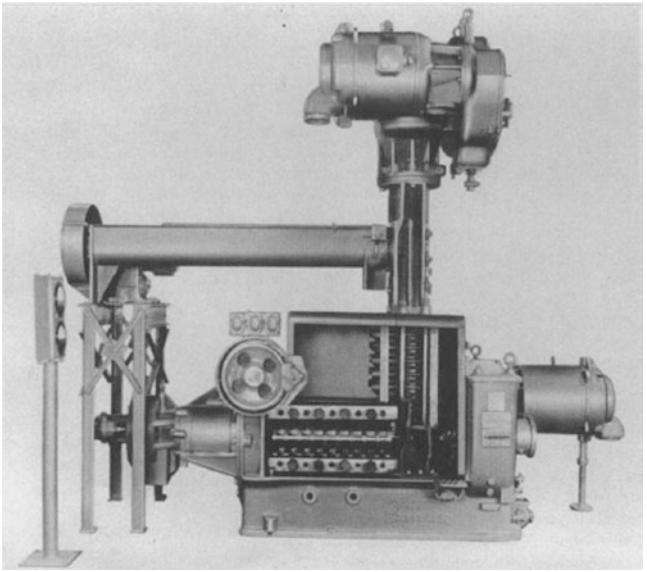


Fig. 34.4 Anderson Expeller® Press, model 55 in. TDMS.™ Note elevated conditioner carrying product from *left* to *right* across *top* of press; vertical screw first-stage press section (*right* side); higher pressure second-stage press screw section carrying product from *right* to *left*. Some hard presses have both stages on one shaft. (Courtesy of Anderson International Corp., Cleveland, OH)

Most oilseeds contain excessive fat for extensive animal feeding. "Scalping" oilseeds such as cottonseed and soybean by preheating and partially pressing to about 9–12% residual oil (which is sold) is becoming popular among large animal feeders, feed manufacturers, and farmer cooperatives. Toxic components, such as trypsin inhibitor (in soybean) and gossypol (in cottonseed), are partially inactivated, and the meals are improved for feeding selected animals.

Decanters and Centrifuges

Two major types of centrifugal separators are used in press-type oil/fat extractions and *wet rendering:* horizontal decanters and vertical stacked conical disk centrifuges. A drawing of a decanter, which separates solids and liquids, is shown in Fig. 34.5. Decanters are built with different internal designs depending on the solid–liquid ratio to be separated and operate at ~2,500–3,000 × gravity (g). When properly operated, a "dry" solids phase and a liquid phase of two immiscible liquids (aqueous matter and oil) are discharged.

A cut-away of a three-phase stacked-disk centrifuge is shown in Fig. 34.6 [16]. These are vertical separators, operating at ~6,000 × g, which employ a spinning bowl and set of conical stacked disks. Centrifuges are used

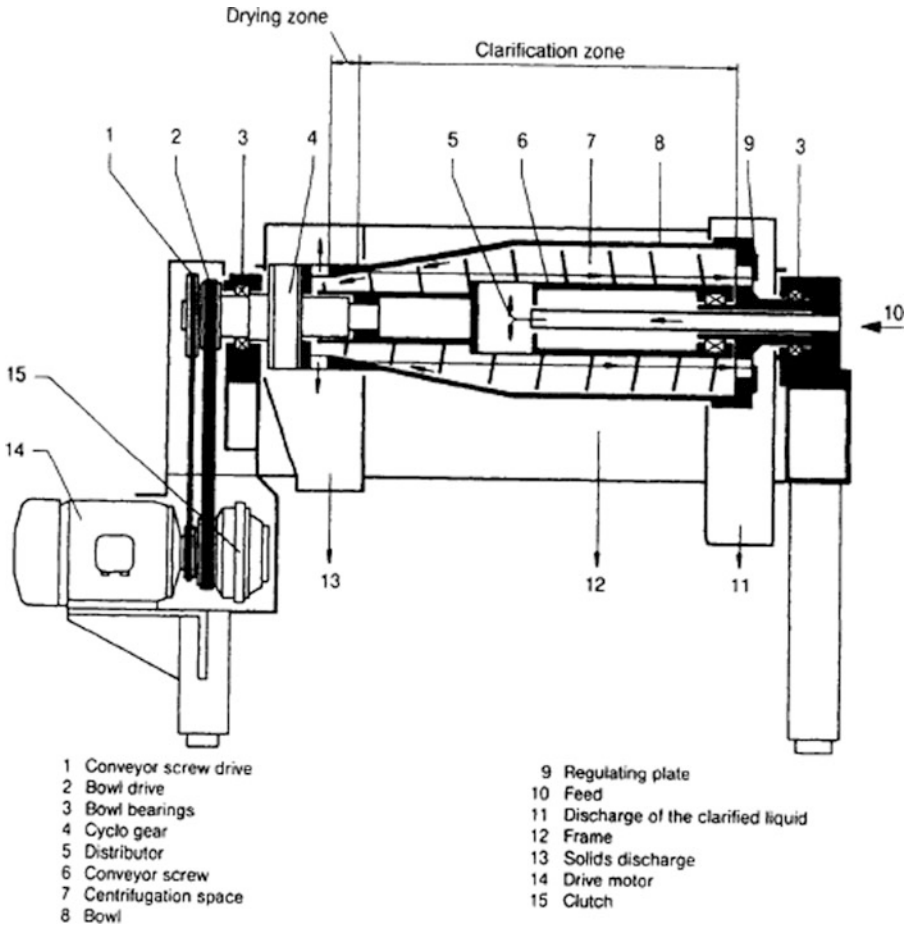


Fig. 34.5 Schematic drawing of Westfalia Model CA 450 Continuous Clarifier Decanter. (Courtesy of GEA Westfalia Separator Company, Northvale, NJ)

primarily in three-phase mode to separate the liquid portion into two immiscible phases and a fine solids (*sludge*) fraction. They are not meant to handle significant amounts of coarse solids. The material to be separated enters the spinning bowl at the bottom through a hollow spindle and is discharged under the lower plates to be thrown against the side of the bowl by centrifugal action. Continual arrival of fresh liquid forces the earlier liquid into the plates, with the heavier aqueous phase remaining at the outside of the bowl, and the oil phase moving into the center. In the past decade, both major manufacturers of centrifuges in the western world have introduced systems for adjusting the aqueous: oil phase ratios exiting their machines while running. The solids, collected at the outer extremities of the bowl, are allowed to escape as heavy slurries by momentarily lowering the bottom of the bowl on a timed *desludging cycle*.

Olive Oil

Traditionally, oil was extracted from fruit of the olive tree, *Olea europea*, by crushing cleaned, ripe olives, including the seed, using stone "edge rollers" or metal grinders; milling by mixing the paste while heating to coalesce the oil droplets; and shrouding it in press cloths or mats for squeezing in lever, wedge, mechanical screw, or hydraulic presses. Next, the *must* (oily liquids escaping the press) was centrifuged to separate the oil and aqueous phases. Lower quality secondary oils were obtained by reworking and repressing the pomace, or by drying it for solvent extraction. Modern olive oil extraction plants: crush the olives and seed using hammer mills; mix the paste while heating; and separate the must from pomace using decanters. The must is heated and separated by disk centrifuges. The solids may be reextracted several times. Some olive oil plants now use bladder presses, similar to those for crushing grapes in making wine, to remove the highest quality oil. Virgin oils are separated by pressing, and usually are usable after filtration. Pomaces are dried and their remaining oil extracted by solvent. Some operations use the desolventized extracted pomaces to fuel steam boilers for the plant [73–75].

Coconut Oil

Coconuts, from the *Cocas nucifera* palm, are dehusked before cracking the nut to drain away the coconut water. Then, the flesh is separated from the adhering shell and dried, raising the oil content from approximately 30% in

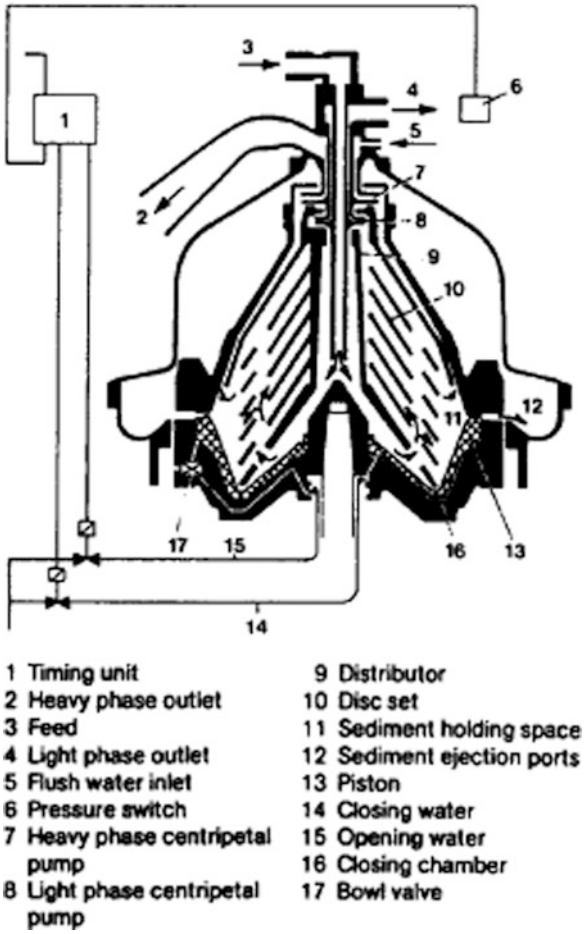


Fig. 34.6 Schematic drawing of Westfalia Model RSA refining separator with self-cleaning bowl. (Courtesy of GEA Westfalia Separator Company, Northvale, NJ)

the "meat" to 50–65% in the resulting copra. Considerable amounts of copra are prepared by hand and sun-dried to supplement family income in tropical countries. Centralized coconut mechanical husking and dehulling facilities, which dry the coconut meat using heat generated from burning the husks, offer advantages of improved moisture control and reduced mold spoilage and aflatoxin problems and are increasing in number. In the oil extraction process, copra is: (1) cleaned by shaker screens to remove trash; (2) size-reduced by hammer or attrition mills, or fluted roller mills; (3) optionally flaked; (4) additionally dried if necessary; and (5) hard pressed or prepress-solvent extracted [76]. Specially designed expanders have been applied to preparing copra for coconut oil extraction.

Palm Oil

Two distinctly different types of oils are produced from the fruit of the Southeast Asia and African oil palm, *Elaeis guineensis*, and its hybrids with the South and Central American palm, *Elaeis oleifera*. Palm oil is obtained from the red-orange fleshy part of the fruit, which resembles an oversized olive about the size of a small chicken egg. Palm kernel oil is derived from the kernel within the nut. Well over 98% of the fatty acids in palm oil belong to the C16 and C18 palmitic-stearic group, whereas approximately 64% of the fatty acids in palm kernel oil consist of the C12 and C14 lauric group.

A palm tree produces 10–15 fresh fruit bunches throughout the year, weighing 5–23 kg (10–50 lb) each. The bunches are cut from the tree with knives attached to long poles and are transported to the oil mill, sometimes by a small-gauge railroad. Although palm fruits somewhat resemble olives, they have a very strong lipase enzyme which is deactivated first by steaming the bunches at about 40 psig for 50–75 min. This also loosens the fruits on the stalk, which are freed in thresher drums and passed through a digester to convert the fleshy pulp to mash. Then, the mash is pressed by twin-screw or hydraulic presses to yield red crude oil. The nuts are dried, shells cracked, and the kernels separated and bagged or bulk-stored for sale and/or solvent extraction in a fashion similar to the processing of row crop oilseeds [77].

Animal Fats and Fish Oils

Extraction of Lards and Tallows

A variety of methods, old and new, is used for extracting animal fats [78]. The method used depends on the required properties of the edible or inedible nonfat product produced and the age of the facility since construction or its last modernization. In recent years, continuous processes generally have replaced batch processes for edible and inedible rendering to take advantage of heat recapture systems, economies and reduction of worker safety problems through automation, and the ability to minimize discharge of offensive odors. Modern edible and inedible rendering plants located near urban areas often are under negative pressure, and the building and processing equipment operate under slight vacuum. Steam vapors from processing are condensed, and air taken into the building is water-scrubbed before return to the atmosphere. Edible and inedible animal fats and fish oils may be subjected to refinery processes similar in principle to those of vegetable oils. Industrial fats often are split by high-pressure steam into fatty acids for further processing by the oleochemicals industry [79].

Edible products for human consumption are processed under federal or state inspection in facilities separate from inedible rendering plants. In the United States, construction of the processing area and designs of equipment selected are previewed and approved before startup by the Food Safety

Inspection Service of the USDA. Only raw materials passed by FSIS inspectors may be used. They may be chilled or frozen and shipped in refrigerated trucks or railroad cars under FSIS seal to the edible rendering facility. On-duty FSIS (or state) inspectors monitor the rendering operation. Edible rendering plants are limited to one species in the United States, and mixing fat of different species is not permitted [80].

Edible beef tallow is produced from the fat of cattle (*Bos taurus*). A counterpart, produced from sheep (*Ovis aries*), is known as mutton tallow. Lard is rendered from the fatty tissue of pigs (*Sus scrofa*). Edible chicken fat is rendered in some countries [81]. Essentially, three methods are used for separation of fat from animal tissues. In older *batch wet rendering* processes, an autoclave is filled with precut raw material, closed, and steam is injected to raise the temperature to about 140°C/280°F. After heating for 2–3 h, the pressure is slowly reduced to atmospheric to avoid emulsification. After a settling period, the free fat is drained from the autoclave; the cracklings are pressed by single-screw machines and sent to drying. Indirect heating is used in *batch dry rendering*. A reactor, equipped with a rotating agitator, and jacket at 6–7 bar (88–103 psi), liberates the fat in 1.5–2 h. On discharge, the fat is drained and the cracklings are pressed. Where batch-type cage presses are still used in other countries, the cake is formed in the shape of large wheels, sometimes called *greaves*.

Much of the edible rendering industry has adopted continuous *wet rendering*, in which the minced raw material is heated first to 60°C/140°F, and then to 90°C/195°F, in an airtight melting section within minutes. The heated material then is separated into solid and liquid fractions by mechanical horizontal decanters (Fig. 34.5) or dewatering screw presses, and the oil is separated from the aqueous portion (stick water) and fines by a three-phase disk-type centrifuge (Fig. 34.6). The pure fat is flash-dried and cooled to approximately 12°C/20°F above melting point by passing through a tube-in-shell or plate heat exchanger before storage and shipping [82].

Lower heating temperatures are used when producing partially defatted beef fatty tissue (PDBFT), or similar edible products of other species, used in making processed meats, including frankfurters. Fatty tissues and trimmings are ground and heated to 43°C/110°F in a mixing tank to melt the fat but still retain the heat-setting properties of the tissues for later use. The slurry is passed through a disintegrator to rupture the fat cells, and then through a horizontal decanter for separation into solid and liquid phases. The solids are cooled for packaging and used in making processed meats. The liquid is heated to 93°C/200°F to coagulate proteins and passed through a desludging disk-type centrifuge to "polish" the oil by separating the stick water and removing any solids [83].

Higher heat treatments, using open cooking kettles, produce darker and more strongly flavored fats and cracklings, also usable as edible food ingredients, which are preferred in specific applications. But, for the most part, bland edible animal fats are preferred and may later be neutralized (alkali refined), bleached, hydrogenated, deodorized, rearranged (interesterified), and fractionated in ways similar to vegetable oils before incorporation into margarines/spreads and shortenings, or used for frying [84].

Inedible Animal Products

Inedible animal products include viscera and inedible parts, carcass parts condemned by inspectors, fatty trimmings from butcher shops, outdated fresh and processed meats, and dead animals that have been skinned. They may be rendered by wet or dry batch processes. In modern rendering, the flesh and bones are ground or chipped, heated to denature the protein and release the aqueous and fat fractions. Next, the slurry is passed through a decanter or dewatering press to separate the solids from the liquid which is further heated to reduce viscosity in separating fat, stick water, and sludge. The meat/bone fraction is dried, reaching high temperatures specified by the federal government to destroy pathogenic bacteria. The solids then are pulverized by hammer mills and sieved for animal feed use, with the separated large pieces recycled to the grinders. Inedible renders, sometimes called *the original recyclers*, play an increasingly significant function as the world wrestles with problems of biodegradable waste disposal.

Restaurant Greases

Used frying oils typically are processed in separate inedible systems. Restaurants and large commercial fryers dump their spent oils into on-site bins, equipped with steam heating coils provided by the grease processor. Pilferage of grease has been a problem in the industry, and covers on the bins are kept locked. The collector may attach a steam line to heating tubes in the bin to melt the fat if required; then, it is pumped to a tank on the collection truck. An exchange of fats occurs between the oil and the product during frying. For example, the used grease may contain substantial quantities of chicken fat from frying. At the processing plant, the liquid grease is heated to 100°C/212°F and flashed into an evaporator flash chamber operating at 82–85°C/180–185°F and 21 in. mercury vacuum to remove the moisture. Next, the dried grease is passed through a decanter to remove any solids and partially cooled before storage [85]. Some inedible renderers also provide services for pumping restaurant and grocery store grease traps. These fats are segregated for handling in separate processing facilities and sold in separate markets.

Table 34.9 Specifications or typical analyses of edible and industrial/feeding animal fats (Compiled from: NRA [80])

Grades	Titre min (°C)	FFA max (%)	FAC[a] color max	Moist. max (%)	Iodine value max	Saturated (%)	Fatty acids distribution unsaturated (%)	Linoleic (%)
Edible[b]								
Beef tallow—USDA certified	41.0	0.75	3	0.10[c]	40–45			
Lard—USDA certified	38.0	0.50	[d]	0.20[c]				
Inedible—industrial[b]								
Top white tallow	41.0	2	5	1 MIU[e]				
All-beef packer tallow	42.0	2	None	1 MIU				
Extra fancy tallow	41.0	3	5	1 MIU				
Fancy tallow	40.5	4	7	1 MIU				
Bleachable fancy tallow	40.5	4	None	1 MIU				
Prime tallow	40.5	6	13–11B	1 MIU				
Special tallow	40.0	10	21	1 MIU				
No. 2 tallow	40.0	35	None	2 MIU				
"A" tallow	39.0	15	39	2 MIU				
Choice white grease	36.0	4	13–11B	1 MIU				
Yellow grease	g	15	39	2 MIU				
Typical analyses—feed grade fats								
FGF (for all feeds)	29–45	40	37	2–4 MIU	40–100	25–50	50–75	4–40
FGF (for milk replacers)	38–41	5	9	1 MIU	47	50	50	4
All-beef tallow	38–43	5	7	1 MIU	47	50	50	4
All-pork fat	32–37	15	37	2 MIU	68	38	62	12
All-poultry fat	28–33	15	19	2 MIU	85	28	72	20
Acidulated vegetable oil soapstock	18–31	70		4–6 MIU	90–140	6–31	69–94	20–75
Palm oil	28–36	5		2	53	42	58	10

[a]*FAC* Fat Analysis Committee, AOCS
[b]American Fats and Oils Association specifications for tallows and greases
[c]Insoluble impurities 0.05% maximum
[d]Lard color maximum = 1.5 red Lovibond color (5.25-in. cell); Lard peroxide value 4.0 meq/kg max
[e]*MIU* moisture, insoluble impurities and unsaponifiables combined
[f]When required, titer to be negotiated between buyer and seller on contract-by-contract basis

Animal Fat Specifications, Production, and Utilization

Specifications, or typical analyses, of edible, industrial, and feed animal fats are shown in Table 34.9 [80, 86]. Much emphasis is placed on Titer, the solidification temperature of fatty acids in a saponified sample of the fat or oil (AOCS Method Cc 12–59). Feed ingredients in the United States may not be as aesthetically attractive as food ingredients, but are required to pass the same toxicology standards.

Rendering produced an estimated 4.18 million metric tons of animal fats in the United States in 2000 [87]. Of this amount, approximately 18 and 6% were edible tallow and lard, respectively, and 41 and 35% were inedible tallow and grease. Approximately 15 and 34% of the edible tallow and lard, respectively, and 37% of the inedible tallow and grease were exported. Of the inedible tallow and grease used in the United States, an estimated 75% was used as animal feed, 16% was converted to fatty acids by the oleochemicals industry, 4% was used in soaps, and 3% in lubricants. Inedible animal fats are the lowest cost domestic fat sources. Their market price per pound sometimes is less than fuel oil, and rendering plants have chosen to burn them as fuels. In 2001, animal fats were included with vegetable oils for federally supported trials of biodiesel fuel.

Fish Oils

Raw materials for producing fish oils include: (1) *pelagic-type* (surface feeding) fish pursued for reduction to meal and oil; (2) waste products produced at facilities that process edible fish; and occasionally (3) *by-catch species* also netted with the primary catch. The type of processing used depends on geographic location, species of fish normally taken in the area, and whether done at an on-shore plant or a factory ship. As in continuous wet rendering, whole fish or trimmings are ground, cooked, pressed, or decanted to yield solids and liquid, and the liquid fraction then centrifuged into stick water and oil [88, 89]. A significant

fish protein industry, using trawlers for netting and mother ships for processing, has developed in Alaska. Local fish species have low oil content, and most of the oil produced is used on board to power steam boilers and engines [90]. Dried animal meals and fish-meals do not contain natural antioxidants, and it is common practice to preserve their fat by using synthetic antioxidants. This is especially important in fish meals, where rapid polymerization can generate sufficient heat to cause spontaneous combustion of stored meals.

Fish oils may be alkali-refined, bleached, hydrogenated, deodorized, and used in making margarine/spreads, other food products, and nutraceuticals. Direct food uses are approved, but seldom made in the United States. Because fish oil contains fatty acids with three or more double bonds, it readily polymerizes in the presence of air and is a major drying oil used for coatings. This property is further enhanced by *kettle bodying* (heating and mixing while bubbling in air). The fatty acid compositions of different fish oils, processing, and uses are presented by Bimbo [91], and Bimbo and Crowther [88]. Nonfood uses include animal feeds, fish attractants and lures, automotive gaskets, caulking compounds, ceramic deflocculants, core oils, fatty acids, fatty acid chemicals, fermentation substrates, fire retardants, fuel oil, illuminating oil, insecticidal preparations, leather tanning, lubricants and greases, mold-release agents, mushroom culture, oilfield chemicals, oiled fabrics, ore flotation, plasticizers, polyurethane lures, pressed wood fiber boards, printing inks, protective coatings, refractory compounds, rubber compounds, rust proofing, soaps, specialty chemicals, and tin-plating oils.

Feeding Animal and Marine Fats

Animal and marine fats provide approximately 2.5 times more calories per unit dry weight than carbohydrates or proteins, but are lower priced. Digestive tract capacities limit growth of broilers and turkeys and productivity of laying hens, and these animals respond well to high-energy diets, another name for fat-containing feeds. This also is true, to a lesser degree, for pigs and fish. However, high intakes of oil can disrupt normal function of rumens, and various bypass techniques are used in feeding cattle. The most common has been to hydrogenate fatty acids to melting points above rumen temperatures. Because of concerns about bovine spongiform encephalitis (BSE or "mad cow disease"), feeding of mammalian meat meals to ruminant animals has been outlawed in the United States and much of Europe, but these restrictions do not apply to feeding of tallows and greases. Concerns also exist about potential crossover of BSE to cats, and ruminant meat and bone meals are avoided in formulating dry cat foods.

Special needs must be addressed in pet foods. The lower melting point animal fats (choice white greases) are more appealing in odor than the tallows. However, lower melting fats can wick into and disfigure paper packaging. Solutions have included using the higher titer fats, including nonpermeable plastic layers in multiwall bags, laminating fat barriers onto paper, and filling into plastic bags. Some foods for guard duty and sled working dogs, and some fish feeds, require 30–40% fat content. However, high-fat formulas do not extrude easily even on modern machinery. Solutions have included using twin-screw extruders, which convey better than single-screw machines, the inclusion of full-fat soybean meal where the oil still is bound within its natural matrix, and enrobing the products with fat after extrusion and drying.

In addition to increasing caloric density and feed palatability, and improving appearance, feed efficiency, and reducing feed costs, feeding of animal, marine, and vegetable fats can:

1. Provide needed molecular structures through dietary EFAs and phospholipids
2. Increase blood glycogen levels and endurance in working animals such as horses and sled dogs.
3. Lower the heat of reaction during digestion and metabolism, thus increasing tolerance of heat by large animals during summertime or in tropical areas.
4. Prevent dermatitis and improve the appearance of skin and hair–an important effect of polyunsaturated fatty acids.
5. Carry fat-soluble vitamins and natural color compounds, for example, yellow pigments to improve the color of egg yolks; red and orange colors for feeding salmon.
6. Prevent segregation of mixed feeds.
7. Lubricate feed-processing machinery.
8. Bind heat-sensitive flavorings, vitamins, medications, "instant gravy mixes" to pet foods and feeds after extrusion and drying.
9. Reduce dustiness of feeds and improving animal health [86].

Row Crop Oilseeds Processing

Extraction Plants

The term *row crop* in this chapter generally means annual crops that are grown in rows. Their seeds have many similarities in extraction and oils processing and often can be handled in the same facilities if provision is made for differences in dehulling requirements. As a group, these oils contain appreciable amounts of phosphatides, which must be

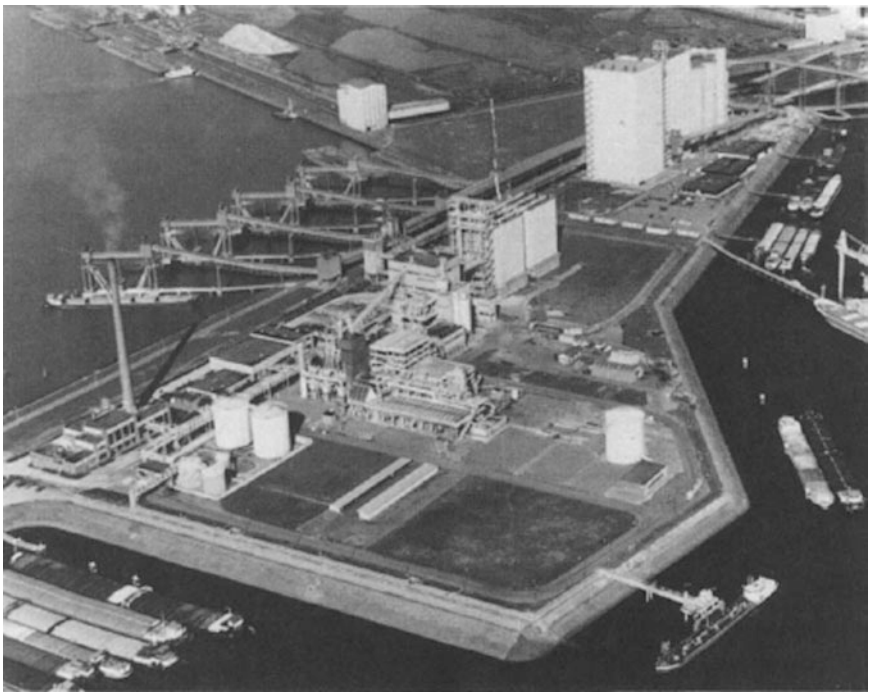


Fig. 34.7 Photograph of an operating soybean extraction plant. (Courtesy of Archer Daniels Midland Company, Decatur, IL)

removed, and are not as readily processed by physical refining as tree seed pulp crops such as palm and olive oils; instead, they must be prepared for lower temperature deodorization.

Concerns about marketing the meal (accounting for 65–75% of returns per bushel of soybean grown), and disposal of refinery byproducts, have reshaped the domestic soybean processing industry in the last 20 years. Soybean extraction plants now are located close to domestic meal feeding markets, and/or on major barge waterways and railways to reduce transportation costs to export facilities. Byproducts of refining are difficult to handle, and their production exceeds market demands. The major oil processors now generally locate extraction plants and oil refineries on the same property to enable spraying and drying surplus gums (crude lecithins) and soapstock on the meal for sale as animal feed. Independent edible oil refineries have almost disappeared, although refineries already associated with an extraction operation may purchase crude oils from other sources.

Economies of scale have led to minimum capacities of about 2,000–3,000 metric tons per day for new United States regional soybean extraction plants, and larger facilities (4,000–6,000 t per day) for soybean plants that pool some of their output for export. At the United States average yield of 38 bushels/acre, each 1,000 metric tons per day solvent plant capacity requires the output of 966.65 acres/day, or 338,328 acres/year (136,975 ha). A 2750 metric tons per day plant would use the soybean crop of 930,402 acres/year (376,681 ha). An extraction plant of this size will support a 500 t per/day refinery. Regional plants are smaller than export plants because accumulating this much soybean, in competition with other processors, can be difficult in some areas of the United States.

The largest solvent extractors can process 8,000 and 10,000 metric tons of soybean per day and are used primarily for the international trade. Two large extractors are used in the world's largest oilseed extraction plant in Argentina, reported to process 16,000 metric tons of soybean per day. Installations typically include: (1) facilities for unloading railroad cars, barges, or ships; (2) storage for at least several weeks' supply of seed, solvent, meal, and crude oil; (3) seed cleaning, preparation, oil extraction, and meal desolventizing equipment; (4) an on-site oil refinery; (5) repair and maintenance shops; (6) a quality control laboratory; and (7) offices and locker rooms for supervisors and workers. A photo of an operating soybean extraction seaport plant is shown in Fig. 34.7.

Seed Preparation for Extraction

A general flow sheet for direct solvent extraction of many row crop oilseeds is shown in Fig. 34.8. Initial quality of the seed and its preparation for extraction have the most effect on yield of extracted oil, subsequent required refinery operations, and yields of (saleable) *neutral oil*. Freshly harvested seed should be cleaned of trash, which may become ignited during drying, or harbor moisture that accelerates seed heating in storage. Oils of most good

quality, dry, row crop seeds contain 0.5–0.75% FFA (AOCS Method Aa 6–38, Ac 5–41) with up to twice this range often accepted in trading without discounts. Rising pile temperature and FFA signals seed deterioration. The maximum moisture content for holding seed for long periods without spoilage varies with storage temperature and ranges from 8 to 13% among species. It is inversely related to the oil content, because less protein and carbohydrate is available to compete for water in high-oil seeds; however, the optimum relative humidity for storage is constant at about 65–70% for all seeds. If not adequately cleaned before storage, the seed should be completely cleaned before further processing to prevent clogging and damage of equipment. The processing system should be well equipped with magnets to arrest tramp metal that arrives with the seed or that is shed by equipment. Electronic metal detectors now are being installed as occurrence of stainless steel tramp metal increases.

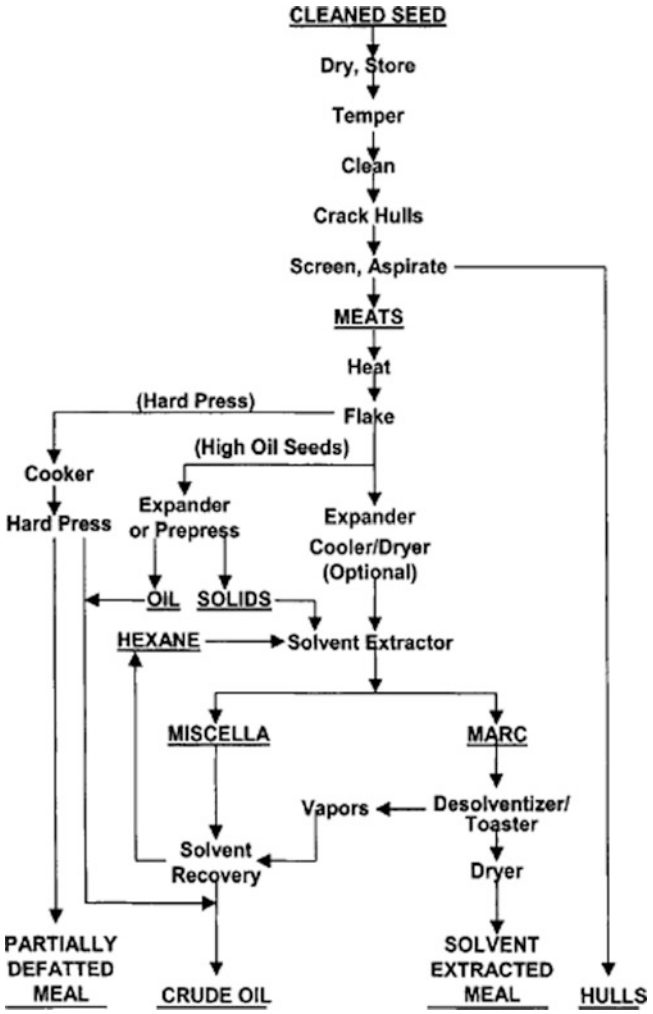


Fig. 34.8 General flow sheet for extraction of row, crop oilseeds

Oilseeds do not have fat cells like those of animals for storing fats. Instead, oil is stored in microscopic globules throughout the cells of dicotyledonous oilseeds, or in corn germ or rice bran. Yields and processing costs are highly dependent on the effectiveness of preextraction operations to disrupt cells and free the oil for recovery. Operations differ among various oilseeds, mainly in techniques of dehulling. Traditional processes have heated soybean and let it stand (temper) for several days to loosen the hull (Fig. 34.9) [92]. They are being replaced by hot dehulling systems which loosen the hull and crack the seed in one operation immediately before flaking and extraction (Fig. 34.10). Avoiding a second heating step saves energy.

Hulls are removed in a two-step process, called *dehulling* or *decortication*, in which seed is first cracked, and the hulls removed by screening and/or aspiration to obtain "meats" for processing. The major objective of removing the hulls is reduction of fiber content in meals for feeding poultry and swine, resulting in increased protein content and reduction of volume of material sent to the extractor. Partial retention of hulls in the meats was required earlier to improve traction in screwpressing operations, but hulls are no longer required with availability of expanders equipped with oil drainage cages. It is common practice either to leave sufficient hulls with the meats to just surpass minimum protein guarantees of meals, or to adjust high protein meals to industry trading standards

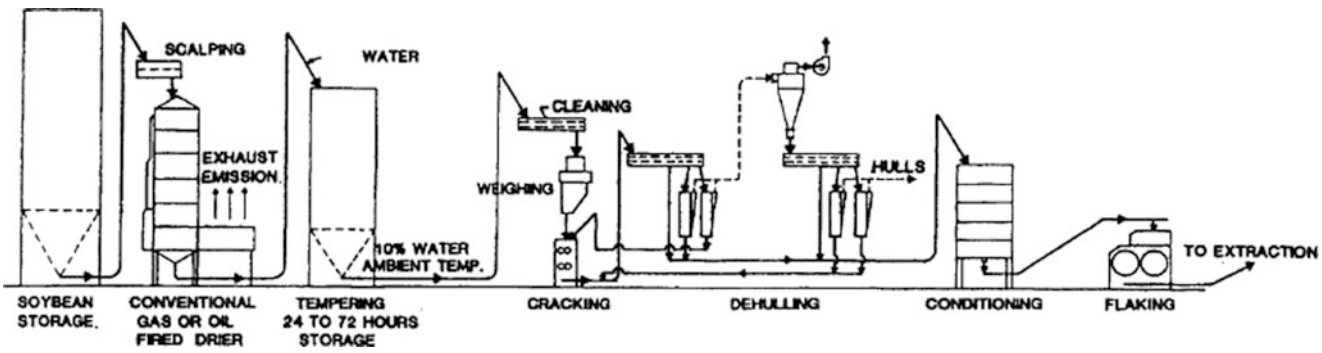


Fig. 34.9 Preparation system for conventional dehulling and flaking of soybeans. (From Moore [92], 141A–144A, With permission)

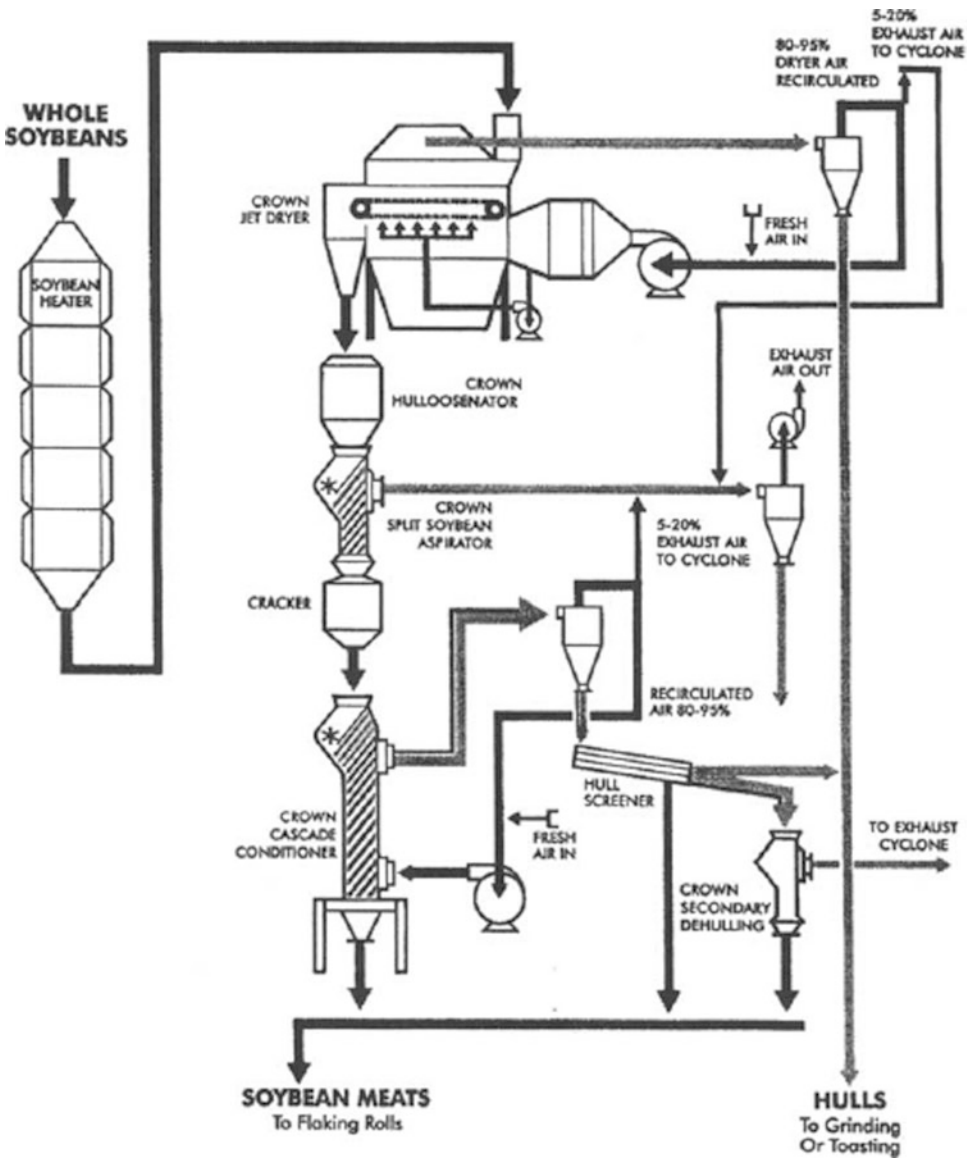


Fig. 34.10 Patented crown iron works hot dehulling system for soybean. (Courtesy of Crown Iron Works Company, Minneapolis, MN)

by adding back hulls after extraction. Currently, dehulled (low fiber) soybean meal trades at 48% protein, nondehulled soybean meal at 44%, cottonseed meal at 41%, and dehulled sunflower seed meal at 42% protein.

The meats are heated by steam injection to soften and increase the moisture content for plasticizing if needed in flaking. Cookers and heaters, used in the oilseeds processing industry, often are shallow circular ring-cooker pans with sweep arms in a multi-stack design, as shown in Fig. 34.16. In earlier processes, seed was heated to about 74°C/165°F before flaking to about 0.3-mm (0.012-in.) thickness. Now, it is realized that *phospholipases*, enzymes that make the phospholipids nonhydratable and more difficult to remove from the oil by water degumming, are highly active at this temperature, and seeds preferably are heated to less than 57°C/135°F or higher than 85°C/185 F to avoid the range of maximum phospholipase activity. Often, the flakes next pass through an expander for rapid heating to 105–121°C/220–250°F for homo-genization and shaping into collets.

Before the mid-1980s, processing concepts were based on classification of oilseeds into two groups. Meats containing over 30% oil on a dehulled or as-processed basis, including rapeseed/canola, oil-type sunflower seed, peanut, safflower seed, and copra, were considered *high-oil seeds*. Typically,

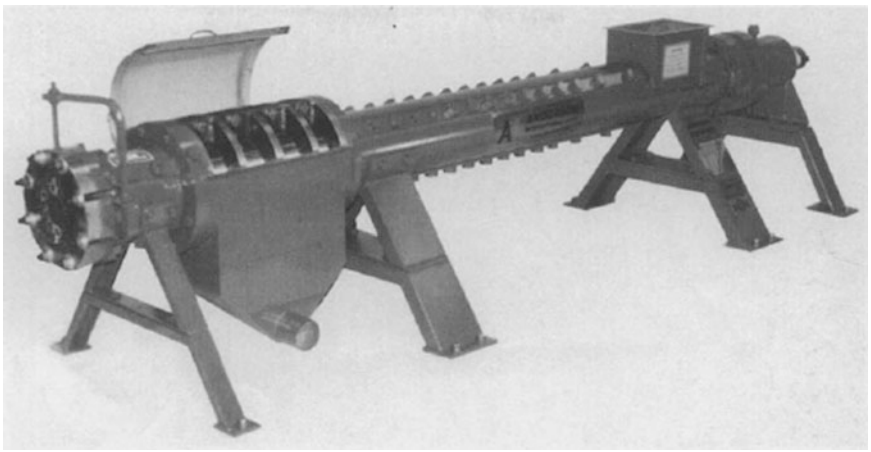


Fig. 34.11 Anderson International Corp. Hivex-Series-Expander™ with oil drainage section for preparing extraction collets from high-oil-content seeds. (Courtesy of Anderson International Corp, Cleveland, OH)

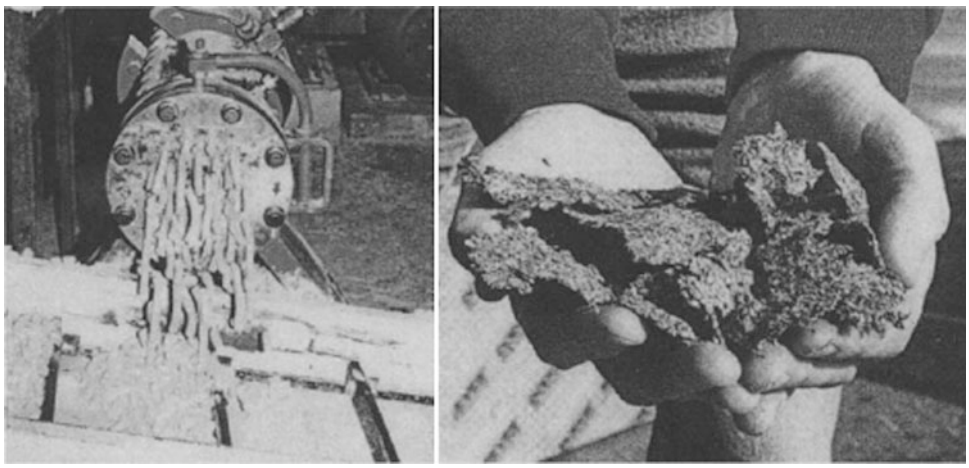


Fig. 34.12 *Left*: Soybean collets for extraction exiting die plate head, Solvex™ expander; strands break into random lengths. *Right*: Puff sheets made by hydraulically positioned cone choke head on expander. (Courtesy of Anderson International Corp., Cleveland, OH)

these seeds were dehulled (shredded in the case of copra); heated, flaked, and hard pressed, leaving 4–6% residual oil in the meal. Processors desiring to recover additional oil would first prepress high-oil seeds to 15–18% oil content using lighter-duty screw presses, and then solvent extract the press cake to less than 1% residual oil content; this process is called *prepress-solvent extraction*. Hard pressing was considered too inefficient for low-oil content seeds such as soybean unless nearby markets were available for the oil-rich meal. Soybean typically has been direct solvent extracted to less than 0.75% residual oil content. Cottonseed was extracted originally by hard press, later by prepress-solvent extraction, and now mainly by expander-direct solvent extraction techniques.

Introduction of the expander, a high-shear extruder with an interrupted-flight screw, in the mid-1980s revolutionized oilseed extraction practices. Essentially all solvent-extracted cottonseed and approximately 70% of domestic soybean tonnage now are processed with expanders. The expander heats, homogenizes, and shapes seeds or flakes into porous collets (pellets) that are more dense (weigh more per unit volume) than flakes, but are more rapidly extracted, approximately doubling the throughput of continuous solvent extractors. In effect, solvent extraction is changed from a diffusion process to a leaching process. Even though the expander homogenizes the seed, prior flaking still enhances oil recovery, but can be done at 0.5-mm (0.020-in.) thickness instead of the typical 0.3 mm (0.012 in.). The flakes or collets are cooled, with some drying occurring, to about 6°C/10°F below the boiling point of the solvent before entering the extractor. Collets also drain more completely than flakes, greatly reducing steam costs for desolventizing the extracted meal.

The Anderson International Company of Cleveland, Ohio, has patented an expander with a drainage cage (Fig. 34.11) to reduce the oil content of high-oil seeds to less than 20%, thus enabling the production of collets for direct solvent extraction from completely dehulled seeds such as sunflower seed and peanut. Replacement of the die plate (Fig. 34.12) with a hydraulically operated cone discharge head in the mid-1990s solved many of the problems first experienced in using oil-drainage cage-equipped expanders.

Introduction of the expander has enabled extraction plants to handle additional seed species, with purchase of only minimal cleaning and dehulling equipment where needed.

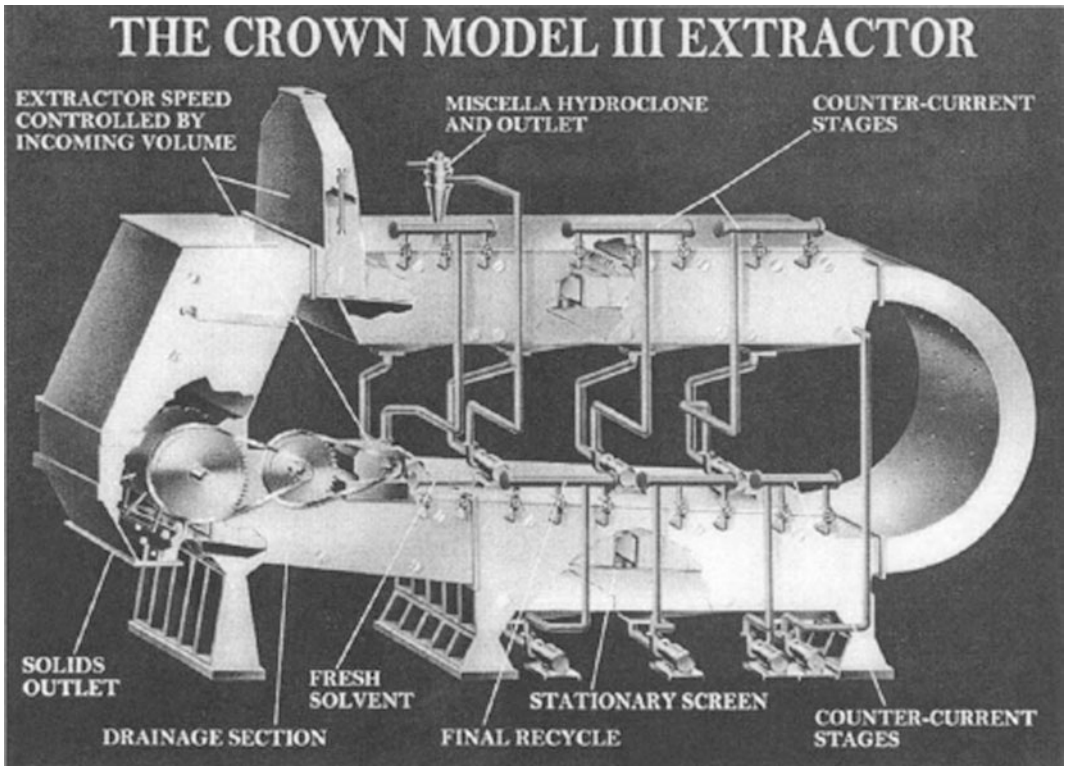


Fig. 34.13 Rectangular loop-type continuous countercurrent solvent extractor. (Courtesy of Crown Iron Works Company, Minneapolis, MN)

Prepress-solvent extraction facilities are being replaced by expander-direct solvent extraction equipment, leaving two basic extraction processes in modern large volume oilseed extraction plants: expander-direct solvent extraction, and hard press for applications where seed supplies are limited, or other considerations do not warrant construction of solvent extraction plants or the expense of skilled personnel and additional safety precautions for their operation. Hydraulic cage presses still are used in processing industrial crops such as castor seed, and for edible oils in developing countries.

Solvent Extractors

Hardly any batch-type oilseed solvent extractors remain. Three of the more popular types currently manufactured include: (1) *shallow bed-type* extractors, where a 0.5–1.5 m thick layer of collets or flakes is pulled across a linear screen and extracted by drenching with a countercurrent flowing miscella consisting of solvent and solubilized oil (Fig. 34.13); (2) *diffusion belt type*, where deeper beds of collets or flakes are conveyed on a woven mesh or folding-pan belt while drenched in countercurrent fashion with miscella (Fig. 34.14); and (3) *deep bed-type* which are constructed as carousels with pie-shaped cells that are filled with collets or flakes (~3 m deep), and extracted in counter-current flowing fashion by drenching with miscella. *Marc* (wet extracted flakes/collets) dropping doors and moving parts have been eliminated in the newer carousel models, and the cells are revolved across a fixed screen (Fig. 34.15). Shallow bed extractors are built in capacities of up to 8,000 metric tons per day, and carousel-type extractors at up to 10,000 metric tons per day.

Solvents

Many solvents have been proposed for extracting oilseeds, but later found ineffective; others were used for a period, but disallowed because of health concerns about residues in food and feed products, or worker exposure [93]. All extraction solvents approved currently are flammable. Most commercial oil extraction currently is with hexane, a mixture of petroleum refinery fractions with a boiling point of 65–68°C/145–155°F, that consists of at least 60% *n*-hexane, with the balance being short-chain homologues and branched compounds. Some plants are using isohexane, which boils at a lower temperature. The US-EPA raised many concerns about extraction solvents in the late 1980s and 1990s. The FDA's position that *n*-hexane is a neurotoxin was put aside after industry-sponsored research showed the problem does not exist in mixed solvent systems [94]. The EPA also raised concerns that discharged volatile organic compounds (VOC) are contributors to ozone production [95]. A major solvent

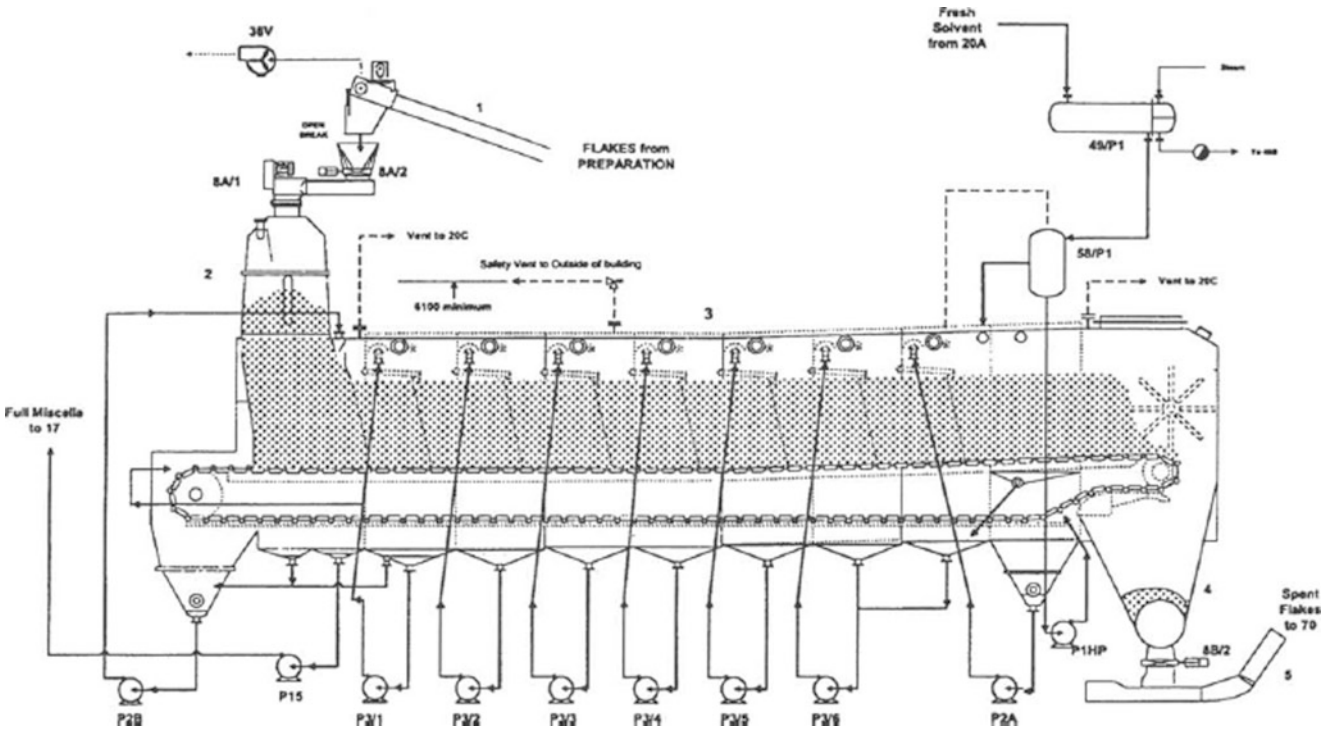


Fig. 34.14 Drawing of DeSmet LM perforated belt diffusion-type extractor. (Courtesy of Desmet Ballestra Oils and Fats, Brussels, Belgium)

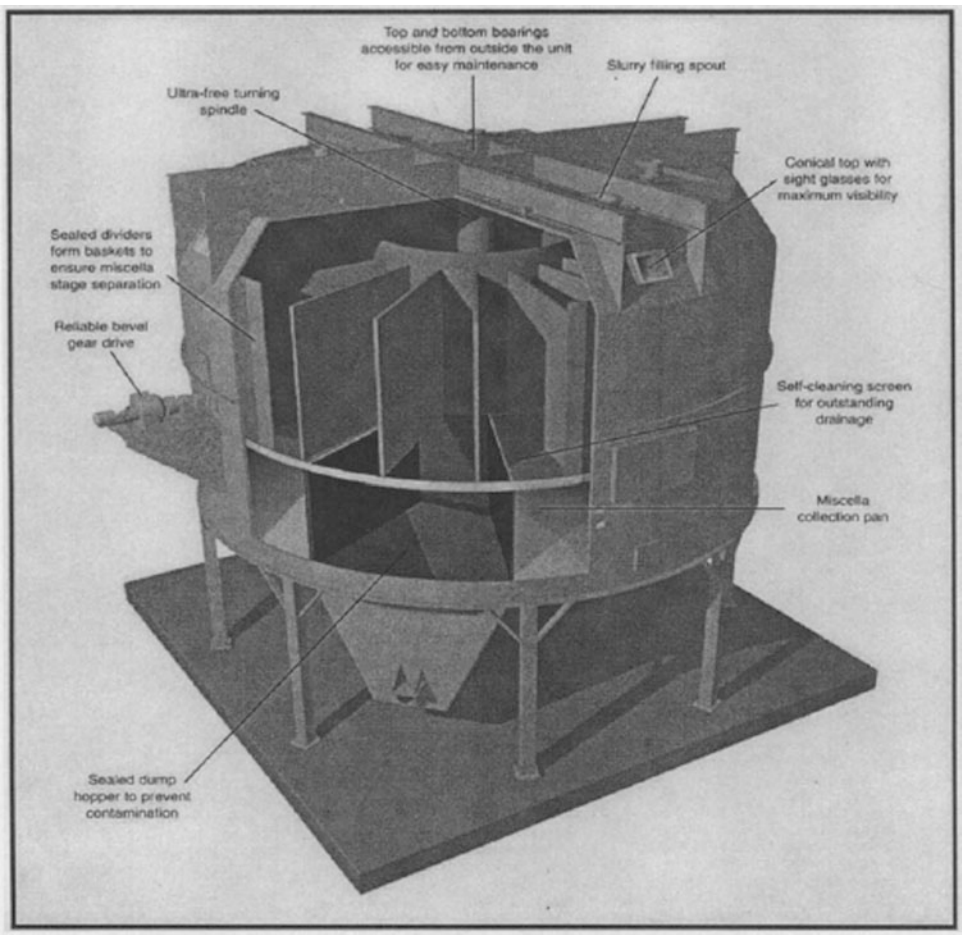


Fig. 34.15 Reflex™ "basket or circular type" 10,000 t/day extractor. *Note*: Basket revolves within shell. (Courtesy of Desmet Ballestra Oils and Fats, Brussels, Belgium)

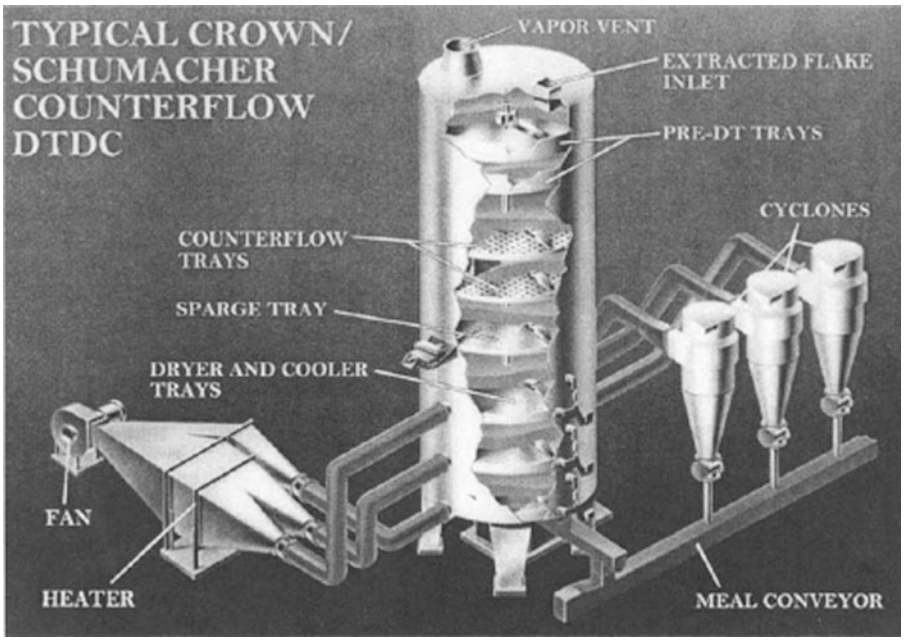


Fig. 34.16 Schumacher type desolventizer–toaster–dryer–cooler (DTDC). (Courtesy of Crown Iron Works Company, Minneapolis, MN)

containment program was instituted and resulted in domestic extraction plants reducing hexane losses from as high as more than 1 gal per ton of seed extracted to 0.25 gal, with some plants reducing losses to less than 0.16 gal per ton seed processed. Extraction solvents are highly flammable, and plants are built, equipped, and operated under Standard 36 of NFPA International, formerly known as the National Fire Prevention Association [96]. Additional worker exposure limits, safety practices, and training are established by the Occupational Safety & Health Administration (OSHA) of the US Department of Labor.

A major project added to the information about isopropyl alcohol (IPA) from earlier trials [97, 98] and showed it can be as effective an extraction solvent as hexane [99]. However, because of high retrofitting costs, IPA is not likely to be implemented while hexane-type hydrocarbons are allowed.

Batch extraction of vegetable oils with high-pressure CO_2 (carbon dioxide) in a critical state (at pressures required for maintaining a liquid phase) was heavily researched in the 1980s [100]. A continuous process has recently been commercialized in which CO_2 is injected into the barrel of a modified screw press (HIPLEX®, High pressure liquid extraction, Crown Iron Works, Harburg-Freudenberger, personal communication). Soy meals produced using this equipment maintain high protein solubility, with PDI's (protein dispersibility index) >70%, and a residual oil context <4%. This technology is being implemented where markets for food application demand "organic" labeling of ingredients and high protein solubility is a functional necessity for the product. Eighteen 400 metric ton/day critical propane extraction plants were processing soybeans in China in 2002. But, domestic critical propane demonstration lines have experienced safety problems. A critical CO_2 extraction laboratory instrument, for rapid analysis of fat content in seed and meals, has been marketed domestically since the mid-1990s.

Desolventizing-Toasting

The extracted, drained marc contains approximately 25% hexane holdup in soybean collets and 33% in flakes, which is vaporized in a desolventizer-toaster (DT) under vacuum. Some DTs have cooling sections, but separate dryer-coolers (DCs) often are used in large installations. Steam is sparged into the marc as the heat source for volatilizing the solvent. The condensate must be removed subsequently by drying. The moist "toasting" operation destroys enzymes and antigrowth factors such as trypsin inhibitors and hemagglutinins in soybean [101] and reduces meal protein solubility and digestibility by rumen microorganisms, thus improving rumen by-pass or escape in feeding cattle and sheep. Figure 34.16 shows a cutaway drawing of a Crown/Schumacher design desolventizer-toaster-dryer-cooler (DTDC) line. The drained marc enters at the top of a stack of circular trays and is mixed by sweep arms and pushed to fall through slots to lower trays. The bottoms of the initial trays also are steam jacketed. As the marc progresses downwards, it encounters rising steam and solvent vapors and is "toasted" by moist heat. The steam provides heat for vaporizing the solvent, but leaves condensate. The solvent-water vapors, drawn off at the top of the DT, are condensed and the solvent recovered. The desolventized flakes or

collets continue to work down through the trays where they are dried by hot air and then cooled by ambient air.

Miscella Refining

In processing most oilseeds, hexane is stripped from the miscella by distillation to produce a crude oil that subsequently is alkali or physically refined. However, gossypol and other pigments become extremely difficult to *bleach* if left in warm cottonseed oil for more than a few days. It is normal practice for cottonseed oil mills to send their crude oil immediately to an alkali refinery or to operate an on-site miscella refinery, where phosphatides, FFA, and color pigments are removed by alkali treatment of the oil-extraction solvent mixture. Cooling the crude oil as produced, until refining, also slows *fixing* of color.

In the process, miscella leaves the extractor at about 30–35% oil and is concentrated to approximately 65% oil by evaporation. The FFA in the concentrate then is reacted with alkali (sodium hydroxide solution) to produce soaps that are removed with other water-soluble compounds by centrifugation. Next, the solvent is removed from the miscella-refined oil by further evaporation, and the soapstock is spread on the meal in the DT to recover its solvent. Hexane vapors from the miscella and the DT are condensed, and the solvent is recycled to the extractor for reuse. The non-condensable gases are passed through a mineral oil stripper to recover the last traces of hexane.

Refining of Vegetable Fats and Oils

Technically, *refining* means alkali neutralization of FFA in the oil. But over time, all postextraction processing of oils has become known as *refining*, and the facility in which it is conducted a *refinery*. Conversions of the resulting ingredients into margarines and spreads, and bottling oils, often are done at different locations or companies. The objectives in refining and processing edible fats and oils include: removal of FFA, phospholipids (*gums*), oxidation products, color and off flavor/odor compounds, and toxic substances to produce light-colored, bland products with long shelf lives; obtaining a mixture of TAG with the desired solids content profiles over the temperature range of product use; and preparation and storage of semi-solid products with desired textures. A flow sheet for refining and processing fats and oils is shown in Fig. 34.17. Refining procedures reliably purify oils extracted from cottonseed, peanut, and corn germ that have been contaminated with (water-soluble) mycotoxins or pesticides, but the resulting meals may have to be destroyed, used as fertilizer, or further treated to inactivate aflatoxins.

Oil Receiving and Handling

Maximizing yields of saleable oil requires even more detailed analyses and attention to lot-to-lot differences during refining than in preparing oilseed lots for extraction. Using soybean oil as an example, the first priority on receiving a shipment, or the output of an adjoining extraction plant, is to characterize the overall quality of the oil and determine what needs to be done to prepare it for market. The responsibilities of the refinery may include preparing freshly extracted oil ready for sale as *Crude Degummed Soybean Oil, Once Refined Soybean Oil,* or *Fully Refined Soybean Oil* for export under National Oil Processors Association (NOPA) Trading Rules [102], or other agreements made with the buyer.

To prevent hydration and precipitation of phosphatides during storage and shipping, the phosphorous content of crude soybean oil must be reduced to less than 0.02% (200 ppm) before entering the trade. This usually is accomplished by water degumming.

If the refinery purchases soybean oils for processing, one of the first tasks is to check composition of the received oil against the contract (usually NOPA Trading Rules), in as much as this determines the final price paid:

- *Flash point* (indicator of residual extraction solvent)—AOCS Method Cc 9c-95(97) (>250°F)
- *Unsaponifiable matter*—Method Ca 6a-40(97) (<1.5%)
- *Free fatty acids* (FFA), as oleic—AOCS Method Ca 5a-40(97) (<0.75%)
- *Moisture and volatile matter* (M&V)—AOCS Method Ca 2d-25(97) and insoluble impurities—AOCS Method Ca 3a-46(97) (<0.3%)
- *Phosphorous*—AOCS Method Ca 12-55(97) (<0.02%)

Additionally, the analytical laboratory estimates how much saleable oil can be produced from the lot, usually by neutral oil and loss (NOL) analysis (AOCS Method Ca 9f-57). In this procedure, a solvent-diluted sample of the oil is poured over a column packed with activated alumina (aluminum oxide). After evaporation of the solvent, the weight percentage of the oil that passed through the column is considered *neutral oil,* and the weight of oil retained is the "loss." The analyst may run a *bleach test* (AOCS Method Cc 83–63) or a *refining test* (AOCS Method Ca 9d-52, seldom used currently) if concerns exist about reducing the color of the oil to an acceptable range.

Phosphatides Degumming, Lecithin Uses

Phosphatides are essentially removed in modern oil processing to minimize fouling the bleaching earth, poisoning hydrogenation catalysts, and darkening the oil color by heat during deodorization and deep fat frying. Phosphatide contents

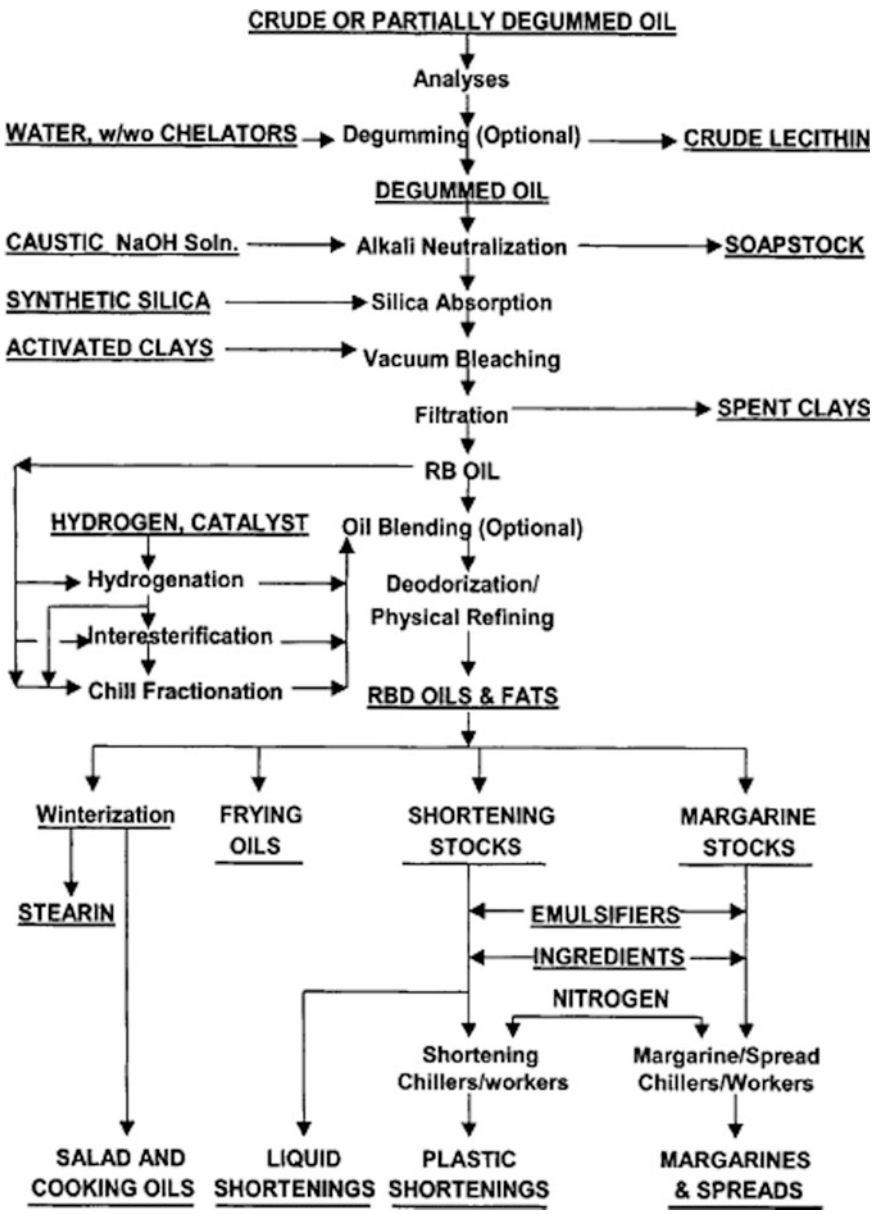


Fig. 34.17 Composite flow sheet of oils and fats refining and processing

of common vegetable oils are shown in Table 34.10. Soy, corn, and canola phosphatides are separated in North America, and some of the former Soviet Union countries separate sunflower seed phosphatides. For soybean oil, the relationship between phosphatide and phosphorous content is:

$$[\text{phosphatide } (\%) \times 10^4]/31.7 = \text{phosphorous ppm}$$

If lecithin is saved at the refinery, the hydratable phosphatides are separated by simple *water degumming* (hydration with deionized water, followed by centrifugation). However, some of the phosphatides will have been converted to NHP by enzyme action. In this case, a chelating agent (phosphoric acid usually because of lower cost) is added to the alkali in the FFA neutralization step to return the NHP to hydratable form. Palm oil has very low phosphatide levels and is physically refined after acid degumming and bleaching. The addition of chelating acids to crude row crop oils before alkali refining results in removal of hydrated phosphatides with the centrifuged soapstock, but viscosity is high and appreciable losses of neutral oil can occur by occlusion. Thus, many soybean oil refineries, without markets for crude lecithin, still run preliminary degumming operations and spread the gums with the later removed soapstock over the desolventized marc for drying in the dryer-cooler and sale as part of the soybean meal [103].

Commercial lecithin is produced by water degumming (precipitation from oil with ion-exchange treated water), separation by stacked disk centrifuge, and vacuum drying to less than 1% moisture content. Crude lecithins contain

Table 34.10 Phosphatide contents of common vegetable oil (From: Farr [103], With permission)

Type of oil	Phosphatide content As (%)	As Phosphorous[a] (ppm)
Soybean	1.0–3.0	311–940
Corn	0.7–0.9	220–280
Safflower	0.4–0.6	130–290
Sunflower	0.5–0.9	160–290
Peanut	0.3–0.4	95–190
Canola (super degummed)	0.16	50
Canola (crude)	1.0–3.0	311–940

[a]Phosphorous calculated as: [phosphatede (%) $\times$ 10^4]/31.7 = phosphorous (ppm)

70–72% acetone insolubles (AI) and are standardized to 62–64% and an acid value of 30 by addition of oil and fatty acids before sale. Crude lecithins may be treated with acetone to obtain free-flowing powders with 95–98% AI. Lecithin can be additionally purified, bleached, fractionated, hydrogenated, hydroxylated, acetylated, sulfonated, and halogenated [104]. One domestic company makes 13 kinds of lecithin for food uses alone.

Food applications of lecithins include: emulsification, wetting and dispersing agents, modification of baking properties, pan release agents, viscosity reduction of melted chocolate, anti-spattering agents in margarine, antioxidant effects, and nutritional supplements. Feed uses include wetting and dispersing agents in calf starters, and nutritional supplementation. Choline is a recognized vitamin, and inositol has been found essential in feeding some species of fish. Industrial uses include: emulsification and dispersion of active agents in pesticides, dispersing agents and stabilizers in paints and magnetic tapes, softening agents and penetrants for leather, and softening and lubrication of textiles. Cosmetic uses include: foam stabilizers and emollients in hair care, and emulsification, emollient, refitting and wetting agents in skin care. Pharmaceutical applications include: emulsifiers in parentoral nutrition, carriers and softening agents in suppositories, and emulsification and penetration improvement in cremes and lotions [105].

Some natural NHP always are present in crude oil, but development of additional NHP during seed extraction can be minimized by heat inactivation of phospholipases as explained earlier. In preparation for degumming, a tank large enough to supply the refinery with uniform oil feed stock for a suitable period of time is filled and mixed. Samples are taken for FFA, calcium, and magnesium analyses. Earlier practices of adding an amount of water equal to the weight of the phosphatides have been defined more precisely, and:

$$\text{added water} = (\text{ppm } P \times 3.17 \times 10^{-4}) \times 0.7$$

is recommended. The amount of phosphoric acid used is:

$$H_3PO_4 = [(Ca + Mg)/2] \times 10$$

with all components expressed in ppm.

The phosphoric acid and water are added to the warmed (65°C/150°F) crude oil stream, pass through a high-shear mixer, and are pumped to the stirred hydration tank. Details of the process, using an Alfa Laval (Lund, Sweden) PX-90 centrifuge rated at 33,000 kg/h for degumming, are shown in Fig. 34.18 [7]. After degumming, the crude oil is vacuum dried to <0.3% moisture and volatiles content and cooled to 50°C/120°F for storage or shipment. But, this step can be omitted if the oil is refined immediately [103].

The objective in acid degumming is to chelate the calcium and magnesium ions and render the nonhydratable phosphatide forms hydratable. In addition to phosphoric acid, citric and malic acids are effective, as well as ethylenediaminetetraacetic acid (EDTA). Acid-treated phosphatides are not used for production of commercial lecithins. Extensive reviews on oil degumming have been prepared [106, 107]. Lurgi, a German equipment manufacturer, has developed an EnzyMax™ process that cleaves the NHP with a phospholipase B at the triglyceride's second carbon to produce a lysophosphatide that is insoluble in oil and is removed by centrifuging [108].

In earlier times, the NHP content was determined by analyzing a water degummed sample for phosphorous, but the procedure took too long for commercial use. In reality, phosphorous is only a marker and loss of hydration actually results from the presence of divalent cations, primarily calcium and magnesium. Refineries now use induction coupled plasma (ICP) spectrographs for analyzing divalent cations content rapidly in aspirated crude oil and adjust the amount of phosphoric acid used for each "day tank lot" of analyzed oil. ICP units cost in the range of $75,000–125,000, but, reportedly, pay for themselves through increased oil yields in as little as 6 months in mid-size (500 t/day) refineries.

The crude oil from which gums are taken for lecithin production still contains non-hydratable phosphatides, but can be treated with a chelating agent before alkali neutralization and will be removed with the soapstock by centrifugation. Provision must be made for the added acid in calculating the amount of neutralizing alkali added.

Alkali Neutralization

The elimination of neutralized oil wash water is the major breakthrough of the decade in oils refining, with *modified caustic refining* or *silica refining* processes still being optimized. Phosphatides are removed by degumming, as already described, and FFA in the crude oil is still

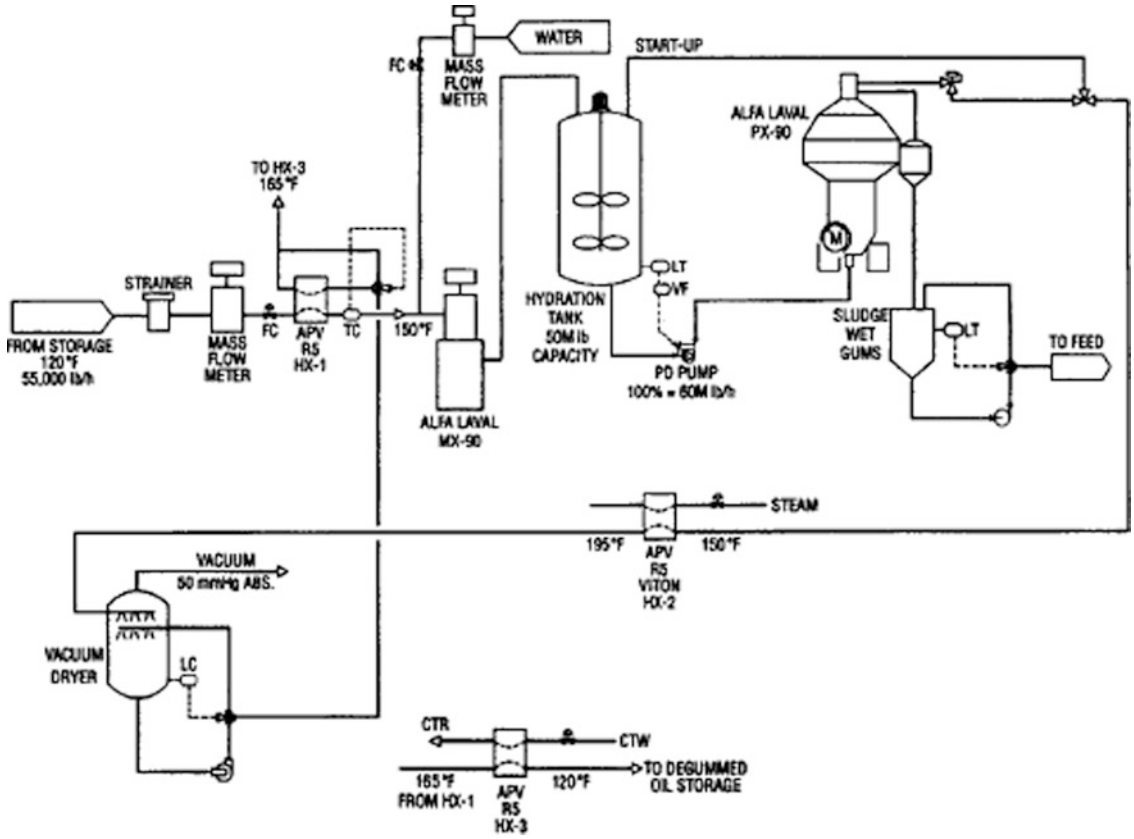


Fig. 34.18 low sheet of a modern water or acid degumming line. (From Farr [103], With permission)

neutralized with sodium hydroxide (*caustic*) solution (20–50°Be for cottonseed oil, and 16–24°Be for soybean, sunflower, safflower, peanut, and corn *oils*). But, the refinery then has the choice of water-washing the oil after removal of soapstock, or adsorbing the residual soaps on silica hydrogel before bleaching, thus eliminating problems of disposing the wash water. Process demonstration by the W. R. Grace Company began in 1986, with increasing growth in the commercial use of Trisyl™ in the 1990s. Several silica hydrogel suppliers now exist [103].

Two major processes have been used for alkali neutralization of FFA in row crop oils: the *long mix* and the *short mix*. The short mix process evolved in Europe, runs at a higher temperature, and reportedly is effective with a number of oils. The long mix process was developed in the United States and has been championed for refining soybean oil. It respects the principle that chemical reactions occur more rapidly and are harder to control, at higher temperatures (van't Hoff rule that the speed of reaction doubles with each 10°C rise in temperature). Traditionally, the long-mix process starts with crude soybean oil at ambient temperature, uses a low-concentration caustic solution, and has a mixer retention time of 15 min after which the oil–caustic mixture is heated to 70°C/160°F to reduce its viscosity before centrifuging. In the short-mix process, crude oil is heated to 90°C/194°F, mixed with high-concentration caustic solution for 1 min and centrifuged [109]. The throughput per hour of both systems is the same because the additional volume for the holding time is built into the long mix line.

A flow chart of a long mix neutralization process is shown in Fig. 34.19. The recommended retention time for soybean oil in this system is 6 min and was shortened by a major improvement in caustic–oil retention mixers developed by the Alfa Laval Company, Tumba, Sweden, in the mid-1990s [103].

The amount of caustic treat to be added for neutralization of soybean oil is calculated as:

$$\text{percent treat} = [(\text{factor} \times \text{percent FFA}) + (\text{percent excess})/\text{percent NaOH}] \times 100$$

where factor = 0.142, NaOH is determined from the 20°Be of the caustic solution, and percent excess is selected from the following ranges based on experience in the specific refinery: degummed soybean oil, 0.01–0.05; nondegummed soybean oil, 0.15–0.25. Continuing with Fig. 34.19, soybean oil from storage is adjusted to 38°C/100°F, passed through strainers, mixed with the treat in the rapid mixer, held in the retention mixers for 6 min, heated to 60°C/140°F, and passed through the primary (first) centrifuge [103]. The soapstock is returned to the extraction plant with surplus

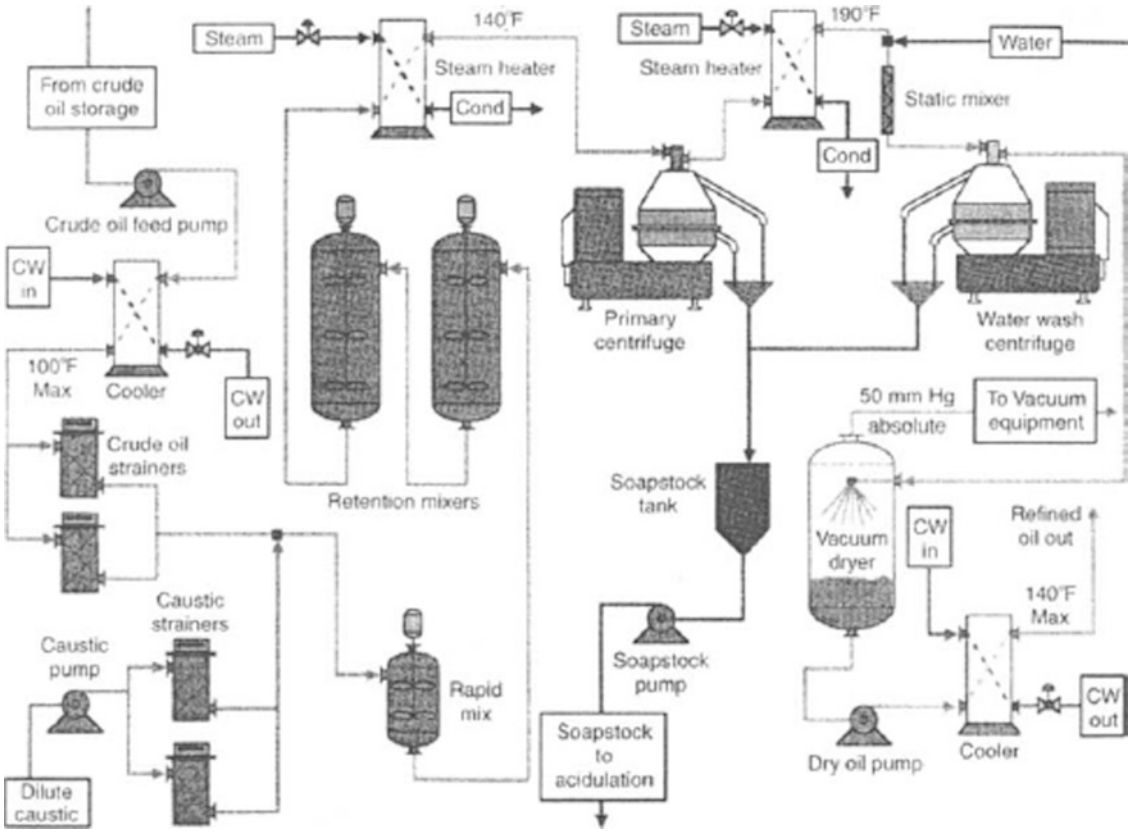


Fig. 34.19 Flow sheet of continuous refining of soybean oil (long mix process) with water wash option. (From Farr [103], With permission)

or acid-degummed phosphatides to be spread over the meal before the dryer-cooler. The refinery then can water wash and vacuum dry the oil by traditional methods, or treat it by silica gel adsorption. If a water wash is used, the oil is heated to 88°C/190°F with 12–15% soft water, held in an agitated tank for ~0.5 h, and centrifuged to produce an oil with <20 ppm soap. The soap can be reduced to "0" by addition of a small amount of phosphoric acid in the water-wash retention tank. The oil is next sprayed into a drying tank at 50 mmHg absolute [103].

Sodium silicate neutralization also has shown promise as a potential commercial method. The resulting soaps form a granular agglomerate, which can be removed by filtration to produce oil containing less than 100-ppm soaps. Thus, the costs of purchasing and maintaining primary and water-wash centrifuges and wash water disposal are avoided. The filtered oil can be treated with neutral or activated clays to remove color, peroxides, residual phosphatides, and soaps to produce oils with FFA fatty acids contents of less than 0.05% and "0" PV (*peroxide value*) [110]. The method has been patented and is being evaluated commercially.

Various researchers have reported on attempts to remove fatty acids from oils by ultrafiltration membranes. In the absence of membranes that can withstand extraction solvents, success generally has been limited. However, progress has been made on membrane degumming [111].

Silica Gel Adsorption

Silica hydrogels are very effective in removing phosphatides, residual soaps, and metal ions (all poisonous to hydrogenation catalysts), thus reducing the amount of bleaching clay required (by 50–75%) and leaving its function primarily to remove chlorophyll and secondary oxidation products. By eliminating soapy wash water, water discharged from refineries is reduced by ~50% in volume and has much lower biological oxidative demand (BOD). Additionally, cost and expenses of a second washing centrifuge are avoided [103].

The method of using silica hydrogel has changed during perfection of the process. Variations in procedure exist, but silica hydrogel can accept oil from the centrifuge at 0.2–0.4% water content. The currently recommended process consists of blending the silica hydrogel with oil directly from the soap removal centrifuge, with minimum, if any, drying of the oil. Silica hydrogel then is removed by filtration before mixing the oil with the bleaching earth [103].

Bleaching

Bleaching originally was a process for reducing color in oils, but the name has become a misnomer of this industry. Although limited color reduction occurs during the process, the major reduction of red and yellow colors occurs during the high heat of the deodorization process. The current practical function of bleaching is to remove chlorophyll and oxidation-degraded compounds and prepare the oil for hydrogenation or interesterification by scavenging the remaining soaps, phosphatides, and minerals that would poison the catalyst. Several authors have reviewed the theory and practical aspects of bleaching [112–114].

Bleaching earths are made from naturally occurring minerals, including palygorskite—also known as attapulgite, sepiolite, bentonite, and montmorillonite—and other minerals belonging to the aluminum silicate family. They may be used as such, but typically are preactivated by treatment with hydrochloric or sulfuric acids which: increase absorption by increasing surface area several fold; provide acid centers with catalytic properties; and impart ion-exchange properties to the clay. These properties are important in adsorbing various undesirable impurities in the oil, and in rendering complex organic structures adsorbable. In addition to adsorbing phosphatides and soaps, the process also removes pesticides, polycyclic aromatic hydrocarbons, *trans* and conjugated fatty acids, dimers, and polymers. Activated earths also provide a catalytic surface for breaking down peroxides. Decomposition is an exothermic reaction, with the heat apparently enhancing the *press effect* in color reduction of carotenoids in the filter press. The cation exchange property of the activated earth is credited with removing magnesium from the center of the chlorophyll complex and arresting its activity as a pro-oxidant. Cation exchange also is used for the removal of heavy trace metal pro-oxidants such as iron and copper, and for removing trace nickel in postbleaching of hydrogenated oil [114]. Although peroxides content is reduced, *p*-Anisidine Value (AV; AOCS Method Cs 18–90) increases. The AV is believed to estimate aldehydes (2-alkenals and 2,4-dienals) in animal and vegetable oils with the potential for later breakdown.

Bleaching clay load (typically 0.1–2.0%) and operating temperatures depend on the type and quality of oil processed [114]. Modern bleaching processes are conducted under vacuum (50 mmHg) to minimize later oil oxidation, and subsequent nitrogen blanketing of the oil during shipping and storage is recommended.

Close coupling of the refining and bleaching operations is highly recommended, especially when using the modified caustic refining or silica refining processes [103]. Because of the high level of unsaturated oils and peroxides in spent bleaching earth, it is very susceptible to spontaneous combustion unless quenched with water. Disposal in landfills is becoming increasingly difficult. Spreading spent bleaching clay on soybean meal for animal feeding is done in limited quantities, but caution should be taken because, by absorbing pesticides and mycotoxins, bleaching is one of the two safety valves in processing oils. The other is collection of volatile pesticides in the condensed deodorizer distillate.

Oils and Fats Modification

If processing proceeded next through deodorization, the resulting product would be liquid and known as "RBD oil" (refined, bleached, deodorized), and suitable for cooking and table use. However, consumers often want: oils that remain crystal clear when stored in household refrigerators; fat solids for an array of products such as butter-, ghee-, and lard-replacement spreads; air-entrapping shortenings for making tender, light-textured cakes; brittle or soft fats for toppings and frostings; cocoa butter replacements and substitutes; prolonged and prolonged bottled oil and frying lives; and fresh flavor in fried cereal-based snacks and nuts. Various techniques are used to craft fats with temperature-solids profiles such as the selected shortenings shown in Fig. 34.20 [115] from liquid oils. Modification processes include thermal fractionation, hydrogenation, and interesterification usually done before deodorization. Thermal fractionation and hydrogenation can use well-purified RB oil. Interesterification requires RBD oil with low FFA content. Hydrogenated and interesterified oils are postbleached and deodorized.

Solid Fat Index/Solid Fat Content

Two systems are used to characterize solids content of temperature-profiled fats. The Solid Fat Index (SFI) (AOCS Method AOCS Method Cd 10–57) uses dilatometers and was developed in the United States. It is the older method and is effective for fats containing up to 50% solids at 10°C/50°F. The Solid Fat Content (SFC) (AOCS Method Cd 16–81) uses pulsed nuclear magnetic resonance (NMR) techniques to quantify crystalization. It was developed more recently to accommodate palm oil and its products and is used in most other countries. SFC is effective for solids contents up to 95%; however, additional care in sample tempering may be required at the upper solids limits for either SFI or SFC. In both methods, a sample of the fat is completely melted to destroy its crystal memory, then chilled to 0°C to set the crystals. Readings are then taken at selected temperatures (10°C/50°F, 21.1°C/70°F, 26.7°C/80°F, 33.3°C/92°F, 37.8°C/100°F, and 40°C/104°F) to develop SFI or SFC curves. In some industries, five-point or three-point readings are taken; readings also may be made

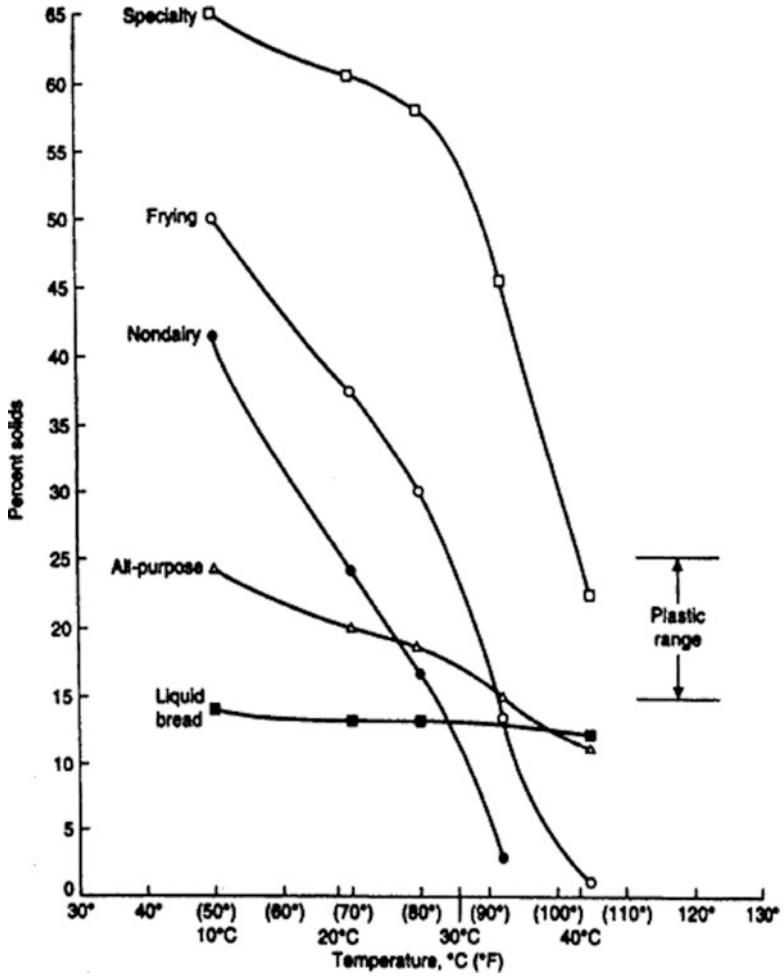


Fig. 34.20 Solids–temperature curves for various types of shortenings. (From O'Brien [115], With permission)

at higher temperatures. SFI and SFC give similar, but not identical results. A recent comparison of the two methods concluded that SFC reads higher at lower temperatures (10 and 21.1°C), but similar to SFI at higher temperatures [116]. The following equations for converting SFC of fats to SFI, with correlation coefficients, R^2, of 0.98–0.99 were offered: Commercial spreads:

$$\text{SFI} = 1.98 + (0.72 \times \text{SFC}) - (0.035 \times \text{temp.})$$

Base stocks:

$$\text{SFI} = 40.94 + (1.22 \times \text{SFC}) + (1.03 \times \text{temp.})$$

Bends (base stocks/liquid oil):

$$\text{SFI} = 0.94 + (0.82 \times \text{SFC}) + (0.02 \times \text{temp.}) + (0.02 \times \text{percent})$$

Profiles of margarine and table spread fats are shown later. Information available from SFI/SFC profiles includes solids contents at removal from most refrigerators (10°C/50°F), in typical kitchens (21.1–26.5°C/70–80°F), and at body temperature (37.8°C/100°F). The Steepness of the profile indicates relative effects of temperature change on fat firmness.

Melting properties of fats in the mouth are important. Generally, consumers can detect a greasy characteristic if more than 3% solids remain in spreads at mouth temperatures, or if more than 5–6% fat solids remain in baked, fried, and snack foods. Thus, doughnuts and bakery products are best eaten while warm to avoid greasy mouth-feel. The fried snack foods industry must choose between these alternatives: (1) snacks fried in oil may impart a cloudy appearance to see-through panels in the package, feel oily when picked up by the fingers, and stain clothing if dropped. (This is expected in long-time favorites such as corn chips, but may not be acceptable in newly introduced snacks.); and (2) Processors who want a "dry feeling" on pickup of the snack may select a fat that is solid at room temperature, but melts rapidly in the mouth to avoid the greasy sensation. Some snacks leave a greasy lining in the mouth if they are eaten at the same time the consumer drinks a cold soda pop. A fat, such as the one marked "Nondairy" in Fig. 34.20, could be used in coffee whiteners.

Another important factor is *plastic range*. Generally, 15–25% solids at ambient temperature are considered acceptable for working a fat-containing product (dough) without it becoming too oily to handle. Doughs containing the "all-purpose shortening" shown in Fig. 34.20 can be machined over a wide range of temperatures in a warm bakery. Stick margarines often are compounded to be softer and easier to spread than butter when taken from the refrigerator, to remain firmer at kitchen temperatures, and to melt completely without greasy mouthfeel when eaten. Soft (*tub*) margarine is ready to spread as taken from the refrigerator.

Thermal Fractionation

The simplest type of thermal fractionation is *winterization* for cosmetic reasons to obtain salad and cooking oils that remain clear when stored in the refrigerator. The oil is chilled in tanks with slow mixing to crystallize the higher melting point waxes, or TAG which are natural or produced by light hydrogenation to delay oxidation of the oil. A filter aid is added to assist filtration. After separation of the liquid (*olein*), the filtering apparatus is heated to melt and recover the fat solids (*stearin*), which can be used in compounding shortenings and other products [117]. The resulting oil is known as RBWD (refined, bleached, winterized, deodorized) and is expected to pass the "cold test" (AOCS Method CC 11–53) by resisting clouding for 5.5 h at 0°C. Shallow unstirred tanks in cool rooms were used for crystallization in earlier days. The rooms became warmer as crystallization progressed, demonstrating it as an exothermic reaction, and oils will readily assume the more compact crystal forms provided they are able to shed the energy as heat.

Thermal fractionation technology is most developed in the palm oil industry, where most oils are fractionated before sales. Solids profiles of stearins that have been fractionated from crude palm oil by chilling to different temperatures are shown in Fig. 34.21 [118]. Thermal fractionation and double fractionation can be useful tools in obtaining fat fractions with the specific desired characteristics (Fig. 34.22) [119].

Three major techniques are used in fractionation. In *dry fractionation,* oil is chilled with slow stirring and often seeded with crystals from an earlier batch. The resulting mixture can be quite viscous and present difficulties in draining oil from the crystals during filtration. In *solvent fractionation,* chilling and crystalization of oil occurs in a solvent, often acetone. The viscosity of the liquid phase is greatly reduced, resulting in easier separation and improved purity of crystals. Solvent fraction must be conducted in explosion-proof facilities. In *detergent fractionation,* a surfactant is added to the chill-crystallized oil–fat mixture and greatly improves drainage [77, 120]. Significant progress in

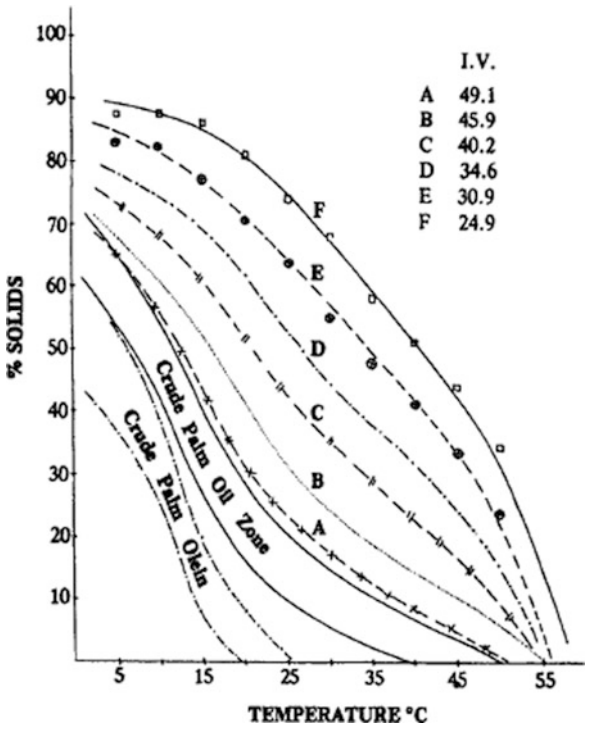


Fig. 34.21 Examples of stearins separated from crude palm oil by chill fractionation. (From Tan and Flingoh [118], With permission)

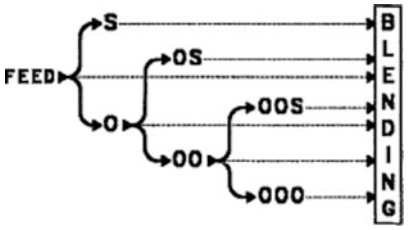


Fig. 34.22 Fat fractions from cascade fractionation. (From Tirtiaux [106], With permission)

recent years in dry fractionation technology has greatly simplified processing and reduced problems of handling solvents and byproduct streams [121]. A variation of the detergent fractionation principle has been used in dewaxing sunflower seed oil. Advantage is taken of the soap content (1,000–2,000 ppm) and 3–4% water remaining in un-washed alkalineutralized oil. After alkali neutralization, sunflower seed oil is pumped from the primary centrifuge directly to a heat exchanger for crystallization. The oil is held at 5–7°C/41–45°F for about 4 h for crystal growth, then heated by heat exchanger to 12–15°C/54–59°F, centrifuged to remove the wax crystals along with some water and soaps, washed with hot water, and centrifuged [122].

Until the mid-1980s, continuous-belt vacuum filters mainly were used for separating oleins from stearins.

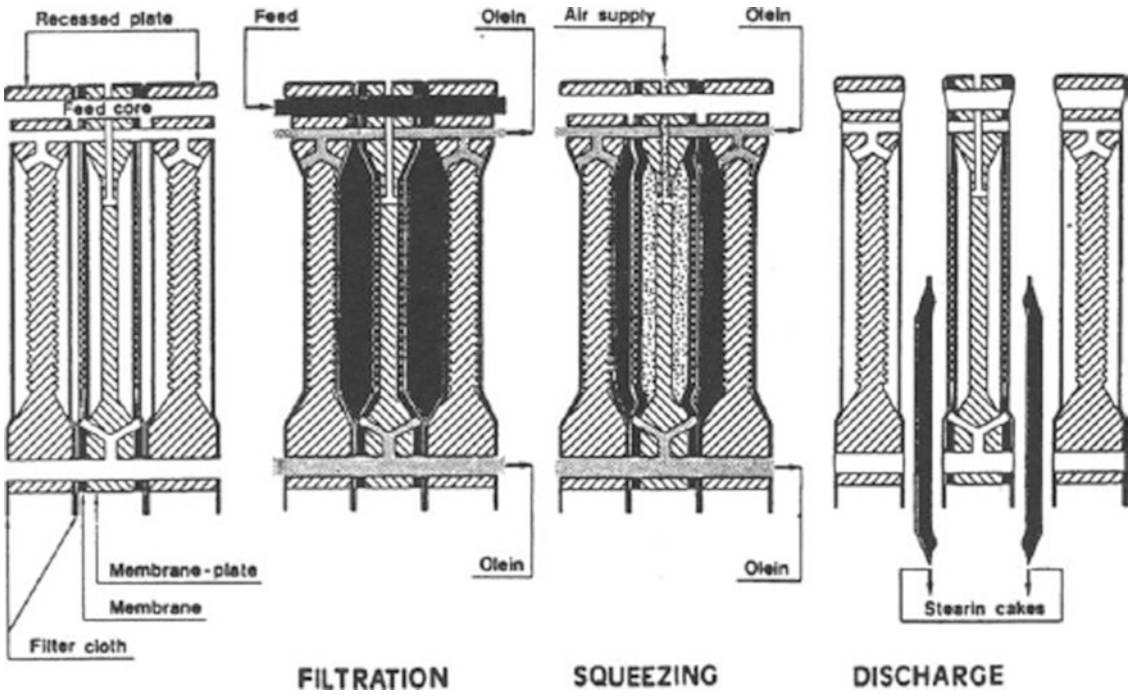


Fig. 34.23 Principle of membrane-type filtration of olein and stearin. (From Tirtiaux [106], With permission)

These are expensive and complex machines, requiring controlled temperatures in various sections and clearing of the belt for the subsequent filtration cycle. Simpler membrane filters have gained in popularity. As shown in Fig. 34.23, the active members resemble a plate and frame filter. Each cavity is lined on both sides with "membrane" filter stock, between which the crystal–oil mixture is pumped. Initially, free oil escapes through the filter stock, until the cavity is filled with crystals. Addition of the oil–crystals slurry is then stopped, and compressed air applied between the membrane and the frame to squeeze oil out from the enclosed crystal mass. When completed, the frames open, allowing the crystal cake to fall into a take-away screw. The frames then reclose, and the cycle is repeated. Stearins produced by membrane filters contain significantly less free oil than those from vacuum belt filters [119].

Oil is an effective solvent for higher temperature melting TAG, and results of thermal fractionation of common fats can be surprising. An example is milk fat (butterfat), which on extensive study has yielded 123 fractions melting as high at 54°C/129°F. Many tropical countries allow inclusion of up to 5% high melting hydrogenated fats in chocolate to raise the melting point and prevent blooming (loss of sheen, paling of color, and development of coarse crystals) resulting from repeated melting and resolidification. This also is a problem during the summer months in temperate countries. However, the latter countries often prohibit inclusion of fats other than cocoa butter in chocolate. The problem has been reduced in milk chocolate by adding high melting fractionated milk fat. Milk fat also has been used in higher-priced shortbread cookies, laminated pastries, and other bakery products where it provides a shortening effect, but doesn't melt and appear greasy.

Hydrogenation

Hydrogenation is the catalytically assisted addition of hydrogen to carbon–carbon double bonds. Its main uses are to increase fryer life of oils and shelf life of table oils and bakery products and to create solids for making shortenings, margarines and spreads, and various confectionery and specialty products. Many process reviews have been published [124–131].

Food technologists prefer to minimize the C18:3 content of oils to improve fryer and bottled oil shelf lives by reducing oxidation tendencies (Table 34.4). This has been partially accomplished by applying selective breeding and biotechnology to oilseeds, but the GMO products still are in the introductory phase. Because small amounts of linoleic (C18:2) and linolenic (C18:3) fatty acids are dietary essential, it is not desirable to eliminate them completely. For many applications, soybean and canola oils are partially stabilized against oxidation by (light) *brush hydrogenation*.

Selectivity, the tendency of the catalyst or process to remove one type of bond in favor of another, has several meanings in hydrogenation catalysts. *Preferential* or

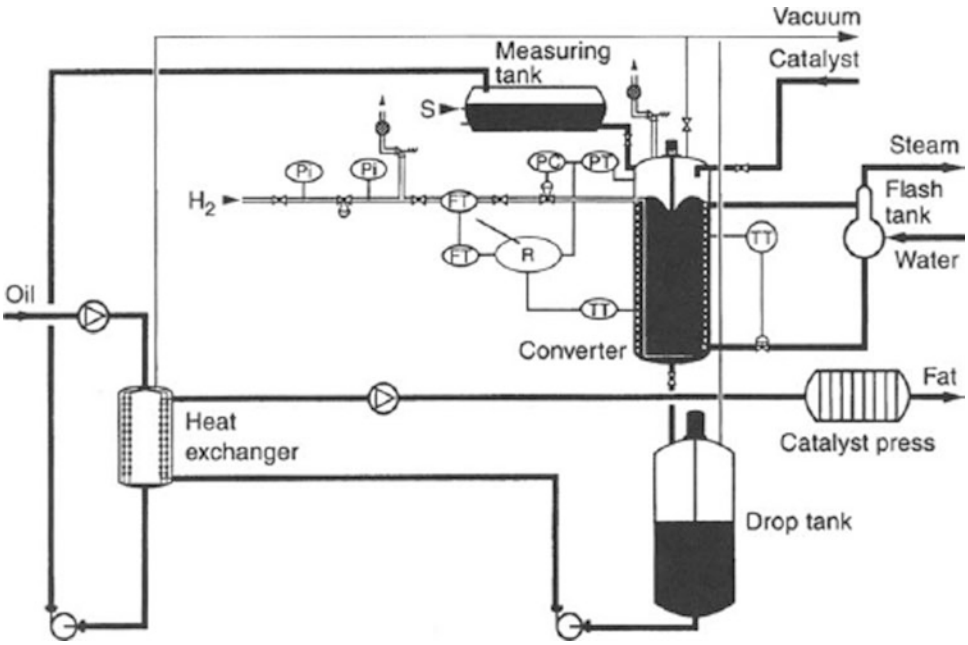


Fig. 34.24 Hydrogenation line. (From Hastert [130], With permission)

saturate selectivity indicates a focus on saturating a specific bond, for example, the C18:3 bond of linolenic acid to form C18:2 linoleic acid. Preferential selectivity is estimated from the following kinetic relationships:

$$\mathrm{C18:3} \xrightarrow{k_1} \mathrm{C18:2} \xrightarrow{k_2} \mathrm{C18:1} \xrightarrow{k_3} \mathrm{C18:0}$$

with linolenic selectivity ratio (SR) defined as SR $1 = k_1/k_2$ and linoleic selectivity as SR $2 = k_2/k_3$. Linolenic acid selectivity for nickel catalysts varies from 2 to 3 and is as high as 6 for copper-based catalysts. Better control of linoleic selectivity, with SR 1 varying from 3 to 4 to 60, is achievable by the choice of catalysts, catalyst poisons, and reaction conditions. This gives the operator greater flexibility in establishing melting behavior and stability of the hydrogenated product [125].

Trans isomer selectivity is less directed and favors formation of *trans* bonds. Catalysts vary in selectivity, with performance greatly affected by catalyst dosage, effectiveness of mixing, temperature, and hydrogen pressure in the reactor. Bonds become conjugated during hydrogenation, but not all atoms fall back neatly into their former positions after the process. The new types of TAG produced increase diversity, which is desirable in controlling later crystallization processes. The production of *trans* (partially saturated) bonds is intentional and can be partially controlled [129].

Hydrogenation is conducted in hardening plants (Fig. 34.24). The *converter* is a pressurized reaction tank, equipped with a highspeed mixer and assisting baffles, means for adding and removing the oil, a gas distributor, a means to add catalyst, and heating and cooling coils. The hardening plant additionally has means for premeasuring and heating the oil, a drop tank, heat exchangers, and a catalyst filter. Purities of the oil and hydrogen affect the life of the catalyst, typically a thin film of nickel on an inert carrier [130].

In brush hydrogenation of soybean oil selective catalysts: (1) reduce IV by 15–25 to ~115 units; (2) produce ~15% *trans* isomers; (3) reduce C18:3 content to 3% maximum; and (4) increase C18:0 content by ~1% [131].

In preparing margarine bases, selective catalysts reduce IV to ~70 and produce about 50% *trans* isomers. Selective or nonselective catalysts used in preparing shortening bases reduce IV to ~75 and produce about 35% *trans* isomers. A high-activity catalyst is used in producing stearin flakes; the IV is reduced to ~5–10 with hardly any *trans* isomers remaining. The flakes are scraped off the surface of a chilled roll, or beadlets can be produced using a shot tower with chilled air.

Maintaining high levels of polyunsaturates is desirable in producing coating fats. A sulfided nickel catalyst is used to reduce IV to ~70 and produce about 65% *trans* isomers with production of saturates (C18:0) minimized to 2–4% increase [131].

Factors affecting the hydrogenation reaction include reactor design, purity of feedstock and hydrogen, operating conditions, and choice and efficiency of the catalyst. Operating conditions include hydrogen pressure, reaction temperature, catalyst dosage, and agitation. Because *trans* formation is indicative of incomplete saturation, conditions that favor keeping the catalyst covered with hydrogen favor saturate selectivity. Progress in the hydrogenation process typically is monitored online by refractive index, calibrated to IV for each process and product [131].

Production of temperature-profiled fat products, such as margarines/spreads and shortenings, often includes preparation of four to six base stocks hydrogenated to different IVs (Fig. 34.25), which are blended with oil and hardstocks to obtain the desired temperature-fat solids profile [132].

An example of broadening the plastic range (15–25% fat solids) of two base stocks by addition of hardstocks is shown in Fig. 34.26. By itself, the 80 IV base stock is in the 15–25% solids (machinable) range only between the temperatures of 10 and 20°C. But, by addition of 8% (5 IV) hardstock, the range was broadened to ~30°C. Addition of 12% hardstock to the 85 IV base stock broadened its working range from ~10–12 to 38°C, which is more typical of bakery operating temperatures [124].

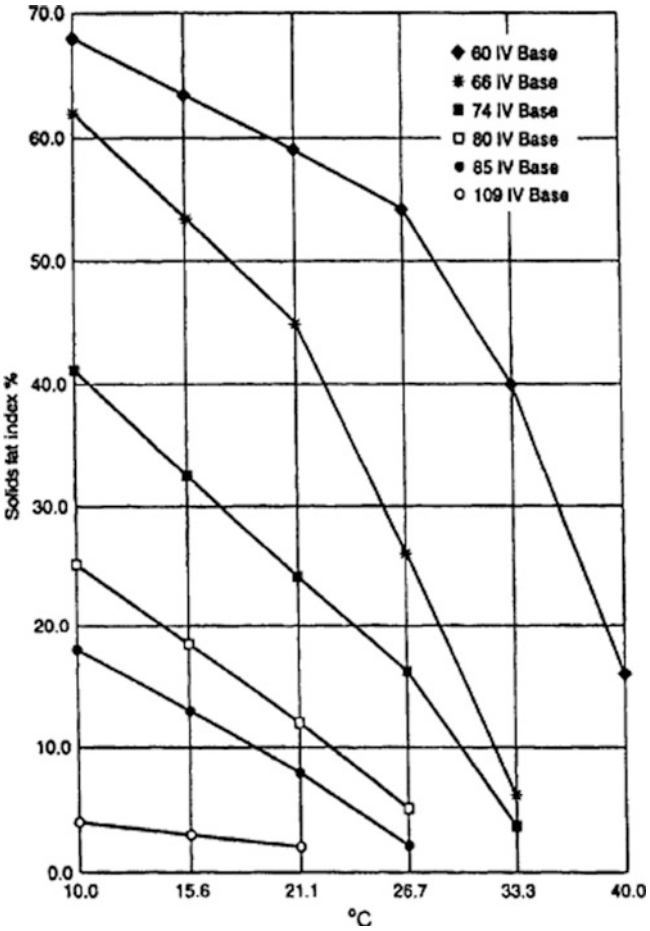
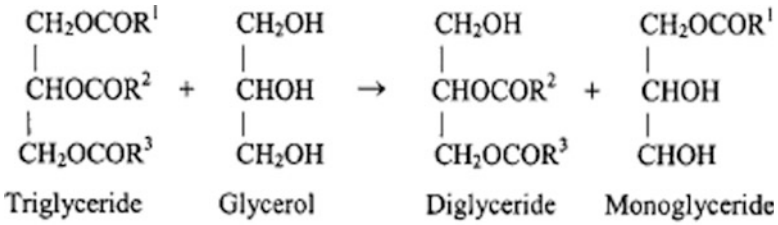


Fig. 34.25 Solid Fat Index (SFI) profiles for six hydrogenated soybean oil (H-SBO) base stocks. (From O'Brien [132], With permission)

Interesterification

Interesterification (INES) is the exchange of acyl radicals between an ester and an acid (*acidolysis*), an ester and an alcohol (*alcoholysis*), or an ester and an ester (*transesterification*) and can be random, directed, or enzymatic. The process has been called *intraesterification* if an exchange of positions occurs within the same molecule, and *randomization* if exchange occurs between molecules [44, 48]. The principles can be used to position fatty acids on molecules with hydroxyl sites to produce monoglycerides (emulsifiers), fatty acid methyl esters (FAME) for analytical purposes, liquid fuels such as methyl soyate (biodiesel), specialty fats such as medium chain triglycerides (MCT), and sugar-ester noncaloric fat substitutes such as Olean™.



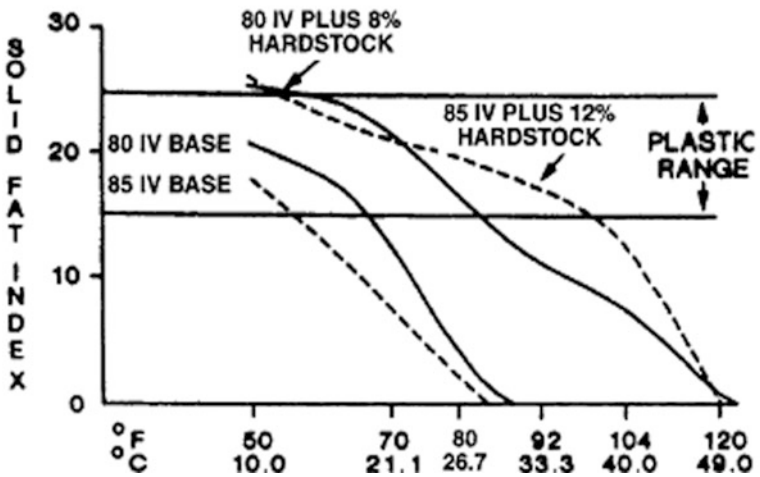


Fig. 34.26 Effects of adding hardstock (<5 IV) to broaden plastic range working temperatures of two base stocks. (From Hastert [124], With permission)

Table 34.11 Triglyceride classes of native and interesterified oils and fats and of noninteresterified and interesterified blends (1 : 1) of fully hydrogenated soybean oil with vegetable oils[a]

		Single oils					1: 1 Blends with hardened soybean oil			
		S_3	S_2U	SU_2	U_3	M.P.	S_3	S_2U	SU_2	U_3
		(%)	(%)	(%)	(%)	(°C)[b]	(%)	(%)	(%)	(%)
Palm oil	n	6	50	38	6	39.8	57	13	20	10
	r	13	39	37	11	47.0	41	43	14	2
Soybean oil	n	0	6	38	56	−7.0	50	2	17	31
	r	1	8	36	55	5.5	13	47	32	9
Cottonseed oil	n	<1	18	51	30	10.5	51	9	24	16
	r	3	18	44	35	34.0	25	34	31	10
Sunflower oil	n	0	1	24	75	–	51	0.3	11	38
	r	<0.2	4	27	69	–	11	47	34	8
Peanut oil	n	0	11	40	49	–	53	3	15	29
	r	1	10	38	51	–	16	47	31	6
Rapeseed oil	n	0	1	16	83	–	51	1	9	39
	r	0	1	17	82	–	10	44	37	9
Coconut oil	n	81	12	7	0	26.0	57	13	20	10
	r	74	24	2	<0.1	28.2	41	43	14	2
Palm kernel oil	n	76	15	9	0	–				
	r	53	37	9	0.7	–				
Cocoa butter	n	2	85	12	1	34.4				
	r	24	43	27	5	52.5				
Lard	n	8	30	50	12	43.0				
	r	10	32	40	18	43.0				
Beef tallow	n	22	60	18	0	46.2				
	r	13	38	17	12	44.6				

[a]From: Bookish [48], With permission
[b]From: Sonntag [136], With permission
n native; *r* randomized

Research publications exist from at least as early as 1852, and United States patents from 1939 [133].

The basic acidolysis reaction is:

$$R^1COOR^2 + R^3COOH \rightarrow R^3COOR^2 + R^1COOH$$

The alcoholysis reaction is:

$$RCOOR^1 + R^2OH \rightarrow RCOOR^2 + R^1OH$$

with methyl alcohol used for preparing FAME when determining the fatty acids components of TAG, and in making much of the biodiesel. Ethanol and other alcohols, up to four carbons in length (butanol), also have been used [44].

Glycerolysis has been used to prepare mono- and diglyceride emulsifiers by reacting TAG with an excess of glycerol [44].

Standard "mono- and diglyceride" products contain 40–50% monoglycerides, whose content can be raised to 53% without distillation. Distilled monoglycerides contain a minimum of 90% α-monoglycerides [44].

In the *sucrosolysis* preparation of Olean™, the generic name for Proctor & Gamble Company's olestra, six to eight fatty acids, selected for functionality purposes, are positioned on sucrose. Although many noncaloric fats are limited or nondigestible, they are made from traditional vegetable oils. Akoh has summarized uses of these and similar products [134].

Except for enzyme-directed processes to place certain fatty acids in specific positions on TAG, such as production of coating fats, cocoa butter substitutes, or reduced-calorie fats [135], the majority of esterification processes are randomizations.

As mentioned earlier, nature arranges the fatty acids in plant oils to achieve the lowest melting point. The abbreviations S and U, for saturated and unsaturated fatty acids, respectively, also are used in indicating their prevalence on TAG: thus S_3, S_2U, SU_2, and U_3. Distributions of these combinations in nature and in randomized products are shown in Table 34.11 [48, 136]. The literature indicates that stability against oxidation often is reduced by withdrawing the unsaturated fatty acids from the *sn*-2 position [44]. Randomization always raises the melting point, more so for vegetable oils than for animal fats, with an increase of 8.5°C for soybean oil. S_3 TAG hardly exists in natural vegetable oils, with only low concentrations occurring in animal fats. However, some are formed during randomization.

Directed randomization is a specific technique that precipitates S_3 and S_2U TAG as formed, depending on operating temperatures chosen. Removal of saturated fatty acids from cottonseed oil has been demonstrated recently

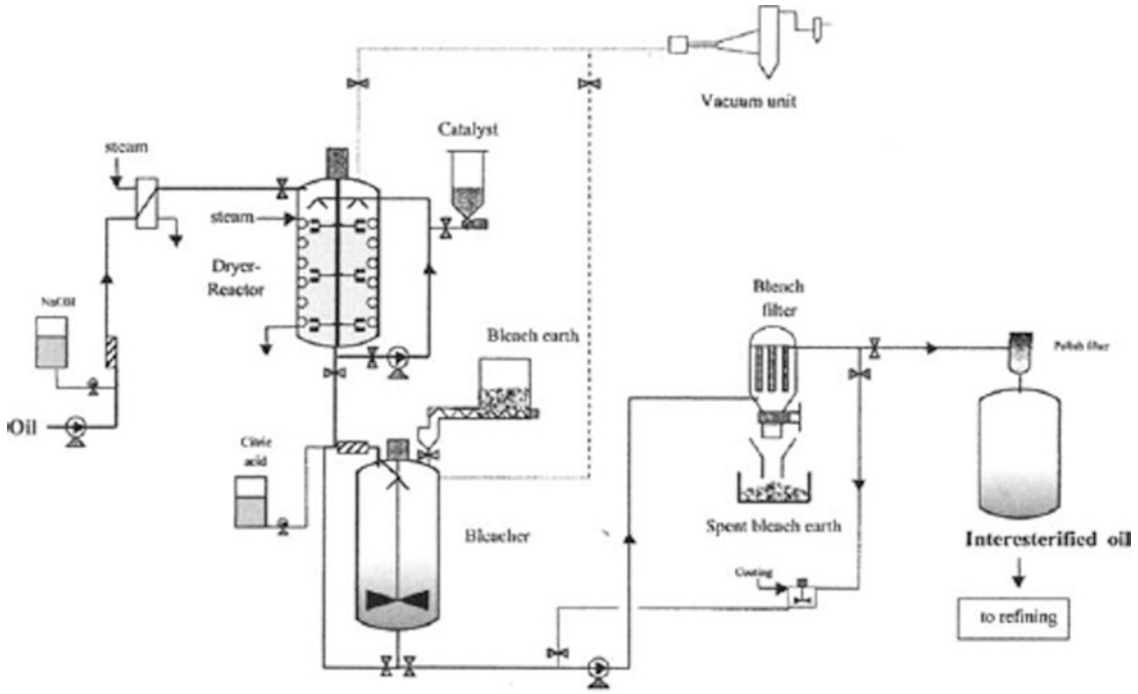


Fig. 34.27 Semi-continuous (chemical) interesterification line with postbleaching. (Courtesy of Desmet Ballestra Oils and Fats, Brussels, Belgium)

[137]. Directed randomization can be used to modify either the olein or stearin fractions.

A flow sheet for a semi-continuous interesterification line with postbleaching ability is shown in Fig. 34.27. The oil must be degummed, well-refined (<0.05% FFA), and free from peroxides and moisture that causes production of soaps. Palm oil stearin and completely saturated (<5 IV) C18 hydrogenated fats generally are *trans* free and may be used as part of the feed. Reactions are run under vacuum, and oil is best stored under nitrogen between processes [44].

A variety of catalysts is available, including alkali metals, alkoxides, alkali hydroxides, sodium hydroxide and glycerol mixtures, metal soaps, and metal hydrides [44]. Alkaline hydroxides (KOH or NaOH) in combination with glycerol were used in earlier days because of their low cost [138]. Currently, sodium methylate and sodium ethylate are popular because of their efficiency. Rozendaal has proposed that the actual interesterification catalyst is a sodium derivative of a diacylglycerol, activated during the process [139].

The oil is loaded into the reactor, shown with both an agitator and a pumped circulation-spray loop, and heated under vacuum (110–130°C) to reduce water and peroxide contents. Next, the oil is cooled to 70–90°C and the catalyst is added as dry powder at 0.05–0.15% or suspended in dry oil. Randomization requires about 30 min, with an additional 15–30 min allowed for completion. After the reaction is complete, the batch is transferred to a postbleacher where the process is arrested by inactivating the catalyst by addition of water or an (phosphoric or citric) acid solution. Bleaching earth added to absorb the inactivated catalyst and soaps removed by filtration and the oil sent to blending or deodorization. Losses from the formation of FFA and FAME are ~10 times the catalyst weight, with an additional 0.5–1.0% lost in the formation of mono- and diglycerides, for a total of 1.5–2.0%. Continuous processes also are available. Interesterification progress can be monitored by online ultraviolet (UV) spectrophotometry and completion of the process by melting point determination and other measurements [44].

The main objective in interesterification is to produce solids free from *trans* fatty acids for later use in compounded fat products. The final fat, or a series of base stocks, can be made for future blending. Randomization can improve the functionality of a fat, as shown for lard in.

Figure 34.28. Natural lard is within the 15–25% solids plastic range between 9 and 24°C; by randomizing, the temperature range is moved to 0–17°C; both conditions greatly restrict its use. But, by directed interesterification, the machinable range is moved to the more acceptable ranges of 0–32°C. In contrast, natural cocoa butter (Fig. 34.29) is almost brittle at 26°C, melts rapidly by taking energy from the tongue, causes a pleasant cooling sensation in the mouth, and is completely liquid with good palate "cleanup" at 35°C. Randomizing destroys these properties, changing the fat into a softer mass, which does not completely melt below 56°C [48].

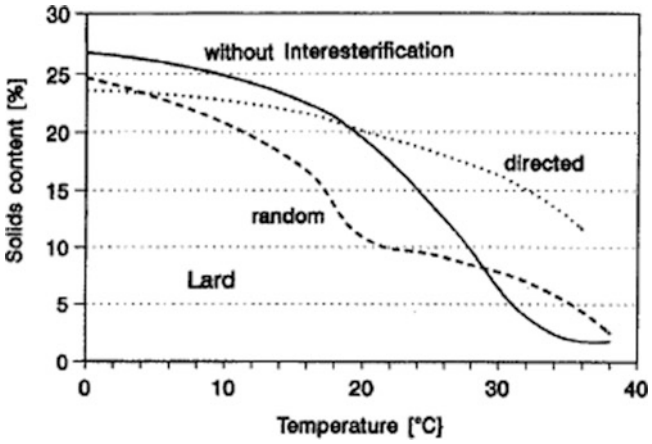


Fig. 34.28 Solids content of natural, random esterified, and directed interesterified lards. (From Bockish [48], With permission)

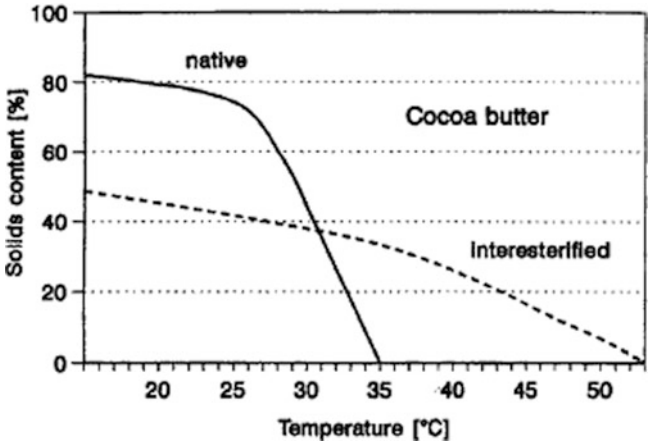


Fig. 34.29 Solids content of natural and randomized (interesterified) cocoa butter.(From Bockish [48], With permission)

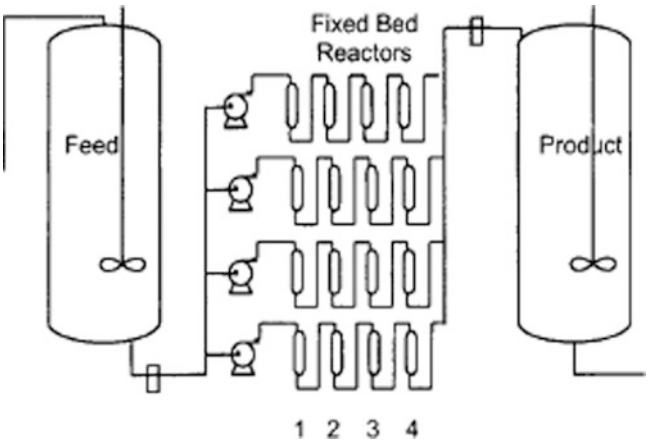


Fig. 34.30 Schematic drawing of multiple enzyme reactor system for enzymatic interesterification of *trans*-free margarine and shortening oils. (Courtesy of Novozymes A.S, Bagsvaerd, Denmark)

Interesterification is being pursued on the basis that *trans* production during hydrogenation increases the melting points of TAG and fatty acids, increases blood cholesterol levels, and increases atherosclerosis (plaque deposits in arteries) and coronary heart disease (CHD) incidence. However, considerable documentation also shows that the presence of saturated fatty acids (primarily palmitic, and to a lesser degree myristic and stearic) at the TAG *sn*-2 position strongly favors atherogenesis. Pork lard contains 70% of its palmitic fatty acid in the *sn*-2 position, whereas only 17% of the palmitic acid in beef tallow is in this position. Lard is considered more atherogenic to laboratory animals than tallow; randomization reduces this propety. However, atherogenicity of tallow is increased by randomization. Levels of saturated fatty acids at the *sn*-2 position are very low in natural vegetable oils, but are increased by randomization, with accompanying atherogenesis in feeding trials [140, 141]. Skepticism exists that switching to interesterification as a means of generating fat solids will reduce health concerns about hypercholesterolemic and atherogenic effects of fats.

Enzyme interesterification is rapidly becoming popular and has the advantage of selection of TAG positions at which fatty acids are interchanged. When 1,3 lipases are used, the current fatty acid at 2-position remains in place, avoiding transposition with saturated fatty acids. A simple way to conduct enzyme interesterification is by contracting for a fixed-bed reactor service. The supplier assists in installing the process and takes responsibility for providing portable reactor beds charged with specified 1,3-lipases to treat established quantities of oil. A schematic of a multiple enzyme reactor system is shown in Fig. 34.30. The freshest reactor is connected to the tank receiving the product and is preceded by a sequence of increasingly used reactors back to the most spent reactor connected to the feed tank. As spent reactors are retired, they are moved forward from positions "4" toward "1." In this fashion, full use is made of remaining enzyme activity as feed flows through the system. The partially exhausted reactors filter the least processed feed and intercept competitive inhibitors that otherwise could reduce performance of fresh reactors. The reactors are shipped between supplier and user by truck. Large facilities can repack reactors in house [142].

Deodorization/Physical Refining

Deodorization is the final step in the production of RBD oils and modified fats. The process is called *deodorization* if most of the FFA is removed by alkali neutralization as with row crop ("soft") oils, and *physical refining* if, by omitting alkali neutralization, the FFA are left in the oil for

removal by steam distillation as with palm oil. Thorough degumming and bleaching must first be done before physical refining of all oils.

The volatile peroxides, other oxidation decomposition products, and odiferous compounds form reduced-boiling point azeotropes with water in the steam, at high temperatures, 250–260°C/482–500°F, and very low absolute pressures (~3 mbar). This is above the smoke point of soybean oil, but below the flash point, and oxygen must be excluded. Considerable heat bleaching of yellow–red carotenoids also occurs at this temperature. Typically: the deodorization process requires 20–40 min after come-up time, uses 0.5–2.0% sparged steam (the higher level if tocopherols are recovered), operates at between 2 and 4 mbar, and produces a product with about 0.03–0.05% FFA [143].

Historically, the standard deodorizer held 60,000 lb of oil (one railroad tank car). Except for refineries making only a few kinds of oil, as for export, building of continuous deodorizers slowed with the advent of just-in-time (JIT) delivery, supplier self-certification, and customers buying on the basis of their projected production schedules. This has led to development of improved batch-continuous systems, which are designed to handle many batches of different oil blends per day, with minimum cross-contamination and delays for process.

For many years, deodorizers (operating at above 270°C/520°F) were heated by several types of mineral oil-like thermal fluids which, in turn, could be heated in direct-fire furnaces at 315°C/600°F in plumbing and coils at 3.2 bar (46 psig). During the 1970s, some consumer health problems in Europe were ascribed to leakage of thermal fluids into oils during deodorization. As a result, the European market required that the local and imported oils industry shift to using high-pressure steam generators, operating at ~80 bar (1,150 psig) to provide a temperature of 295°C/560°F. Soon, other import countries also started adopting European standards. This essentially meant that heating coils and jackets of deodorizers, owned by suppliers wanting to sell oil in Europe, had to be rebuilt or new deodorizers and high-pressure steam generators purchased [144].

Deodorizers are built in many vertical and horizontal designs [143–145]. They typically are located outdoors and look like multistory plumbed silos or petroleum refinery reactors. A drawing of a modern deodorizer is shown in Fig. 34.31. The components have been gathered into one shell to take advantage of heat recovery opportunities, and the temperature gradient within the vessel gradually decreases from top to bottom. As with all manufacturers, improved designs are continuously evolving. The unit is operated at lower temperatures, 220–235°C/428–455°F, and a deeper vacuum (2 mbar) to minimize *trans* and polymer formation and loss of valuable minor components such as tocopherols. The supporting high-pressure steam boiler and vacuum system (typically a four-phase steam-jet ejector with barometric condensers, mechanical liquid ring vacuum pumps, or dry "ice" condensing system) is not shown. In the deodorization process, a well-prepared pre-warmed RB oil is passed through a deaerator to remove dissolved air, then heated in an exchanger by oil exiting from the deodorization stage. It is additionally heated by steam coils and passes into the deodorization tray, where it is deodorized by sparged steam. Next it passes through a heat recovery exchanger, heating the incoming oil. After partial cooling, citric acid (20–50 ppm) in solution is added to sequester iron or copper that may be picked up later by the oil. The oil is still hot and under vacuum, and the moisture flashes off. Then, the oil is cooled and passes through a polishing filter on its way to temporary storage under nitrogen before shipment.

The liquid used to *scrub* the vapors is previously condensed deodorizer distillate that is chilled, recycled, and drawn off as necessary to maintain a constant level in the scrubber. The condensate may entrap vapors of pesticides if they get this far in the refinery. Deodorizer distillate is rich in tocotrienols or tocopherols, some of which have vitamin E activity. During the time that consumption of vitamin E supplements in the United States was growing, and strong markets for natural antioxidants existed, deodorizer distillate was very much in demand and the domestic supply from refineries was committed by contracts with vitamin E producers. As much as 60% of the tocopherols in soybean oil could be extracted at the deodorizer, but in doing so, the refineries no longer are available to stabilize the shelf life of the oil or provide its full natural nutritional benefits. In recent years, tocopherols and tocotrienols from palm oil processing have eased supplies.

At this point in processing, the peroxide value in the oil should barely be detectable (<1 ppm), but will soon start increasing again. Thus, margarine and other profiled-temperature fats are blended before shipment. A rule of thumb in the deodorization department is: "Don't deodorize oil until it is sold and ready to be shipped."

After cooling to appropriate temperatures, processors may add additional oil-soluble ingredients, antioxidants, vitamins, colors, and others that customers might have difficulty dispersing in the oil/fat at their processing sites. Unless the fat needs to be texturized into a soft-plastic form by the addition of nitrogen and chilling to a shortening for specific handling requirements, it is shipped and kept at about 10°C above the melting point. Nitrogen purging of oil during pumping, and storage under a *nitrogen blanket,* are common if held for more than several days before use by the processor. Contact with copper- and iron-bearing materials and contamination with water should be avoided. Typically, one to two percent *trans* fats are produced during deodorization, with lesser quantities formed at lower temperatures. Ultra-high vacuum steam distillation, operating at microbars

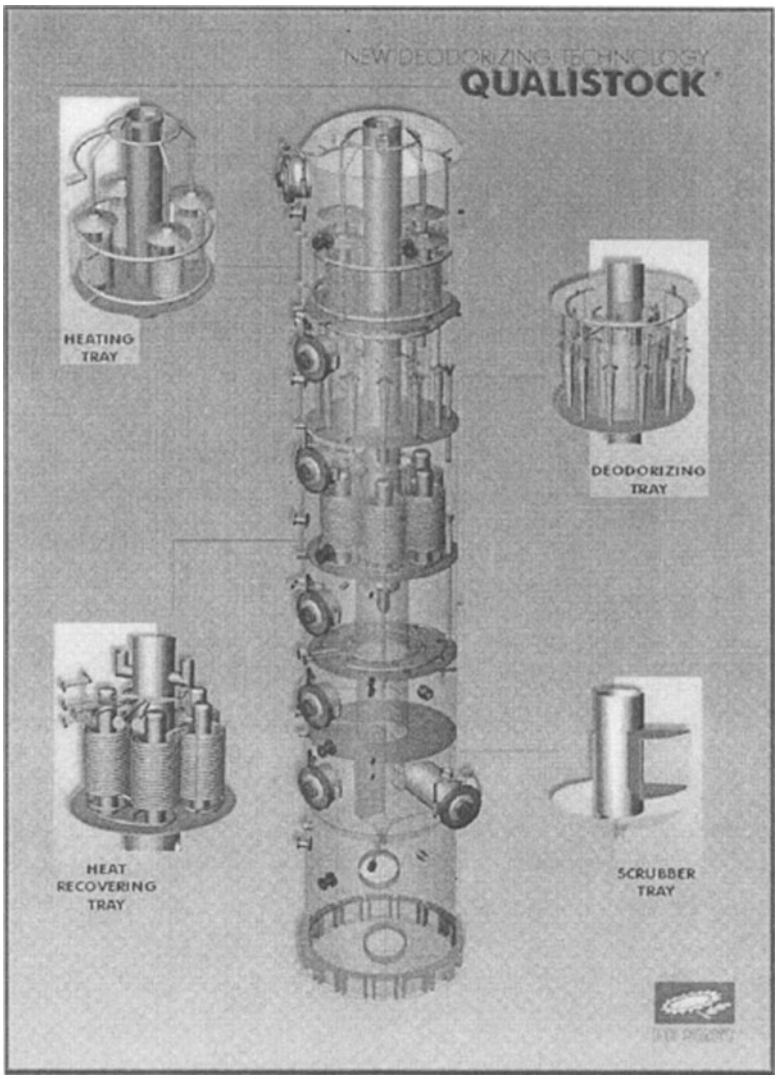


Fig 34.31 Cut-away drawing of DeSmet Qualistock® Continuous Deodorizer. (Courtesy of Desmet Ballestra Oils and Fats, Brussels, Belgium)

rather than millibars, has successfully deodorized oils and fats in laboratory and pilot plant scale and is used in the production of higher-priced products. However, fats and oils scientists have reported that the flavor of this oil is not as acceptable as from traditional deodorization/physical refining. Several steam distillation methods for the removal of cholesterol from animal fats were developed and patented after the fast foods industry switched from tallow to vegetable oils for frying French fries in the 1980s. Currently, the ability of tallow to regain this former market seems doubtful.

Notes on Major Row Crop Oilseeds

Soybean

Soybean (*Glycine max* L.) was domesticated in north China, probably during 1700–1100 BC in the Shang Dynasty or earlier [146]. Samples found their way to Europe during the 1700s, where it was grown as a curiosity in botanical gardens [147]. Documentation exists for soybean brought, grown, and made into soy sauce near Savannah, Georgia in 1765, by Samuel Bowen, an English seaman who had sailed to Canton, China earlier as an employee of the East India Company. Benjamin Franklin sent seed from London to a botanist in Philadelphia in 1770 [148]. A sample, from a salvaged Japanese junk, was brought from San Francisco to Alton, Illinois, in 1851, where it was grown and also distributed to botanists in other states.149 Additional samples were brought back by Commodore Matthew Perry's expedition to Japan in 1854, sent by missionaries in the Far East, and distributed in the United States before establishment of the Department of Agriculture in 1864 [149]. However, the plant mainly was grown for feeding cattle and as green manure to enrich soils.

The Treaty of Portsmouth (New Hampshire) to settle the 1904–1905 Russo–Japanese War gave Japan control of the Liaotung Peninsula in Manchuria. This area was leased previously from China by Russia during construction of

the Trans-Siberian (Moscow to Vladivostok) Railroad for establishing all-weather naval and trading ports in Port Arthur (now Lüshun) and Dairen (Lütita, Talien, Dalian) [150]. The withdrawal of Japanese occupation troops from Manchuria resulted in a local surplus of the soybean crop, which had been expanded to feed the soldiers. Manchurian soybean was shipped to England in 1907 [151], and to Germany, other Northern European countries, and the US Pacific coast, by 1910 [152]. Dairen, Manchuria became the international soybean processing and export center for the early part of the 1900s. An English hydraulic press mill had been sold to China in 1868 [153], but Manchurian and Japanese soybean extraction continued mainly by crushing seed with stone edge runners and pressing with wedge presses, which produced press cake that could not survive shipment to Europe [152, 154, 155].

Europe wanted the soybean for oil and the meal for animal feed, but was dissatisfied with leaving 5–6% to six percent oil in the cake, characteristic of box presses and expellers (screw presses). England and Germany initiated work on batch solvent extraction processes, but World War I interrupted progress. The Bollman basket countercurrent extractor was patented in Germany in 1919, followed by the Hildebrandt U-tube extractor in 1934 [152].

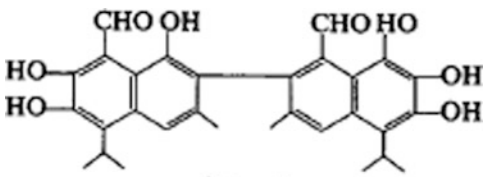
The first domestic crushing of soybean occurred in Seattle, Washington, in 1910, using seed imported from Manchuria [152]. Domestically produced soybean was crushed at cottonseed oil mills in the South and linseed (flaxseed) oil mills in the Midwest during the 1910–1920 era [152, 156]. The first commercially successful domestic soybean solvent continuous extraction plants were installed by Archer Daniels Midland Company (ADM) and the Glidden Company in Chicago in 1934, both using 100 tpd Hildebrandt U-tube extractors and commercial hexane as solvent. They also were equipped to produce phosphatides [153].

United States production of soybean, for domestic processing and exporting to Europe, grew slowly until acceleration by World War II, which devastated the German oilseed crushing industry [157]. This left the United States in the position of the world's largest soybean producer and processor. Soybean utilization increased during the reconstruction of Europe and Japan, by uses in famine abatement programs throughout the world, to meet growing world population food needs, and as feed to support world growth of the broiler industry which started about 1960. Eventually, land-rich countries in South America also became major soybean producers.

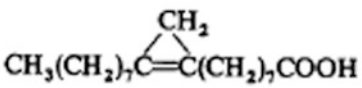
Cottonseed

Cotton (*Gossypium arboreum* and *G. herbaceum*) was grown in the Indus River Valley (modern Pakistan) as early as 3000 BC. "New World" cottons were grown in Peru (*G. hirsutum*) about 2500 BC, and Sea Island cottons (*G. barbadense*) in the Caribbean Islands. Most of the world's cotton today is *G. hirsutum*, with a fuzz-covered seed that requires removal of the fibers by *delinting* before dehulling and subsequent processing. Pima and Egyptian cottons (*G. Barbadense* type) have fuzz-free (*naked*) seed and can be processed directly. Cottonseed is among the first examples of a reclaimed byproduct in our industrial age. Invention of the cotton gin by Eli Whitney in 1793 led to increased domestic production of cotton and also to seed disposal problems. The state of Mississippi passed the first antipollution law in the nation in 1857, prohibiting throwing cottonseed into rivers and requiring its orderly disposal from gins located less than one-half mile from a town.

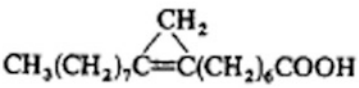
Cottonseed contains the polyphenolic yellow-red pigment gossypol, 1,1′,6,6′,7,7′-hexahydroxy-5,5′-diisopropyl-3,3′- dimethyl (2,2′-binapthalene)-8,8′-dicarboxaldehyde, in discrete bodies called *gossypol glands*. Processing challenges include removal of gossypol, or its 15 or more derivatives, from the oil to reduce color, and deactivate its toxic effects (through binding to the protein with moist heat) to enable feeding the meal to monogastric animals. Cottonseed oil also contains the cyclopropenoic acids, C18:CE malvalic acid (8,9-methylene-8-heptadecenoic acid) and C19:CE sterculic acid (9,10-methylene-9-octadecenoic acid), which form the pink color in the Halphen Test used to detect its adulteration of higher-priced olive oil [158]. Concerns about adulteration of olive oil appeared again when fractionated palm oil was introduced to Europe.



Gossypol



Sterculic acid



Malvalic acid

Cottonseed oil has long sold at a slight premium over soybean oil because of greater stability to oxidation and desirable flavor in fried snack foods such as potato chips. However, gossypol content and lower protein quality put the meal at a price disadvantage. Feeding whole cottonseed to dairy cattle, whose rumen microorganisms can detoxify

limited amounts of gossypol, now utilizes over 70% of the supply and may portend eventual abandonment of oil extraction.

Rapeseed/Canola

Rapeseed/Canola belongs to the turnip rutabaga, cabbage, Brussels sprouts, and mustard family of crops that can be grown at low temperatures and moderate humidity. Three species have been grown as oilseeds: *Brassica napus*, known in Europe as rape, oil rape, Swede rape, and Argentine rape; *B. campestris*, known as rapeseed, oil turnip, turnip rape, and Polish rape; and *B. juncea*, known as leaf mustard, brown mustard, Oriental mustard, and Indian mustard. *B. campestris* was grown in India as early as 2000–1500 BC.

This crop is the classic example of an effective crop improvement program mobilized by a country in response to impending loss of international markets. When it was reported in the early 1960s that erucic acid (12-docosenoic, C22:1 *n*–9) in rapeseed oil could cause heart damage and other diseases, the Canadian government established a crash development program that led to the release of the first low-erucic acid rapeseed (LEAR) in 1969. Continuing efforts to develop varieties with even lower erucic acid content led to later release of double zero (low-erucic, low-glucosinolate) varieties, which were named canola in 1980. Because of reduced glucosinolate levels, considerably more of the meal could be used in animal feed than earlier. Canola oil, which contains less than 2% erucic acid compared with 20–40% in earlier rapeseeds, was granted GRAS status by the US FDA in 1985 [159].

However, the introduction of canola left unmet needs for erucic acid in industrial markets. High-erucic acid rapeseed then was imported from Northern Europe for extraction, followed by efforts to increase erucic acid contents in domestic industrial rapeseed as well as development of crambe (*Crambe abyssinica*) specifically for its erucic acid content. At the current state of development, equipment corrosion and poisoning of hydrogenation catalysts by sulfur in canola oil still are problems. Also, oil from the new canola varieties favors formation of β crystals, in contrast to β' formation in the earlier rapeseed varieties.

High *oleic acid canola* varieties were introduced recently to directly compete in applications formerly using olive oil.

Sunflower Seed

Sunflower (*Helianthus annus* var. *Marco-carpus*) is a New World crop, known to have been grown in Arizona–New Mexico in 3000 BC and in the Mississippi–Missouri Basin at least since 900 BC. A midsummer weed relative, with small multihead flowers, is common in the central United States. The crop was taken to Europe by early explorers and developed as a source of edible oil in Russia. The gray and white striped seed is known as *confectionery-type*. Its kernel is loose within the hull, and the seed usually is shelled for eating. No major antinutrition factors are known to exist in the raw seed. *Oil-type* varieties predominantly are black-hulled, with seeds about one third the size of confectionery types. The seed adheres tightly to the hull and provides a challenge in dehulling. It has been repeatedly shown that, although the setting of seed by sunflower plants is not as sensitive to day length as for soybean, the oleic acid content is inversely related to the temperature of seed maturation. Early users desiring polyunsaturated oil with high linoleic acid content specified northern-grown sunflower seed oil, whereas those desiring extended oil stability, as in the production of fried foods, have preferred oil from seeds matured during the summer in the southern states. Sunflower varieties with high-oleic acid content (85–92%) have been developed with the intention of using the oil as a feedstock in chemicals manufacturing processes [122]. Recently, the sunflower seed industry has developed mid-oleic acid oil, containing ~65% oleic acid. Also, high-oleic confectionery-type sunflower seed has been developed, enabling extension of the shelf life of roasted seed.

Peanut

Peanut, groundnut (*Arachis hypogae*), also is a New World crop and was grown in the Upper Plata River Basin of Bolivia in 2000 BC. It was taken to Europe by early explorers and was returned to the southeastern United States from Africa by slave traders. Broad cultivation did not occur domestically until the early 1920s, when the southeastern United States was looking for a crop substitute for cotton, which was severely ravaged by the boll weevil [160]. Most domestically grown peanut is consumed as food, with over one half of the crop produced used in making peanut butter. Peanut is very susceptible to *Aspergillus flavus* mold invasion in the soil, which produces carcinogenic aflatoxins. World production of peanut for oil has slowed because of limitations on feed uses of the meal. Direct food uses of peanut have increased in developing countries.

Some Miscellaneous Oils Processed at the Food Protein R&D Center, Texas A&M University

Pistachio Oil

Pistachio oil is extracted from the fruit of *Pistacia vera* by expeller or screw press. Compared to other nut oils, pistachio

oil has a strong flavor. It tastes like the nut from which it is extracted. Pistachio oil is high in Vitamin E, containing 20–25 mg/100 g. It contains 12.8% saturated fats, 54.8% monounsaturated fats, 33.7% linoleic acid, and 0.7% omega-3 fatty acid. Pistachio oil is used as a table oil to add flavor to foods such as steamed vegetables. The fruit is a drupe, containing an elongated seed, which is the edible portion. The fruit has a hard, whitish exterior shell. The seed has a light green flesh, with a distinctive flavor. When the fruit ripens, the shell changes from green to a yellow or red and abruptly splits. This is known as dehiscence. Each pistachio tree averages around 40–50 kg of seeds, or around 60,000, every 2 years. The shell of the pistachio is naturally a beige color, but it is sometimes dyed red or green in commercial pistachios. Most pistachios are now picked by machine and the shells remain unstained, making dyeing unnecessary except to meet consumer expectations. The kernels are often eaten whole, either fresh or roasted and salted. Pistachios are also used in ice cream, pistachio butter, and confections. Recently, the FDA approved the first qualified health claim specific to nuts lowering the risk of heart disease.

Emu Fat/Oil

Emu is the largest bird native to Australia. The soft-feathered, brown, flightless birds reache up to 2 m (6.6 ft) in height. They have long thin necks and legs. Emus are farmed primarily for their meat, leather, and oil.

The Food Protein R&D Center at Texas A&M University has special expertise in emu fat processing to produce premium quality emu oil. There are presently no established special methods to process emu oil. However, current oil processing technology can be used. The entire refining process involves rendering the fat, cooking, fat separation, and fat drying. The crude oil is treated by caustic (caustic neutralization) for free fatty acid removal followed by bleaching and a deodorization. The general physical properties of emu oil are similar to those of a vegetable oil with intermediate content of saturated fatty acid. Emu oil is similar in oleic acid content to oils such as peanut or canola. With regard to saturated fatty acid, emu oil resembles cottonseed oil. The ultimate quality of the refined emu oil depends strongly on the starting material. For example, if the crude oil has blood tissues producing a high content of free fatty acids, even though the refining process will eliminate the acidity of the oil, the final product will contain a high concentration of mono- and diglycerides which easily degrades during storage. Emu meat is a low-fat meat (less than 1.5% fat), and with cholesterol at 80–90 mg/100 g, it is comparable to other lean meats. There is some evidence that the oil may have anti-inflammatory properties.

Mink Oil

Mink oil is produced from the thick fatty layer which lies just under the skin. This fat is removed from the pelt when the mink is skinned and is then rendered into mink oil. The crude oil is dark yellow in color. Crude mink oil is directly bleached and deodorized without being caustic neutralization. The bleached and deodorized oil is light yellow in color. Mink oil and its fatty acids are unique among animal-derived fats and oils. The total unsaturated fatty acids in mink oil account for more than 75% of the fatty acid content, but the oil, nevertheless, has a greater oxidative stability than other animal or vegetable oils. Mink oil is a source of palmitoleic acid, which possesses physical properties similar to human sebum. It is used in several medical and cosmetic products, and also for treating, conditioning, and preserving nearly all kinds of leather.

Ostrich Oil

The Ostrich (*Struthio camelus*) is a large flightless bird native to Africa. It is farmed around the world, particularly for its feathers, which are decorative and are used as feather dusters. Its skin is used for leather products and its meat is marketed commercially. The refining process for ostrich oil is similar to that for EMU oil. It starts with the cleaning of fat to eliminate blood, skin, dirt followed by fat separation (separate the solids by decantation), fat drying (heat under vacuum), refining (remove free fatty acid), bleaching (to eliminate color, peroxides, metals), and deodorization (to remove odor, peroxides, free fatty acids). Ostrich oil is high in omega-3, omega-6, and omega-9 EFAs. It contains around 20% saturated fatty acid followed by 35% monounsaturated and 39% polyunsaturated fatty acids. It is used in cosmetic and in the treatment of lesions, burns, contact dermatitis, dry skin, and many other ailments. Ostrich oil and EMU oil have very similar properties.

Trans Fats Nutritional Labeling

Trans fats have been created, often intentionally, during hydrogenation of TAG to obtain fat solids with specific properties for use in shortenings, spreads, confections, and other semisolid foods. Lesser amounts result during hydrogenation to reduce linolenic acid content and slow the oxidation of fats and their breakdown during frying. Small quantities (seldom more than 2.0%) are created during high-heat treatments in deodorization or physical refining. *Trans* fat formation is part of the oxidative sequence at ambient temperatures and is accelerated in frying. *Trans* fats in ruminant meat and dairy products, produced by biohydrogenation, are considered "natural" as described earlier. The US FDA has estimated the average domestic intake

of *trans* fat at about 5.8 g, or 2.6% of calories per day for individuals 20 years of age or over. Consumption of saturated fat is estimated at four to five times more. Estimated sources of *trans* fat are: cakes, cookies, crackers, pies, bread, and the like ~40%; animal products ~21%; margarine and spreads ~7%; fried potatoes ~8%; potato chips, corn chips, popcorn ~5%; household shortening ~4%; salad dressing ~3%; and breakfast cereals and candy ~1% each [161].

In response to a petition by a consumer advocate group, the FDA published a proposal in the *Federal Register* [64] (221, 62745–62825, Nov 17, 1999) to include *trans* fat information in Nutrition Facts labels of packaged foods. (Listing of saturated fat and dietary cholesterol has been required since 1993.) The proposal initiated one of the most intensive dialogues ever in domestic food regulation between consumer advocates, public sector researchers, commodity producers, food processors, and government officials. The net effect was that separate listing of *trans* fat content was required on packaged food Nutrition Facts panels as of January 1, 2006. Also, dietary supplements, which contain 0.5 g or more *trans* or saturated fats per serving, must list their amounts in the Supplement Facts panels. The Nutrition Facts per serving format is:

	Percent daily value[a]
Total fat, 12 g	18
Saturated fat, 3 g	15
Trans fat, 1.5 g	—
Cholesterol, 30 mg	10

[a]Percent daily values are based on a 2000-cal diet

Daily value (DV) has not been established for *trans* fats; thus, calculation of a DV is not possible. Amounts of *trans* fat less than 0.5 g per serving are recognized as "*Trans* fat 0 g." Processors, who wanted more favorable nutrition facts labels on their packaged foods, reformulated their products. Those, choosing to claim "0 *trans*," *typically* provided fat solids from interesterified fats, fully hydrogenated fats (because these do not contain *trans* bonds), or higher melting fractions of palm and other oils. Exclusion of conjugated structures from the FDA *trans* fats definition enables claiming products where all the fat is from ruminant sources (butter, cheese, cream, dips, ice cream, beef, and tallow) as containing "0 trans." Saturated fat content also must be shown on the label. *Trans* fats are unsaturated. Currently, some nutritionists and regulators are seeking means to inform restaurant, institutional, and fast foods customers about *trans* fats contents of specific products sold at these outlets.

The FDA's regulatory chemical definition for *trans fatty acids* is: "all unsaturated fatty acids that contain one or more isolated (i.e., nonconjugated) double bonds in a *trans* configuration." Under this wording, CLA would be excluded from the definition of *trans* fat, but *trans* vaccenic acid would be included. This definition was reconfirmed as of June 24, 2004 [162].

Copies of announcements, communications, and transcripts of open hearings during regulation making are available at the US-FDA Internet Web site. Readers may gain insight into regulator–nutritionist thinking on the *trans* issue from the transcript of the Nutrition Subcommittee Meeting on Total Fat and *Trans* Fat on April 27–28, 2004 [163].

During the review process, each responding interest group typically rationalized its position using generally accepted research findings. However, the diverse findings have yet to be integrated into a coherent system. FDA's communications have taught that consumption of saturated and *trans* fats causes undesired increases of total cholesterol in blood serum. They also has taught that *trans* fats cause undesired increase of LDL (LDL that carry cholesterol), which is termed "bad" cholesterol and is the rationale for listing *trans* fat in Nutrition Facts labels. However, it is generally accepted in the scientific community that not all saturated fats are equal, and likewise for *trans* fats. More specifically, stearic acid has been considered "neutral" in raising total cholesterol or LDL based on research initiated nearly a half-century ago and frequently reconfirmed. In response to concerns about defamation of palm oil as its world sales increased, that industry initiated extensive nutrition research, even involving noted United States scientists, on palm oil's dietary effects in the mid-1980s. Palm oil contains approximately 44% palmitic acid, 5% stearic acid, 39% oleic acid, and 10% linolenic acid. Repeatedly, diets containing palm oil (palm olein) raised neither total cholesterol nor LDL, and in some experiments decreased total cholesterol and increased "good" HDL (high density lipoprotein). In comparative experiments, *trans* fats fared negatively compared to palm oil, as also did palm kernel and coconut oils and lard. (In palm oil, 75% of the fatty acids in TAG position 2 are unsaturated.) It has been suggested that myristic acid (C 14) leads in increasing LDL, followed by lauric acid (C12). But, myristic and lauric acids, in limited amounts, also play essential nutrition roles. Current nutrition thought is shifting to dietary ratios of saturated and unsaturated fatty acids as more important in the diet than individual fatty acids. However, the world's major saturated fatty acid is palmitic, and together with stearic acid (which occurs in beef tallow consisting of approximately 25% palmitic acid, 19% stearic acid, 36% oleic acid, and 3% linolenic acid) accounts for the far majority of domestic dietary saturated fat intake. This leads to the question: If the majority of saturated fatty

acids are essentially cholesterol neutral, why are they grouped with the LDL-raising saturated fatty acids in nutritional labeling?

With exception of the dairy and ruminant animal industries, which are recommending exemption of *trans*-vaccenic acid, no one is promoting increased consumption of *trans* fats. However, the dichotomy of procholesterolemic and cholesterol-neutral saturated fats has divided the nutrition community into two groups, each with well-respected members and spokespersons. Many scientists strongly recommended against combining saturated fat and *trans* fat into one number on the Food Nutrition Facts label in invited letters to the FDA. Others repeated that a better system for classifying "good" and "bad" nutrients is needed. Some nutritionists have suggested that earlier FDA Nutrition Facts labeling and the USDA Food Pyramid have: (1) been interpreted by the public as "all fats are bad;" (2) participated in causing current national obesity problems; and (3) led to development of "low carb" weight loss diets which include increased fat intake [163]. More discussions and new diets can be expected in the future.

Historically, the presence of CLA in vegetable oils was considered minimal, well below 1%, and little was known publicly about their actual occurrence in hydrogenated fats. In 2002, a group of Korean researchers published a pioneering study on effects of catalyst types and concentration, hydrogen pressure, and operating conditions on CLA formation in different oil species. Using selective catalysts, they obtained 23.2, 23.7, and 23.3% total CLA production in corn, cottonseed, and soybean oils (originally containing ~58, 51, and 51% linoleic acid, respectively). As much as 2.4% 9 *cis*-11 *trans*-18:2 and 1.7% 10 *trans*-12 *cis* 18:2 were obtained in mixtures from individual trials [164]. Biological activity of the CLA was shown later. Another publication from the same laboratory, incorporating the latest separation techniques developed in the United States CLA research program, and mass spectroscopy for CLA identification, reported separation and identification of 20 different CLA isomers in hydrogenated soybean oil [165]. These studies report that CLA production can be a result of hydrogenation conditions, and concentrations as much as eight times greater can be produced chemically than in ruminant sources. Thus, CLA are no longer unique to ruminant fats, and potentially can be made available in quantity. However, because of the unknown biological activity of other CLA isomers produced simultaneously, they should be carefully reviewed before broad authorization in the food supply.

New regulations can markedly change equipment requirements and practices of an industry. While regulators, lobbyists, and lawyers negotiated the new law, the fats and oils industry had to start preparing for new market requirements, and food formulators had to develop new products. Likely, the first consideration was selection of ingredients that make Nutrition Facts panels look attractive compared to competitor's products and also have functional properties necessary for making the products. But formulators are well experienced in matters such as ingredients listings. Research is continuing on ways to better control *trans* fat production during hydrogenation [166], but the industry has to formulate with currently available technologies. Reserving the use of hydrogenation for making fully hydrogenated hardstocks (~5 IV), the two most promising routes for obtaining fat solids are blending selected fractionated fat solids, hard stocks, and oils and interesterification of the above. However, as mentioned earlier, skepticism exists about increasing the number of saturated fatty acids in the TAG 2 position by randomization. Enzymatic interesterification at the 1,3 positions seems more appealing in theory.

Trans-free margarines and spreads were well established in Canada and European markets, before promotion in the United States. Many major domestic snack food fryers have adopted *clean ingredient listings* in which only potatoes or corn, vegetable oil, salt, and flavorings are listed (but no hydrogenated products or preservatives). Formulators of more complex foods have options of using emulsifiers, antioxidants, and an ever-increasing variety of hydrocolloids and gums.

Not all fat products have been reformulated for "0 *trans*" labels. Margarines must contain 80% fat, just like butter. Both have been largely replaced by spreads, or "lite" spreads, which contain lower amount of fat; a far majority of spreads claim "0 *trans*." Many home makers prefer to cook or bake with the higher fat content margarines, or (100% fat) shortenings, which often show positive *trans* fat content on their labels.

Edible Uses of Fats and Oils

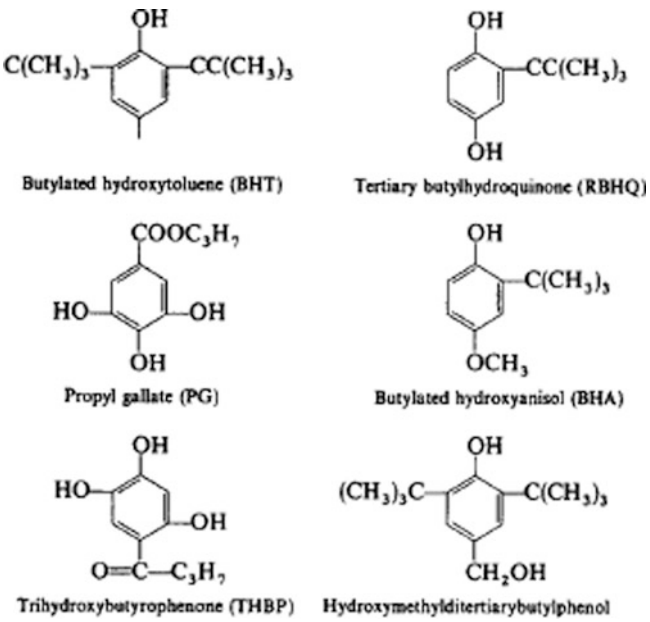
Antioxidants

Fats and fat-containing products may be stabilized against oxidation by the addition of antioxidants as adjuvants. These compounds are believed to act as hydrogen donors or as free radical acceptors that intercept and hold quantums of energy that otherwise might induce oxidation. The major food grade synthetic antioxidants used include: butylated hydroxyanisol (BHA), butylated hydroxytoluene (BHT), tertiary butylhydroquinine (TBHQ), propyl gallate (PG), and 2,4,5-trihydroxybutyrophenone (THBP). Generally, they are allowed in food products at 0.01% of total fat weight each, with a total of 0.02% if a combination is used.

Synergists used in combination with antioxidants include citric acid, isopropyl acid, phosphoric acid, ascorbic acid, ascorbyl palmitate, iso-ascorbic acid, tartaric acid, and lecithin, most of which act as chelators of pro-oxidative metals.

Natural antioxidants include gum guaiac, tocopherols (including vitamin E), and oil of rosemary (containing rosmaridiphenol). antioxidant properties but are not counted in the maximum amounts of antioxidants permitted in the food. Types, mechanisms, and health effects of natural antioxidants are described in the references [168, 169].

The cross-linking that occurs in drying oils also is an oxidation reaction. Polymerization of oils can occur rapidly in products such as fish meal that contain significant amounts of polyunsaturated triacylglycerols, even to the point of building up sufficient heat for a pile to spontaneously burst into flame. Thus, feed grade antioxidants, such as ethoxyquin, often are added before storage. Ethoxyquin also has been used for sparing the natural tocopherols for vitamin E activity in nutrition.



Because of cost, they usually are reserved for premium-priced foods. Many types of tocopherols and associated compounds exist, and understanding of the mode of action is continually improving. The forms that give the most antioxidant protection do not always show the greatest vitamin E nutrition activity [167].

Assemblers of grocery store or food service convenience foods have the same general limitations. However, they also have access to natural cereal ingredients and herbs, herb extracts such as oils of rosemary, sage, and other materials in formulation that possess.

Synthetic and natural antioxidants are known to be heat- and steam-distillable and preferably should be added to oil products after the maximum heat encountered in processing. It further is known that many natural phenolic compounds in cereal–oilseed products, as well as reaction products of Maillard (nonenzymatic amino acid-reducing sugar) browning and natural wood smoke, have antioxidant effects. Additional techniques for reducing oxidative activity include maintaining nitrogen blankets on oils stored in tanks and distributing oils in opaque containers or brown bottles to limit exposure to ultraviolet light, although this is not popular with many marketing departments who want to display clear, light-colored oils.

Nonionic Surfactants and Emulsifiers

Nonionic surfactants and emulsifiers, whose molecules have both aqueous (polar) and alkane (nonpolar) compatible sectors, also are common adjuvants. Their molecules have regions that are sufficiently similar to become part of either the water or oils phases, and other regions sufficiently dissimilar to repel that phase. For example, when added to a crystallizing fat, some nonionic surfactants may orient themselves to become part of the crystal, thus preventing further replication and limiting crystal size. Likewise, some will react with gelatinized starch in aqueous and bread systems and prevent its recrystallization (retrogradation). Furthermore, surfactants may orient around discrete droplets to stabilize water in oil (W/O) or oil in water (O/W) emulsions. When this occurs, the compatible end becomes associated with the discrete droplet, leaving the other end turned outward to associate with the compatible continuous phase [170].

The major groups of commercial emulsion stabilizers include: (1) glycerol esters, favoring W/O emulsions; (2) esters of mono-acylglycerols with hydroxycarboxylic acids (including lactic, succinic, malic, and tartaric); (3) sodium stearoyl-2-lactylate (SSL), favoring O/W emulsions; (4) fatty acid monoesters of ethylene glycol; (5) sorbitan fatty acid esters, known as SPANS favoring W/O, and TWEENS favoring O/W emulsions; (6) phosphorlipids; (7) water-soluble gums, including gum arabic, tragacanth, xanthin, agar, pectin carrageenan, and methyl- and carboxymethyl-cellulose; and (8) proteins [170, 171].

Glycerol has three exposed hydroxyl groups, resulting in a compound completely miscible in water at all concentrations. Fatty acids have both hydrophilic (water-attracting) and lipophilic (oil-attracting) ends. As they are esterified to glycerol, the molecular structure that originally was primarily water-soluble becomes increasingly oil-soluble. Finally, when all three positions are esterified to fatty acids, the molecule is nonpolar and soluble only in organic solvents.

Table 34.12 HLB (hydrophile–lipophile balance) numbers for some surfactants

Name	CAS number	HLB value
Oleic acid	112-80-1	1.0
Acetylated monoglycerides (film formers)	–	1.5
Sorbitan trioleate (SPAN 85[a])	26266-58-6	1.8
Glycerol dioleate	25637-84-7	1.8
Sorbitan tristearate (SPAN 65[a])	26658-19-5	2.1
Glycerol monooleate	25496-72-4	3.4
Glycerol monostearate	31566-31-1	3.8
Sorbitan monooleate (SPAN 80[a])	1333-68-2	4.3
Sorbitan monostearate (SPAN 60[a])	1338-41-6	4.7
Soy lecithin	8020–84–6	8.0
Sodium stearoyllactylate (anionic type)	18200-72-1	8.3
POE sorbitan monooleate (TWEEN 81[a])	9005-65-6	10.0
POE sorbitan monostearate (TWEEN 60[a])	9005-67-8	14.9
POE sorbitan monooleate (TWEEN 80[a])	9005-65-6	15.0
POE stearic acid (monoester) (TWEEN 20[a])	9004-99-3	16.9

[a]Atlas brand names

The hydrophilicity of nonionic surfactants can be characterized numerically as their hydrophile–lipophile balance (HLB). An HLB value of 3–6 indicates that the compound is a likely W/O emulsifier; 7–9, a wetting agent; 8–13, an O/W emulsifier; 13–15, a detergent; and 15–18, a solubilizer (of oil or other non-polar compounds) in water. The HLB values of some common compounds are presented in Table 34.12 [170]. An HLB value of 8.0 is shown in Table 34.12 for lecithin, but manufacturers are able to supply modified lecithins with values of 2–12.

Table Oils

The processing of RBWD table oils has been mentioned earlier. Depending on positioning in the marketplace, these products may also serve as light duty cooking/frying oils and may be brush hydrogenated and contain added natural or synthetic antioxidants and methyl silicones at 0.5–3.0 ppm to slow breakdown, initiation of foaming, and smoking during frying [172]. United States and Northern Europe markets consider light product color and bland flavor as indicators of oil quality. Olive oil aficionados often prefer the green color and its stronger taste as an indication of virgin or minimum processing. All oils revert to stronger flavors in time. Slight flavor reversion generally is acceptable in cottonseed oil, but not in soybean oil. Many years of research were required to reduce the problem in soybean oil, and the mechanism still may not be fully understood. Converting the industry to only stainless steel oil contact surfaces (specifically avoiding iron and copper), reducing residual phosphatides content to essentially "zero," early inactivation of phospholipases and associated enzymes when preparing seed for extraction, nitrogen blanketing and reduced storage temperatures of bulk oil, and the use of antioxidants are believed to have helped.

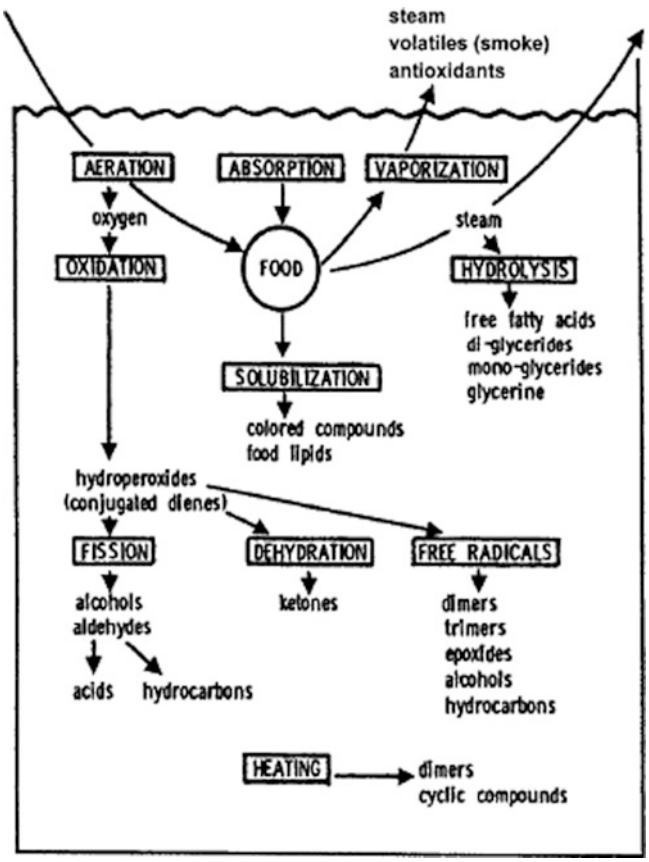


Fig. 34.32 Changes occurring during deep fat frying. (From Fritsch [173], With permission)

Frying Oils

Oil acts as a heat transfer medium during the frying process which rapidly heats, cooks, and sometimes puffs, dehydrates, or forms a crust around the product. The mechanics of deep fat frying are shown in Fig. 34.32 [173]. The entering material carries oxygen that temporarily aerates the hot oil, and water that forms steam, with both rapidly swept out because of low solubility of gases in the hot liquid. Besides enzymes, which are likely to be inactivated rapidly, raw materials also carry oxidation catalysts such as iron in the hemoglobin of fresh meats, chlorophyll, and color pigments. Alkali may accompany the material, especially in chemically leavened doughnut batter and alkali-treated corn snacks. In short, almost every concern mentioned thus far in seed preparation, extraction, and oil processing occurs during frying.

The high temperatures of frying, 177–204°C/350–400°F, are deleterious to oil quality. *Trans* fats are produced, and some of the degradation-prone anisidine value products remaining after refinery deodorization deteriorate. Oils start breaking down into simpler compounds, and also form cyclic compounds and polymers. This process continues while food shop fryers are left hot and inactive during afternoons between preparation of lunch and dinner meals. However, limited self-cleansing occurs in the system by steam distillation, as noted by reduction of carbonyl compounds in oils after inactive fryers are put into service again. An excellent review on frying has been edited by Perkins and Erickson [174].

Unlike in some countries, few United States households have dedicated frying pots containing oil in readiness for meal preparation. Most domestic deep frying is done by commercial operations such as: snack foods processors, producers of convenience fried foods such as Chinese egg rolls and frozen meals, and fast food vendors who prepare French fries, fried chicken, and other products.

Industrial fryers generally are of two types: (1) those who sell all the purchased oil with the product, and (2) those who must recondition and occasionally dispose of oil. Requirements for the selection and use of frying oils in these applications differ [175]. Industrial snack food fryers, designed to use all the oil, are equipped with clean-out systems and inline filters. In theory, they should be able to operate indefinitely, only adding make-up oil as needed. In *clean label,* operations, company policy dictates that no, or minimum, additives can be used. Typically, company personnel periodically inspect and monitor refinery operations of self-certified suppliers. Antioxidants or silicone defoamers are not permitted in these oils. Oils are received in bulk, typically at less than 0.05% FFA, < 1.0 PV, < 4 ppm phosphorous, and <0.75 ppm chlorophyll, and are kept in stainless steel tanks under nitrogen [175].

Stability against oxidation of soybean oil has consistently increased in frying trials as linolenic acid content decreases, whether by plant breeding, mixing with other oils, or by hydrogenation [176–178]. Less than 2% linolenic acid content has been a long-term industry goal, with the way by which linolenic acid is reduced (hydrogenation or breeding) appearing to have little effect on fried product stability [179]. Oils with PVs higher than 2.5 are not used in well-disciplined frying operations.

The freshness of fried snack foods is dependent on use of packaging impermeable to moisture and oxygen, including laminates of windowless aluminized films that block 99+ percent of the light to prevent photo-induced oxidation. Additionally, the pouches are nitrogen flushed before sealing, thus creating pillow packs that further protect the product against crushing. The snacks often are delivered by company delivery personnel, who place them on store shelves or racks. Products may have shelf lives of 6–8 weeks, but inventories are carefully managed to ensure rapid turnover and fresh products [175].

Normally, the warm surface oil serves as the binder ("tacking agent") for adsorbing salt and dry flavorings to snack foods. The concept of reducing or entirely eliminating oil from snack foods appeared during the early 1990s. Rather than deep fat frying, snacks were dried at high temperatures in fluidized bed continuous dryers. A far smaller amount of oil was then sprayed onto the dried product for flavor. Where a "fat-free" snack food was desired, solutions of edible gums or specialty starches were sprayed onto the snack to serve as tacking agents, for water-soluble flavors; the product then required an additional drying step (to less than 1.5–2.0% moisture content to ensure crispiness) [175].

Industrial fryers, who cannot turn the oil over completely, have lengthened its life 3–10 times by using polydimethylsiloxane (methyl silicone), which is not allowed in some countries. Levels as low as 0.2–0.3 ppm have been found effective, with commercial usage of 0.5–5.0 ppm reported. Users are advised to minimize levels of usage to 1.0–3.0 ppm. Dispersion of polydimethylsiloxane in oil is difficult. The compound operates by suppressing foaming and polymerization and increasing smoke points of oils by up to 13.9°C/25°F. Antioxidants steam distill out of the oil during normal frying. Their initial inclusion essentially protects the oil only until the time of use, but some operators insist on periodically adding them to the fryer. For greater effectiveness, antioxidants in fresh oil are best sprayed onto the product after frying, or included in dry seasoning mixes [175]. Additional steps to prolong the use of frying oil include: inline filters, periodic cleaning of fryers to remove settled charred product, neutralization of fatty acids, and refreshing the oil by passing through adsorbent earth filters continuously, or at the end of the day. Numerous kits and advisory services are available.

Large commercial frying operations, and fast food franchises that prepare French fries and chicken, have provisions and personnel trained to care for frying oils. The greatest food safety concerns are about small restaurants which do occasional frying during midday and evening meals. Several countries have imposed standards on the quality of frying oil in use. For example, Germany requires that the smoke point be not lower than 170°C/338°F, and total polar compounds not exceed 24% [180]. Products fried in oils usually would be objectionable in taste to most Americans long before they reach the unusable specifications. Yet, with exceptions of reduced digestibility and depletion of vitamin E (which can be supplemented), laboratory animals directly fed thermally degraded fats have not done as poorly as anticipated from the history of the oil and known presence of mutagens. Obviously, gaps exist in our toxicology and nutrition knowledge. Many practical details are presented in a new book [181].

Specialty Oils

A variety of specialty oils exists. Pumpkin seed oil is popular in Central Europe. Sesame oil is used throughout the Middle East and the Orient; and roasted sesame oil is used in very small amounts to flavor Asiatic foods. Nut oils, grape seed oil, tomato seed oil, and herb-flavored oils are available.

The organic and "natural" foods markets demand nonchemically treated oils. These often are made by hard pressing the source and water degumming the oil, followed by bleaching with "natural" (nonchemically treated) earths and removing FFA by physical refining.

In 2004, ADM Kao LLC, a joint venture of Archer Daniels Midland Company (United States) and Kao Soap Company (Japan), launched a new type of cooking oil, Enova™ Brand in the United States market. Enova™ is a 1,3 diglyceride (diacylglycerol, DAG) intended for use in nutritional beverages/drinks, nutritional bars, salad dressings, and general cooking [182]. Enova™ oil was initially developed by the Kao Corporation and is the best-selling cooking oil in Japan under the "Econa® Healthy Cooking Oil" brand name. The manufacturer claims the US product is made from all natural soybean and canola oils, has the lowest saturated fat content of any cooking and salad oil, contains zero grams of *trans* fat, and is metabolized differently by the body: instead of being stored as fat, the majority of DAG is burned as energy.

In the early 1970s, Triple "F" Incorporated, a feed manufacturer in Des Moines, IA, developed a low-cost extruder for on-farm use, which inactivated trypsin inhibitor in whole soybean by heat produced by friction shearing. This made soybean directly usable by cattle, pigs, and poultry, without sending it to extraction plants and buying back soybean meal. However, the oil content of the product was too high for direct feeding, and purchase of defatted soybean meal often was necessary. In the mid-1980s, the INTSOY program at the University of Illinois developed a procedure for hard-pressing the sheared soybean, reducing fat content of the meal by about a half and producing saleable crude soybean oil. As domestic livestock operations increased in size, large farmers and cooperatives installed the InstaPro International Company ExPress® Extruder/Press System to process soybean, cottonseed, and occasionally other oilseeds for feed. Production of oil byproducts also increased. Research has shown many desirable properties in the crude hard-pressed ("expeller") soybean oil, including highly hydratable phosphatides content which are easily water degummed and a high resistance of the refined oil to oxidation. After physical refining, the oil shows unexpectedly good stability as frying oil, without hydrogenation or formation of *trans* fats while still retaining its linolenic acid (omega-3) content. After 35-h potato frying tests, soybean oil had a total polar compound level of 17.7% (degradation), whereas the "expeller" oil had 9.1%. Soybean oil with TBHQ antioxidant had 8.8% and hydrogenated soybean oil had 9.7%. Potatoes fried in the expeller oil had significantly higher flavor scores than those fried in the other oils [183]. Test results have been repeated in other laboratories [184]. The reason for the good performance is not yet known. Some believe the high heat (~130°C/266°F) generated in the process almost instantaneously inactivates most of the destructive enzymes (lipases, phospholipases, and especially lipoxygenases) at the time the seed is first sheared [185]. Others believe the benefits come from physical refining [186]. The industry is very excited about market potential for expeller-produced oil.

Margarines and Spreads

Margarine is one of the major temperature-profiled fat products. It was invented in France in 1869 intentionally as a butter substitute and was first produced in the United States in 1873. Originally, it was made from animal fat; coconut oil became the lead fat in margarine in 1917, partially hydrogenated cottonseed oil in 1934, and partially hydrogenated soybean oil in 1956. Various legal principles have been tested through margarine. Among the first was protectionism for butter and the dairy industry, with a requirement that a "Oleomargarine Sold Here" sign be posted on the door of every store offering it. (In retrospect, modern marketers might see this as the best free advertising possible.) In response to dairy industry claims of product inferiority, a law was passed in 1923 requiring that margarine be fortified to the same level of vitamin A as butter; vitamin D was added later. The principle that an intended direct substitute be at least as nutritious as the replacement had become part of the FDA's expectations for new products. Sales of colored margarine were approved on a state-bystate basis in the 1950s and 1960s, and United States per capita consumption of margarine surpassed butter in 1956.

The major enabling technical break-throughs were invention of the internal scraped surface heat exchanger (SSHE, "Votator") in 1937 for chilling the margarine oil mixture, and the lifting of emulsifier restrictions in 1992, which permitted development of a wide range of reduced-fat spreads. Margarine typically has had the same fat content as butter in most nations and is 80% in the United States. Spreads contain less than 80% fat and have become the most popular of the group. Some contain as little as 20% fat, the minimum amount being technical rather than legal.

SFI profiles of several margarine types, an all-purpose shortening, frying oil, and two shortenings are shown in Fig. 34.33 [128]. The SFI profile of butterfat varies with

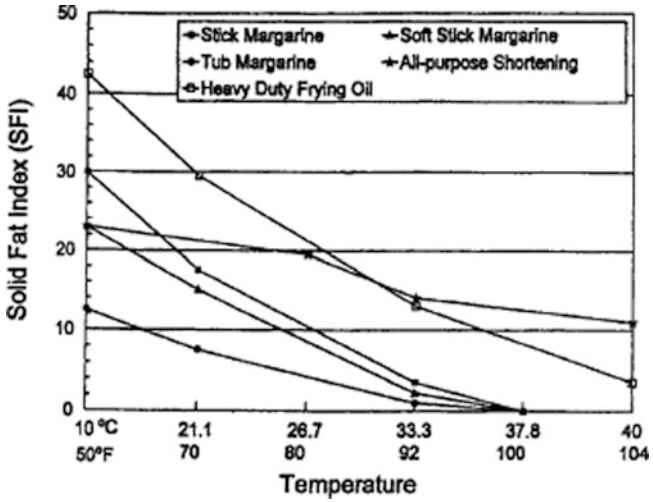


Fig. 34.33 Solid Fat Index (SFI) profiles for hard stick, soft stick and tub margarines, and for all-purpose shortening and heavy duty frying oil. (Data plotted from Erickson and [128])

Table 34.13 Crystal forming tendencies of hydrogenated oils, collected and updated from various sources

Beta prime (β′) type	*Beta* (β) type
Cottonseed	Soybean
Rapessed—HEAR[a]	Canola—LEAR[a]
Lard—modified[b]	Lard—nonmodified[b]
Palm	Palm kernel
Rice bran	Sunflower
Herring	Olive
Menhaden	Corn
Milk fat (butter fat)	Peanut
Tallow	Safflower
	Cocoa butter
	Coconut
	Sesame

[a]By elimination of erucic acid from traditional high erucic acid rapeseed, the C22 fatty acid family also was eliminated. The replacement canola (low-erucic-acid rapeseed) had one less variety of fatty acids and became a β crystallizer

[b]A reverse situation occurred in lard, which has few predominant TAG types. Rearrangement created additional types which led to β' crystallization

the season and feed and typically is in the 40–50% solids range at 10°C/50°F. Soft stick margarine is softer than butter when taken from the refrigerator, and tub margarine is spreadable.

The basic sequence for making margarines/spreads includes:

- Formulation of an oil mixture from hydrogenated base stock or interesterified fats, hard stock, and oil that has the desired SFI or SFC profile.
- Ensuring that sufficient diversity occurs in the species and fractions to provide a variety of TAG that will form small β' crystals.
- Compounding the margarine oil blend at the refinery; final deodorization; shipping the melted blend to the margarine plant; and storage under a nitrogen blanket.
- Preparing an oil-soluble additives mixture containing mono- or diglycerides and other emulsifiers, flavorings, oil-soluble vitamins, and yellow color at the margarine/spread plant.
- Preparing a water-soluble additives mixture containing water, salt, anti-microbial compounds, viscosity thickeners, and water-soluble flavorings. Formula amounts of thickeners and water-soluble flavorings increase as the fat content of a spread is reduced. The water should be microbiologically potable and deionized to remove calcium, magnesium, iron, and copper.
- Blending the heated oil-soluble additives mixture into the warm oil in a mixing tank. Slowly adding the warmed water-soluble additives mixture into the blend to produce a water-in-oil emulsion.
- Pasteurization; partial cooling.
- Chilling and working the emulsion in a series of (typically ammonia-chilled) internal scraped-surface heat exchangers ("A" units) and "picker bar" workers ("B" units), with resting tubes interspersed to ensure adequate time for establishment of the desired crystal structures.
- Filling.
- Holding under controlled temperature conditions for establishment of the desired crystals.
- Shipping.

Much of the physical chemistry for making temperature-profiled fats, including Figs. 34.1 and 34.2, has already been reviewed. Additional references are available [53, 187]. We cannot change the laws of thermodynamics, but can slow or hasten arrival at equilibrium. The margarine literature often shows a table similar to Table 34.13, but does not explain the practical implications. Basically, the beta prime (β′) tending oils contain a greater variety of fatty acids than the beta (β) tending. A greater diversity makes it more difficult for identical TAG to align and crystallize. It is easier to make whole cottonseed oil margarines/spreads than whole soybean oil counterparts because the former contains about 2.5 times more palmitic acid than soybean oil. For years it was common practice to include about 10% cottonseed hard stock in soybean margarines. A reduction in TAG diversity increased the problems of making margarine when erucic acid was eliminated from canola (rapeseed); but increasing diversity, as by rearrangement of lard and increased presence of *trans* fats, has assisted in making smooth-textured margarines. A similar lack of diversity is encountered in making palm oil margarines, and addition of C 18 hard-stocks and lengthening pin working and resting times have been employed. The newer high oleic acid oil varieties often present more difficulties in texture development than the traditional varieties in the same oil species. Crystals grow by aligning

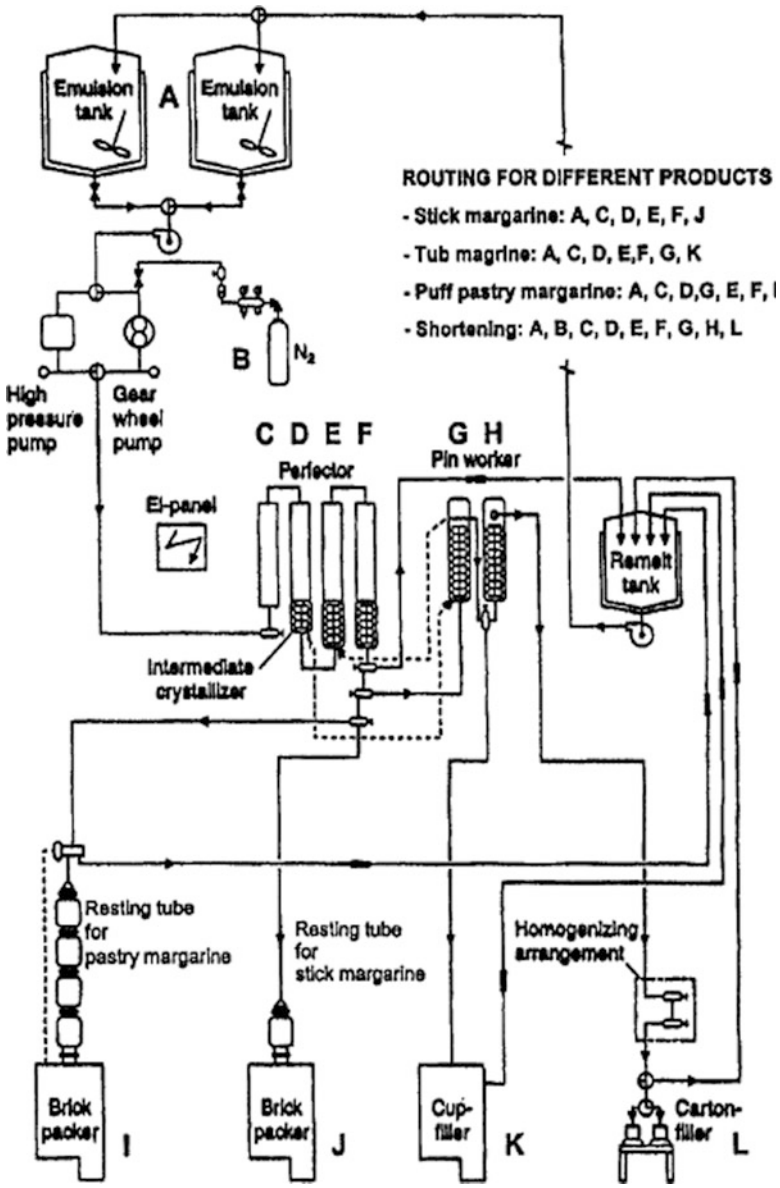


Fig. 34.34 Flexible Perfector Plant™ for making stick, tub, and pastry margarines, and shortening. (Courtesy of Gerstenberg Schröder, Brondby, Denmark)

identical molecules side by side. Emulsifiers, such as mono- or diglycerides, can align next to the crystal and be accepted as part of the lattice. But, not being identical, they foul the surface and stop crystal growth. Increasing the viscosity of lower oil content spreads makes it more difficult for similar TAG to align and crystallize, especially if temperature cycling occurs during storage.

Margarine, like butter, and spreads, is a water-in-oil emulsion. The water and all water-soluble ingredients are encapsulated in a continuous phase of oil. This has many practical advantages. Growth in individual droplets is limited by available nutrients, and bacteria cannot cross over to a second nearby food supply. If the product is salted at 1.5%, the water droplets will have a salt concentration of 7.5%, which is inhibitory to many bacteria. If the emulsion has been properly made and pasteurized, many droplets will be small and not contain bacteria cells. Lecithin is included in margarines/spreads at 0.1–0.5% as an antispattering agent used for frying; it is introduced with the oil-soluble additives initially added to the base oil.

The margarine/spread production flow sheet in Fig. 34.34 shows how these principles are applied. The figure represents a multipurpose plant, in which various products can be made. The legend in the upper right corner shows results of the sequences employed. The emulsions are prepared in tanks (A), although the provisions for pasteurization and cooling before processing are not shown. Consumer margarines must meet FDA Standards of Identity, which specify the permissible additives. Industrial buyers may arrange to have other FDA-approved ingredients added as a means to simplify their dispersion in manufactured products. The emulsion is pumped to an internal scraped-surface chiller and exits at

10–19°C/50–65°F as a soft glass (stiffening when held in the hand). Because this is not the type of final crystal desired, the chilled emulsion is then sent through a series of pin workers (tubes through which the margarine is pumped while a shaft with fingerlike pins mixes it), chillers, and resting stops to craft the desired crystal. The final temperatures for table margarines and margarine–butter blends are −18–−20°C/0–14°F, and −5°C to −1°C/12–23°F) for low-calorie spreads [188].

Figure 34.34 shows that tub margarine is pin-worked considerably more to keep it more liquid until filling. The solids content profile also is different from the stick margarine, and a smooth-textured product with minimum stiffening is desired.

Some bakery products ("puff pastries," phyllo) consist of flaky layers, made by rolling the dough thinly, covering it with shortening, folding, rerolling, and repeating the process many times. On baking, they puff up. The gluten layers must stay intact, and the shortening also must be flexible but not give off free oil during the machining. Puff pastries such as croissants, whose fat melt and clean-up in the mouth, can be made from butter, but must be prepared at low temperatures (10°C/50°F) in refrigerated rooms using chilled equipment. A very flat SFI curve (30.0–33.5 at 10°C; 28.0–30.0 at 21.1°C; 24.5–26.5 at 33.3°C; and 19 minimum at 40.0°C) is recommended for tallow–vegetable oil puff pastry margarines. They melt slightly above mouth temperature, but some people notice greasiness. Historically, puff pastry margarine was made using chilling rolls, but processes exist now for using scraped-surface heat exchangers, "B" units, and large resting tubes [188].

Shortenings

Typically, the function of fats in baking is to "shorten" or control development of wheat flour gluten and avoid or limit toughness in the product. In doing so, starch becomes the predominating matrix, and tenderizing complexes can be established between the fat and carbohydrates. A fat with a flatter solids temperature profile like the "All-purpose shortening" in Fig. 34.33 can accomplish its "shortening effect" during machining of the dough and baking even if it does not melt substantially during eating.

Numerous emulsifiers are available for dough (continuous gluten) and cake (sugar, corn sweetener, starch, and fat emulsion) systems. Emulsifiers act as conditioners in dough systems by: improving tolerances to variations in flour and other ingredients; increasing resistance to mixing and mechanical abuse; providing increased gas retention, shorter proof times, and increased product volume in yeast-leavened systems; improving uniformity of gas cell size, cell walls strength, and grain texture; improving slicing; and extending product freshness by delaying starch retrogradation and staling [171].

Cakes essentially are emulsified slurries before baking. Considerable use is made of sugar (with corn sweeteners increasingly used), starch in low-protein content flours, and fat. Emulsifiers have three functions in cake systems: to improve air incorporation; to disperse shortening into smaller particles to maximize the number of air cells; and to improve moisture retention. Complexes occur between fats, emulsifiers, and starches that result in smooth, tender, moist cakes. Emulsifiers include broad classes of lecithin and lecithin derivatives, mono- and difatty acid glycerol esters, hydroxycarbocylic acid and fatty acid esters, lactylated fatty acid esters, polyglycerol fatty acid esters, ethylene or propylene glycerol fatty acid esters, ethoxylated derivatives of monoglycerides, and Sorbitan™ fatty acid esters [171]. Many oil processors sell proprietary brands of shortenings containing emulsifiers, and large bakers can arrange to have emulsifiers added to their melted fat mixtures before shipping.

As shown in Fig. 34.34, nitrogen is injected into the first scraped-surface chiller, with the shortening oil mixture, to give an opaque white appearance and increase plasticity. Some bakers prefer to use semi-plastic shortenings in applications where oil may shorten the dough too rapidly, and for "creaming" sugar and shortening as in making cake frostings. Some small restaurants prefer semi-solid "shortenings" and have fryers able to accept standard 18.2-kg (40-lb) cubes. Care should be taken to avoid development of large air spaces when melting cubes over the (electric) heating rods to avoid burning the shortening.

Other Edible Applications

Cocoa butter (CB) has a challenging chemistry and has attracted many efforts to develop lower cost, acceptable alternatives. The following definitions provide a quick introduction to this field: (1) cocoa butter equivalents (CBEs) are compounded mostly from tropical oils other than palm. Because their melting and crystallization properties closely resemble CB, they are compatible as diluents at all levels of substitution; (2) cocoa butter replacers (CBRs) are made from nondairy oils (typically soybean, cottonseed, or palm) partially hydrogenated for maximum *trans*-C18 isomer formation to acquire a steep melting profile. They are best used for enrobing bakery products, but their melting profiles can be improved by chill fractionation; and (3) cocoa butter substitutes (CBSs) are made primarily from lauric-type fats (C8–C12 of palm kernel and coconut origin) and are hydrogenated under conditions that favor *trans* formation, but may contain a limited amount of hydrogenated C18 trigly-cerides. CBS limitations include: they must be used

alone because of incompatibility with cocoa butter, they require the use of cocoa for "chocolate" flavor, and all ingredients with active lipase systems must be avoided to prevent the development of a soapy flavor [189].

The reader is referred to the volume by O'Brien [172] for other food applications of fats, including icings for sweet goods; spray-dried nondairy creamers; coffee whiteners; aerated whiteners with encapsulated air to produce a cappuccino effect when added to coffee; dried powders designed to be reconstituted, pasteurized, homogenized, and packaged for restaurant use as creamers; vending machine dry creamers; whipped topping shortenings, also used for making bakery cream pie fillings and cake toppings, aerosol toppings, powdered toppings, and frozen ready-to-use toppings; cheese analogue shortenings, frozen mellorine dessert shortenings, sour cream analogue, and dip base fats; and sweetened milk and sweetened condensed milk analogue fats.

Industrial Uses of Fats and Oils

Timeline

Industrial uses typically means nonfood-nonfeed applications, although feed uses are not consistently excluded. No one knows when man first used oils or fats for lighting, medical, and cosmetic applications, lubricants, or combined them with wood ashes to make soaps. The following sequence has been published for soybean oil [21].

- <AD 980—China: soybean oil likely used for illumination in lubricating fluids and coatings.
- AD 980—China: documented use of soybean oil boat caulking materials.
- 1908—Europe: soybean oils used in soaps; glycerin sought for making explosives for Panama Canal project and printer's inks; oil additionally used in rubber substitutes and linoleum flooring.
- 1910—United States: soybean oil classified as a drying oil; used as cheap replacement for linseed oil in paints.
- 1914–1918—United States: largest soybean oil industrial market is soaps, followed by paint, varnish, enamel, linoleum, oilcloth, asphalt, and other waterproofing materials.
- 1919—Blowing warm air through heated soybean oil found to increase viscosity by initiating oxidation and polymerization; blown oil improves properties of printing inks.
- 1926—Soybean oil used for plasticizing and increasing the elongation of rubber.
- 1930s—United States: Kienle and Hovey of General Electric developed soybean oil alkyd resins used in paints to improve drying, adherence, endurance, and color; Ford Motor Company used soybean oil and its derivatives in enamel paints for automobiles; DuPont's "four-hour enamel," based on soybean oil, is considered the most important factor in furthering soybean oil usage in paint. Japan also initiates programs.
  - Quality of soybean oil first reported suitable for food use and hydrogenation; replacement of cottonseed oil begins.
  - Strong chemurgic movement initiated; credited with nearly 200 industrial uses during its ten-year existence. Ford Motor Company uses significant amounts of soybean oil for enamel paint, glycerin for shock absorbers, in 1937 automobiles.
- 1945—Chemurgic programs decline after World War II.
- 1950s—D. Swern, USDA scientist, develops epoxy plasticizers from oils or monohydric fatty esters for use in plastics.
- Late 1970s—Converting oil triglycerides to methyl or ethyl fatty acid esters by transesterification ("alcoholysis") reduces injector fouling, carbon deposits, and degradation of lubricating oils in diesel engines, compared with direct use of vegetable oils or diesel fuel–vegetable oil mixtures.
- Early 1980s—American Newspaper Publishers Association develops first-generation soybean oil-based inks to replace uncertain mineral oil supplies.
- Mid-1980s—Degummed, alkali-refined cottonseed and soybean oils used in pesticide aerial spays.
- 1987—USDA Federal Grain Inspection Service allows the use of soybean and other edible oil sprays to reduce the risk of grain dust explosions in elevators. Use of one to two percent soybean oil in livestock feeds reduces dust in pig-rearing facilities, improves animal health, and gives five to ten percent increase in weight gains.

Chemurgy Revisited

Chemurgy is the use of replenishable farm crops as feedstocks for industrial processes. The concept became very popular with onset of the Great Depression in the early 1930s because it promised new uses for agricultural crops and development of a self-sustaining national economy. Famous advocates of the era included Henry Ford, industrialist, and George Washington Carver, crop scientist. The movement was heavily subsidized by the federal government, slowed as World War II approached, and ended in the prosperity of the postwar era. Currently, the United States again has agricultural surpluses, especially soybean oil. Naturally, the following question arises: Are business prospects for chemurgy products different now than in 1937, especially with the United States committed to an open global trade policy? New factors include: (1) Replenishable

materials offer the promise of biodegradability, which is becoming increasingly popular with an environment-concerned public. (2) The global politics of petroleum carry many hidden costs, including threats of supply interruption, occasional price fixing, and potential involvement in wars to keep trade sources and routes open. (3) The petroleum companies are driven by economies of scale and have limited flexibility in responding to small, although reliable, markets.

(4) Biotechnology offers the promise of tailored crops, able to produce high levels of specific chemical feedstocks, previously unavailable. But (5) the portion of the public engaged in agriculture and agribusiness is the smallest ever, and federal subsidies may not be easily obtainable in the future.

Nevertheless, current chemurgy research and applications is the highest ever, and many products have been launched by small entrepreneurs to regain markets previously lost by vegetable oils to petroleum feed stocks (Table 34.14). Several factors seem obvious. (1) Supplies of fossil carbon sources (coal and petroleum) and minerals are limited and access to new sources is increasingly expensive. It seems almost certain that plastics and composites will become more important as structural and manufacturing materials, and people will have to increasingly replenish more of their carbon needs through agriculture. (2) The question of where replenishable resources will be grown and converted into industrial and consumer products is heavily political and yet to be answered as national policies compete with global companies. (3) the transition will not occur smoothly. Interests vested in the status quo are likely to first act to preserve current positions as long as possible, but will provide capital when change becomes inevitable.

Table 34.14 Examples of soybean oil and lecithin industrial uses[a]

Soybean oil technical uses	Oleochemicals from oil	Soybean lecithin
Anti-corrosion agents	Methyl esters	*Wetting agents*
Anti-static agents	Soy diesel fuel	Dry powders
Candles	Solvents	Cosmetics
Caulking compounds		Plant pigments
Composite materials	Fatty acids	
Concrete release agents	Fatty alcohols	*Nutritional*
Core oils	Glycerin—industrial and explosive uses	Medical
Crayons		Vitamins—animal feeds
Dust control agents		
Electrical insulation		*Anti-foaming agents*
Epoxy resins		Alcohol
Fungicides		Yeast
Hydraulic fluids		
Printing inks		*Dispersing agents*
Linoleum backing		Inks
Lubricants		Pesticides
Metal casting/ working oils		Magnetic tapes
Oiled fabrics		Paints
Paints		Papers
Pesticide carriers		Synthetic rubber
Plasticizers		
Protective coatings		*Other*
Putty		Viscosity modifications,
Soaps/shampoos/ detergents		concrete, drilling muds
Solvents		Softening and curing leather
Vinyl plastics		
Wallboard		
Waterproof cement		

[a]Courtesy of American Soybean Association, St. Louis, MO

Industrial Oils Utilization

Estimates of recent domestic edible and industrial oils and fats use are shown in Table 34.15, and industrial uses of soybean oil in Table 34.16.

Fatty acids chemistry and processes have been summarized by Johnson and Fritz [190] and oleochemicals manufacture and use by Gunstone and Hamilton [191]. Pathways for converting oils and fats into various oleochemicals are shown in Fig. 34.35 [21, 192].

Crude soybean oil has limited uses as sprays. Spray nozzles are in danger of clogging by phospholipids, which also leave repeatedly sprayed surfaces sticky. Generally, *once-refined oil* (degummed, alkali-neutralized, water-washed, and dried) is the minimum quality used for dust control and aerial spraying of pesticides. Anticorrosion and anti-polymerization agents are added in lubricants and also in hydraulic fluids. Current industrial applications include: inks, paints and coatings, biodiesel fuels and additives, lubricants, ion exchange resins, adhesives, foams, fatty alcohols, fatty amines, and associated processing [191, 193–196].

Fatty Acid Methyl Esters, Biodiesel

Fatty acid methyl esters (FAME) are the gateway to many products. Use for glycerol, a byproduct of alcoholysis interesterification. Current FAME uses include: cleaning graffiti stains and sticky deposits, light lubricants, degreasing baths, inclusion in penetrating oils, asphalt and concrete

Table 34.15 Reported fats and oils uses in the United States, 2002 (million pounds)[a,b]

Fat or off	Amount (million pounds)	Percent of reported Crop oil	Total edible oils
Edible uses			
Coconut oil, Total edible	294	100.0	1.3
Corn oil, Total edible	950	100.0	4.3
Cottonseed oil:			
Baking or frying fats	200	37.1	0.9
Salad or cooking oil	317	58.8	1.4
Total edible	539	100.0	2.4
Lard:			
Margarine[c]	14	5.9	0.1
Total edible	238	100.0	1.1
Palm oil, total edible[d]	W	–	–
Peanut oil, total edible[d]	W	–	–
Canola oil (Edible rapeseed):			
Salad or cooking oil	732	81.0	3.3
Total edible	904	100.0	4.0
Soybean oil			
Baking or frying fats	8,572	48.1	38.3
Margarines	1,242	7.0	5.6
Salad or cooking oil	7,880	44.2	35.2
Other edible	125	0.7	0.6
Total edible	17,818	100.0	79.7
Sunflower oil, total edible	269	100.0	1.2
Tallow, total edible	252	100.0	1.1
Nonidentified edible	1,101	–	4.9
Total fats and oils:			
Baking or frying fats	9,704	–	43.4
Margarines	1,333	–	6.0
Salad or cooking oils	10,924	–	48.8
Other edible	403	–	1.8
Total edible uses	22,365	–	100.0
Selected Industrial Uses			
Fatty acids	2,178	32.8	–
Animal feds	2,670	40.2	–
Soaps	374	5.6	–
Paints and varnishes	111	1.7	–
Resins and plastics	138	2.1	–
Lubricants and similar oils	112	1.7	–
Other inedible products	1,054	15.9	–
Total Industrial Uses	6,637	100.0	–
Total US uses	29,002	–	–

[a]From Oil Crops Situation and Outlook Yearbook, Economic Research Service US Department of Agriculture, October 2003, OCS-2003
[b]US Census Bureau statistics
[c]Includes lard and edible tallows
[d]W = Withheld to avoid disclosing figures for individual companies

Table 34.16 Estimated uses of soybean oil in US industrial applications, 2003.[a]

Market	Soy oil (million lb)
Biodiesel	214.0
Solvents/specialty	1.8
Plastics/coatings	149.8
Paints/coatings	129.5
Other coatings/inks	99.5
Ttl. loss/metalwork lubes	10.7
Polyols (carpets, foams)	29.9
Soaps, fatty acids	80.2
Other uses	200.0
Total	915.4

[a]Courtesy of United Soybean Board, St. Louis, MO

mold release agents, and adjuvants in various applications. FAME are called *methyl soyate* if made from soybean oil. Large investments in manufacturing facilities are being made in expectation of rapid growth of this industry.

Vegetable oil fuels have been prepared by various methods, including micro-emulsification, transesterification, and pyrolysis. Tests during the mid-1970s and early 1980s showed that diesel engines can initially run on vegetable oils or animal fats, or their mixtures with diesel fuel; but, despite various additives to the fuel and engine oil, problems eventually were encountered with fuel injection valve clogging, cylinder head carbon deposits, and engine oil fouling by fuel blow-by.

The fuel properties of some vegetable oils and soybean FAME are presented in Table 34.17. The heat of combustion of various vegetable oils is nearly 90% that of No. 2 diesel fuel, but engine viscosity is 10–20 times greater. Conversion of soybean oil to methyl soyate reduces fuel viscosity to approximately twice that of diesel fuel. Cetane numbers (CN) indicate the comparative ignition delay time of fuels in the combustion chamber: the shorter the ignition delay, the higher the CN [195]. A flow sheet of a process currently installed for making methyl or ethyl fatty acid esters is shown in Fig. 34.36.

Problems encountered in handling vegetable oil-based fuels include: higher viscosity and higher cloud and pour points, which may require supplemental heating of fuel tanks in cooler weather. Various techniques have been tried to reduce cold temperature viscosity of methyl soyate. Winterization lowered the crystallization temperature by 7.1°C [197]. Increasing the molecular diversity by the addition of isopropyl and 2-butyl (branched alcohol) esters lowered the crystallization temperature of soybean methyl esters by 7–11°C and 12–14°C, respectively [198]. But, molecular diversity effect is reported significantly diluted in 20:80 mixtures of methyl soyate and No. 2 diesel fuel [195].

Domestically, methyl esters are made from soybean oil, spent frying oils, and inedible animal fats. Palm oil is used in Southeast Asia, and rapeseed in Europe. Although appreciable in quantity, supplies of such materials actually are small compared with the amount of TAG that would be required if significant quantities of methyl esters were used in fuels. Governmental support of biodiesel development has included funding of research and demonstration projects, and reducing or eliminating state or federal taxes collected for its fuel use. In turn, this funds the amount of methyl esters that can be blended to make biodiesel competitive with nonblended fuels.

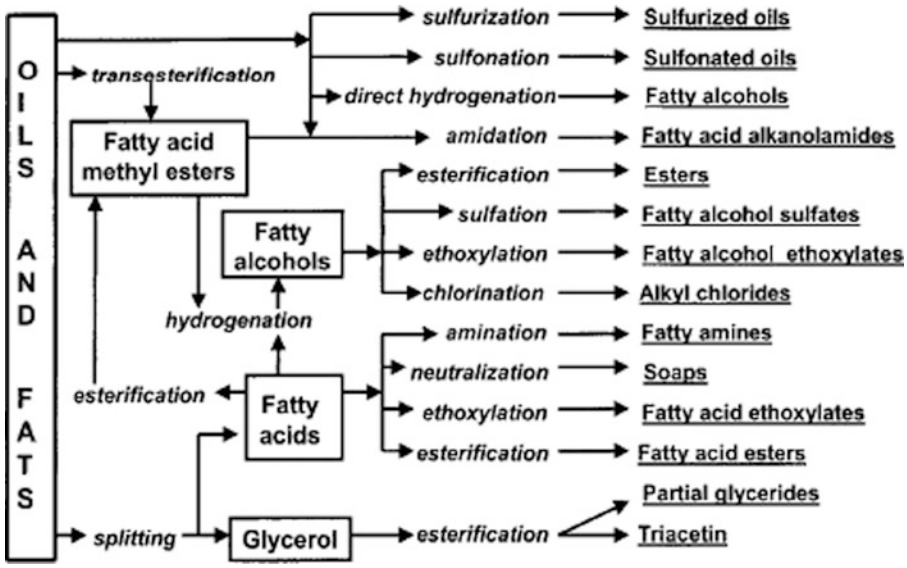


Fig. 34.35 Oleochemical derivatization pathways. (Modified from Zoebelein [192])

Table 34.17 Fuel properties of some vegetable oils and soybean esters[a]

Oil or ester	Viscosity (mm^2/s)	Cetane no.	Gross heat of combustion (kJ/kg)	Cloud point (°C)	Pour point (°C)
Oils[b]					
Castor	297.0	–	37,274	None	−31.7
Corn	34.9	37.6	39,500	−1.1	−40.0
Cottonseed	33.5	41.8	39,468	1.7	−15.0
Crambe	53.6	44.6	40,482	10.0	−12.2
Linseed	27.2	34.6	39,307	1.7	−15.0
Peanut	39.6	41.8	39,782	12.8	−6.7
Rapeseed	37.0	37.6	39,709	−3.9	−31.7
Safflower	31.3	41.3	39,519	18.3	−6.7
High oleic safflower	41.2	49.1	39,516	−12.2	−20.6
Sesame	35.5	40.2	39,349	−3.9	−9.4
Soybean	32.6	37.9	39,623	−3.9	−12.2
Sunflower	33.9	37.1	39,575	7.2	−15.0
Soybean esters[c]					
Methyl soyate	4.1	46.2	39,800	2	−1
Ethyl soyate	4.4	48.2	40,000	1	−4
Butyl soyate	5.2	51.7	40,700	−3	−7
No. 2 diesel fuel	2.7	47.0	45,343	−15.0	−33

[a]From: Foglia et al. [195], With permission
[b]Viscosity determined at 38°C
[c]Viscosity determined at 40°C

The attraction of biodiesel is reduced discharge of undesirable combustion emission compounds into the air. Undoubtedly, effectiveness is related to the degree of petrochemicals replacement. Biodiesel is sold with a numerical designation of the oil/fat-ester content. B20 is a frequent blend, containing 80% petroleum diesel fuel and 20% FAME. A major farm equipment manufacturer has announced it will ship its new equipment with B2 in the fuel tanks. A salt mine has begun using B 100 as a means to improve air quality for its workers.

Progress on biodiesel development can be followed on the National Biodiesel Board (NBB), Jefferson City, MO, Web site (www.biodiesel.org), and the United Soybean Board (USB) St. Louis, MO, Web site (www.unitedsoybean.org) for soybean oil-based fuels; also *Render Magazine*, Camino, CA (www.rendermagazine.com) has kept that industry's members informed on worldwide developments on biodiesel development [199–205].

While a number of bio feedstocks are currently being studied, algae (an autotrophic organism, ranging from unicellular to multicellular forms) have emerged as one of the most promising sources of biodiesel feedstock. Algae have some important advantages over other oil producing crops. It can be grown in almost any enclosed space and it requires

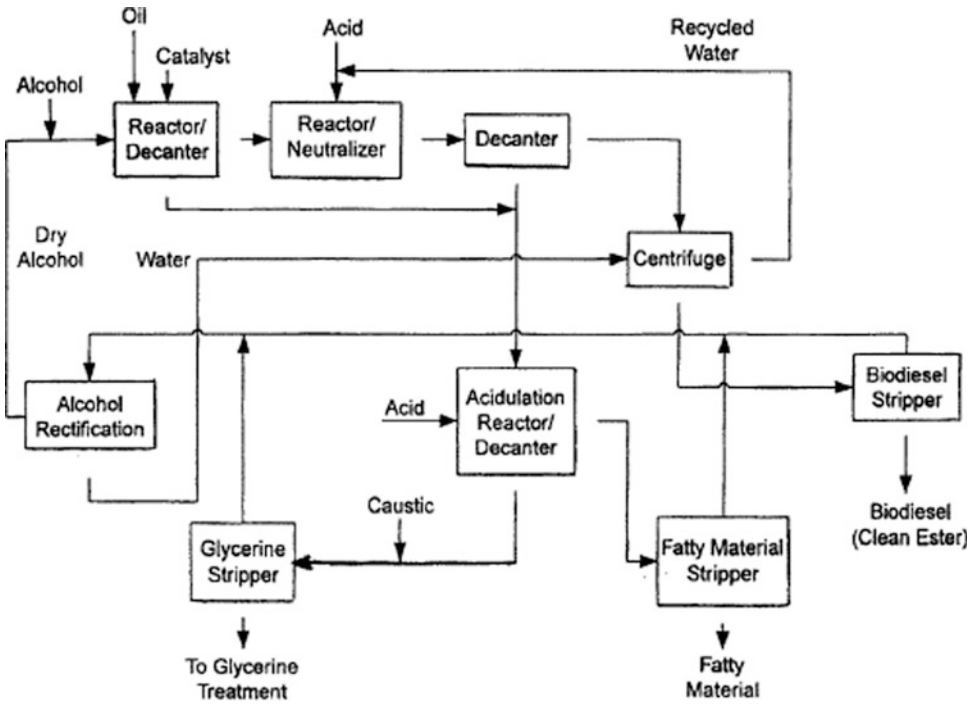


Fig. 34.36 Basic flow diagram of Crown biodiesel ester process. (Courtesy of Crown Iron Works, Minneapolis, MN)

Table 34.18 Global Biodiesel Production, 2008-2010 (metric tons)[a]

Country	2008	2009	2010	% Change (10/09)
EU-27	7,752,825	9,046,000	10,296,033	14
Brazil	1,027,078	1,415,089	2,156,007	52
Argentina	756,802	1,179,204	1,848,006	57
United States	2,302,016	1,815628	1,049399	-42
Thailand	394,241	536,802	580,802	8
Colombia	70,400	290,401	369,601	27
Indonesia	96,800	308,001	352,001	14
Korea, South	158,400	264,001	352,001	33
Malaysia	195,000	222,000	275,000	24
Canada	118,800	164,561	167,201	2
Philippines	63,360	132,000	109,120	-17
Australia	47,520	86,240	52,800	-39
Paraguay	8,800	7,040	10,560	50
Uruguay	2,640	4,400	7,000	59
Turkey	24,992	6,952	6,952	0
Honduras	968	880	880	0
Total	13,020,643	15,479,198	17,633,364	15

[a]*Source*: USDA/Foreign Agriculture Service GAIN reports, National Biodiesel Board, European Biodiesel Board. (Render April 2011)

very little support to grow such as sunlight, water, and carbon dioxide. However, maintaining a pure culture is a major challenge, including during the oil extraction process. Currently, efforts are being focused on these two areas by academicians and by the bio-industry. Algae contain anywhere between 2 and 60% of lipid oil by weight depending on type of strain. Microalgae have been investigated for the production of a number of different biofuels including biodiesel, bio-oil, bio-syngas, and bio-hydrogen.

The global market for biodiesel is changing rapidly, creating both uncertainty and opportunity. The first-generation biodiesel markets in the United States and Europe have reached impressive production levels, but remain constrained by feedstock availability (see Table 34.18). As a result, a surge

in demand for alternative feedstock is driving new growth opportunities in this sector. Biodiesel from non-food feedstock is also gaining attention around the world. For example, jatropha plantations in India and China. In Brazil and Africa, there are significant programs underway dedicated to producing non-food crops such as jatropha and castor for biodiesel. Also, an increasing number of second-generation biodiesel projects are now emerging in anticipation of growing sustainability concerns by governments, and in response to market demands for improved process efficiencies and greater feedstock production yields. A great deal of research is under way on reducing the cost of feed-stocks such as algae, jatropha, castor, used vegetable oils, tallow. Given recent efforts in these areas, it is reasonable to expect significant advances at the industrial scale in the near future.

Other Industrial Applications

Essential oils, used in perfumes and cosmetics, are extracted in several ways by perfusion into fat, distillation, batch solvent extraction, and critical CO_2. The oldest method, used today only for extremely valuable essential oils, is *enf eurage–def eurage*. This consists of layering blossoms of plants to be extracted between lard-coated glass plates and allowing the essential oil to perfuse into the fat. The blossoms are renewed daily. At the end of the season the fat is scraped from the plates, melted, poured into containers, and sold as pomade or is batch-extracted with cold ethanol and sold as extraits. Another technique consists of macerating the material and extracting with hot fat. The most common extraction process for essential oils is steam distillation of a mash of the leaves or seeds to be extracted. Selective solvent batch extraction also is used.

New oilseed crops, currently studied as potential sources of specialty fatty acids, include *Crambe abyssinica* for erucic acid, *Limnanthes alba* for very long-chain fatty acids, *Dimorphotheca pluvialis* for dimor-phecolic acid, *Lesquerella fendleri* for lesquerolic acid, *Calendula officinalis* for calendic acid, and *Euphorbia lagascae* and various *Vernonia* species for vernolic acid.194 The lowest cost sources (inedible fats and oils and palm oil fractions) are most likely to be exhausted first as world trade in industrial applications grows. Cornstarch is becoming a major feedstock for plastics production. This may compete with potential oil uses, but also will increase production of corn oil.

Other current areas of soybean oil industrial applications research include plastics, coatings, lubricants, and hydraulic fluids. Potential applications are only limited by imagination, economics, and the business skills of the respective entrepreneur. The United Soybean Board maintains a Web site (www.unitedsoybean.org) of current soybean oil-based industrial products manufacturers, listed under the categories of adjuvants, alternative fuels and fuel additives, building and construction, cleaners, concrete, dust suppressants, engine oils, hydraulic fluids, ingredients, metal working fluids, printing, and miscellaneous. The categories list suppliers and as many as several hundred products each. In many cases, suppliers list their Web sites for interested persons to learn more about uses and specifications of their products.

Analytical Methods

Selected analytical methods, adopted by the American Oil Chemists' Society (AOCS) [22] for characterizing the composition, structure, physical properties, and stability of fats and oils, are summarized below. Prescribed equipment must be used and conditions followed. Some of these techniques are limited to specific oil species, but adaptations are available for other species. Procedures for sample drawing and preparation also are specified.

AOM for fat stability (Cd 12–57): determines the time (in hours) for a sample of fat or oil to attain a predetermined peroxide value (PV) under the conditions of the test. The method is used to estimate the comparative oxidative stability of fats and oils. The method has been placed in surplus, in favor of Cd 12b-92 (Oil Stability Index), but retains official status and is still used in domestic industry. *p*-anisidine value (AV) (*Cd 18–90*): determines the amount of aldehydes (principally 2-alkenals and 2,4-dienals) in animal and vegetable fats and oils. These are degradation products of peroxides, which are not removed by bleaching. Some fats and oils chemists propose increased use of this method in purchase specifications.

Bleaching Test for Soybean Oil (Cc 8e-s63): determines the color of a sample of soybean oil after treatment with a specified bleaching earth. Specific methods exist for other oil species.

Boemer Number, Foreign Fats in Lard (Cb 5–40): estimates the presence of tallows and similar fats, based on differences in melting points of foreign glycerides and fatty acids as compared with pure pork fat. *Cloud Point Test (Cc 6–25)*: determines the temperature at which a cloud first forms in cooling a sample of melted fat to the first stage of crystallization

Cold Test (Cc 11–53): measures the relative resistance of a sample to crystallize at an established temperature in terms of time. The 5.5-h test at 0°C is used as an index of stearin removal in the winterization of salad oils.

Color Measurement by Lovibond–Wesson (Cc 13b-45): determines the color of clear oil samples by comparison with glasses of known color characteristics.

Fatty Acid Composition by Gas Chromatography (Ce 1–62): *quantitatively* determines saturated and unsaturated fatty acids with 8–24 carbon atoms in animal fats, vegetable oils, marine oils, and fatty acids after conversion to their methyl ester forms.

Fatty Acid Composition by GLC (Ce Ic-89): measures the fatty acid composition and levels of *trans* unsaturation and *cis, cis* methylene-interrupted unsaturation of vegetable oils using capillary gas liquid chromatography.

Flash Point–Pensky–Martens Closed Cup for Fats and Oils (Cc 9b-55): determines the temperature at which an oil sample will flash when a test flame is applied. This technique sometimes is used to estimate levels of residual hexane and to ensure the safety of workers handling the oil. Some refineries use gas chromatography methods instead.

Free Fatty Acids in Crude and Refined Fats and Oils (*FFA*) *(Ca 5a-40)*: determines FFA, as oleic acid, by ethanolic sodium hydroxide titration.

Halphen Test for Detecting Cottonseed Oil (Cb 1–25): estimates the presence of cottonseed oil in vegetable or animal fats or oils as the result of a pink color formed between the reagent and cyclopropenoic fatty acids (sterculic and malvalic) normally present in cottonseed oil.

Hexane Residues in Fats and Oils (Ca 3b-87): determines, by gas chromatography, the "free" volatile hydrocarbons remaining in fats and oils after extraction with hydrocarbon solvents. The results are expressed in terms of hexane.

Insoluble Impurities in Fats and Oils (Ca 3a-46): determines dirt, meal, and foreign substances that are insoluble in kerosene and petroleum ether.

Iodine Value of Fats and Oils—Cyclohexane Method (IV) (Cd lb-87): measures the unsaturation of fats and oils in terms of centigrams of iodine absorbed per gram of sample. The method is applicable to all normal fats that do not contain conjugated double bonds. It often is used to estimate the degree of hydrogenation of oils.

Melting Point–Capillary Tube Method (Cc 1–25): determines the temperature at which a sample of fat in a closed capillary becomes completely clear and liquid; broadly applicable; popular for tropical fats.

Melting Point–Mettler Dropping Point (Cc 18–80): determines the temperature at which a sample becomes sufficiently fluid to flow in a specified apparatus; the major melting point determination method used by domestic industry.

Melting Point–Open Tube-Softening Point (Cc 3–25): determines the temperature at which a solidified fat, in an open capillary tube, softens sufficiently to slip and rise to the top of the heating bath. This method is applicable to fats such as coconut oil, stearin, hydrogenated fats, and hard tallows. The results sometimes are reported as the "melting slip point," but the method is different from the AOCS Slip Point (Cc 4–25).

Melting Point–Wiley Method (Cc-38): determines the temperature at which a sample disk of solidified fat assumes a spherical shape while suspended in a heating bath with an alcohol–water density gradient. A seldom-used method, primarily replaced by the Mettler Dropping Point.

Moisture-Distillation Method (Ca 2a-45): determines only moisture in triacylglycerols and emulsions by distillation with an immiscible solvent (toluene).

Moisture and Volatile Matter —Air Oven Method (M&V) (Ca 2c-25): determines the moisture and volatile matter by heating in a hot air oven. This method is applicable to animal and vegetable fats, but not to drying oils, coconut group fats, or oils with added monoacylglycerols.

Oil (Aa 4–38): determines oil content in a dried sample of oil-bearing material by extraction with petroleum ether. This method is specific for cottonseed, which first must be fumed with hydrochloric acid to prevent oil adsorption to the fiber. Additional methods exist for other oilseeds.

Oxygen Stability Index (OSI) (Cd 12b-92): measures the oxidation induction period of fat sample (essentially the time for a sample to exhaust its antioxidant properties) under conditions of the test.

Peroxide Value, Fats and Oils (PV) (Cd 8–53): determines all substances, in terms of milliequivalents of peroxide per 1000 g of sample that oxidize potassium iodide (KI). These substances generally are assumed to be peroxides or products of fat oxidation.

Phosphorus in Oils (Ca 13–55): estimates the phospholipid content of crude, degummed, and refined vegetable oils in terms of phosphorus. Refineries often use ICP spectrographs to analyze divalent cations rapidly in aspirated crude oil. The calcium and magnesium measured are mainly responsible for NHP and are determined directly. An AOCS method for analysis by ICP is being developed.

Refining Loss, Vegetable Oils, Crude (Ca 9a-52): determines the loss of free fatty acids and impurities when crude oils are refined under specified procedures.

Residual Lint (Aa 7–55): determines the lint content of cottonseed by fuming (digesting) with hydrochloric acid.

Saponification Value of Fats and Oils (Cd 3–25): determines the number of milligrams of (alcoholic) potassium hydroxide necessary to saponify a 1-g sample of a fat or oil.

Schaal Test (Schaal Oven Method): an accelerated test for determining the oxidative stability of a fat or a fat-containing food product. Results are reported as the time elapsed until a rancid odor is detected. This is not an AOCS method; see American Association of Cereal Chemists' Method Manual. Modifications, using OSI apparatus, have been reported.

Smoke, Flash, and Fire Point—Cleveland Open Cup Method (Cc 9a-48): determines the temperatures at which fats and oils smoke, flash, or burn. Smoke point determinations sometimes are used to follow degradation of frying oils with use.

Solid Fat Content of Fats and Oils by NMR (SFC) (Cd 16–81): estimates the percentage of solids in a semi-solid fat on the basis of the pulsed NMR signal of hydrogen in the liquid fraction. The method is used in the palm oil industry and widely throughout the world.

Solid Fat Index—Dilatometric Method (SFI) (Cd 10–57): estimates the percentage of solids in a semi-solid fat on the basis of changes in volume with temperature. This method utilizes glass dilatometers and is the primary method in the United States. *Totox Value:* an estimate of the degree of oxidation of a fat or oil, calculated as:

$$\text{Totox} = 2 \times (\text{PV}) + \text{AV}.$$

Triglycerides by GLC (Ce 5b-86): quantitatively determines triglycerides (triacylglycerols) in liquid vegetable oils in terms of molecular weight and degree of unsaturation as a function of their equivalent carbon number using high-pressure liquid chromatography.

Unsaponifiable Matter in Fats and Oils, Including Marine Oils (Ca bb-5, 3): determines substances dissolved in fats and oils that cannot be saponified (turned into sodium salts) by the usual caustic treatment, including higher aliphatic alcohols, sterols, pigments, and hydrocarbons. This method is not suitable for marine oils or feed grade fats.

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