

Chapter 2

Oils, Fats, and Waxes

At present about 11.7×10^6 t of edible vegetable oils and about 4.2×10^6 t of edible animal fats and oils are produced in the United States each year.¹ About 7×10^6 t are exported and the remainder is consumed in the United States.

Figure 2.1 depicts the relative consumption by the food, soap, and paint industries of various oils and fats. It also shows the direct competition of the chemical, soap, and paint industries with basic food production. Three types of agricultural products make up the bulk of the farm products that enter into the chemical process industries. Animal fats, both edible and inedible materials, are the largest in quantity and value. Starch (Chap. 30) runs a close second, and vegetable oils are next.^{1a} Fats and oils are found widely distributed in nature, in both the plant and animal kingdoms. Waxes likewise are natural products but differ slightly from fats and oils in basic composition. Whereas fats and oils are mixtures of the glycerides of various fatty acids, waxes are mixed esters of higher polyhydric alcohols, other than glycerol, and fatty acids.

Table 2.1 indicates the characteristic composition of various important oils in regard to their fatty acid content. These acids have an even number of carbons and fall within (1) the saturated series, as exemplified by stearic acid, which is the basis for nondrying oils, (2) the monoolefinic acids, with one double bond between carbons as illustrated by oleic acid, and (3) the polyolefinic series, with more than one such double bond, as exemplified by linoleic and linolenic acids. The latter two classes of acids, being unsaturated, furnish semidrying and drying oils, according to the amounts of unsaturation present. The chief constituents of vegetable oils are 16- and 18-carbon acids, and 20-, 22-, and 24-carbon acids predominate in fish oils. Coconut oil is unique in that it consists of esters of much shorter carbon-chain acids, 12- and 14-carbon acids being present in the greatest amount.

There is a growing, recent demand for polyunsaturated oils in food products; the largest in supply, soybean oil, has 61% polyunsaturated constituents; safflower oil contains 68%; corn oil, 42%; cottonseed oil, 50%; peanut oil, 21%; and olive oil, 7%. The degree of saturation of the acids involved affects the melting point of the ester mixture; the more unsaturated acids give esters with lower melting points, and these are the chief constituents of oils. The more saturated esters, on the other hand, are constituents of fats. Thus we see that the factor determining if one of these compounds is termed a fat or an oil is merely its melting point. These oils are called fixed oils, in distinction from the essential, or volatile, oils described in Chap.

1. Fixed oils cannot be distilled without some decomposition under ordinary atmospheric pressure. Differentiation should also be noted from petroleum oils, discussed in Chap. 37.

¹t = 1000 kg.

^{1a}Statistical Abstract of the United States, 1981; J. Am. Oil Chem. Soc. 59 (1) 7A (1982).

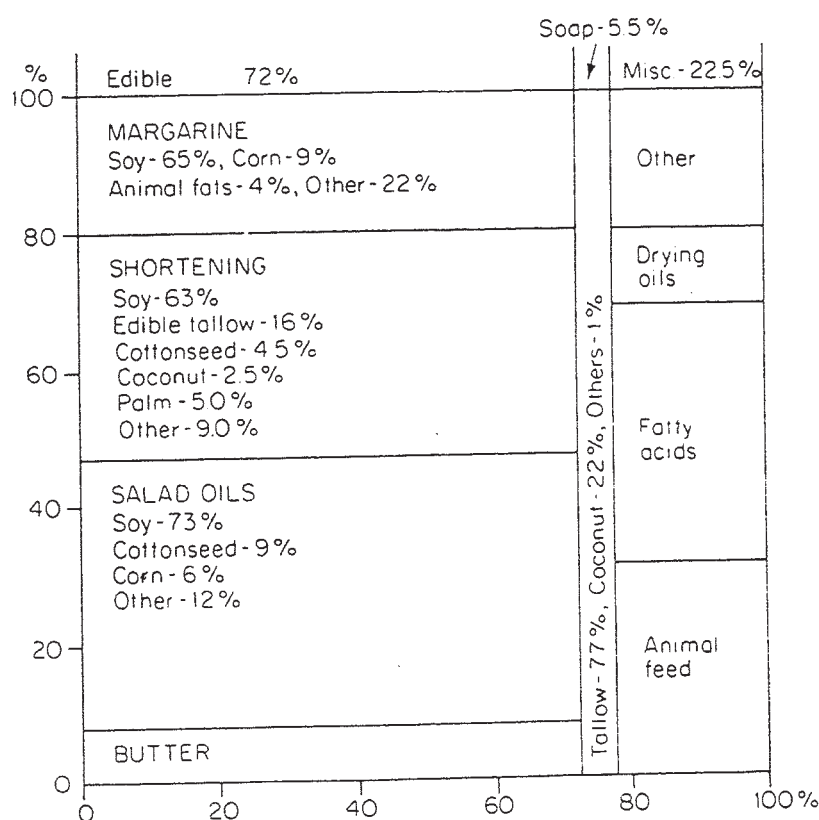


Fig. 2.1. Consumption of fats and oils by various industries, 1980.

HISTORICAL. Since ancient times humans have known how to remove oils and fats from their natural sources and make them fit for their own uses. Animal fats were first consumed as food, but it was not long before they were burned for light and heat. Obtaining oils from vegetable sources is of ancient origin, for the natives in the tropical regions of the globe have long been removing these oils from various nuts after drying them in the sun. The utilization of marine oils began with the whaling industry, which was started by the Basques in the Bay of Biscay in the fifteenth century.

The first chemical reaction applied to fats and oils (excluding oxidation in burning) was that of saponification, to give soap. The early raw materials were mainly of animal origin, the rendering of animal flesh being an old art. The industrialization of oils and fats began with the erection of a cottonseed mill in South Carolina, about 1826. This crude industry did not expand very rapidly until after 1865. In 1850, the use of caustic soda to remove free acids from oil was introduced from France. About this time, the millers became aware of the value of the linters that clung to the hulls, and also of the hulls themselves, for cattle feed. The beginning of the oleomargarine (margarine) industry in Chicago in 1885 gave impetus to the cottonseed-oil industry. The higher quality demanded by this new market produced several processing improvements. Fuller's earth was used to decolorize the oil. In 1893, it was learned that the oil could be deodorized by blowing steam through it at high temperatures. Later it was found that deodorization under reduced pressure improved both flavor and odor. In 1900 the discovery that oils could be upgraded by *hydrogenation* to produce fats revolutionized the entire oil and fat industry and led to hydrogenated shortenings. This discovery also made many of the lesser-known oils marketable. This phase of the industry has advanced until now much shortening is made by hydrogenating unsaturated oils and fats to a higher degree of saturation than originally found, but rarely to total saturation.

Table 2.1 Fatty Acid Content of Various Oils and Fats (in percentage)

no. of C Atoms	Acid	Formula	Butter	Cotton	Soybean	Corn	Menhaden	Whale	Linseed	Coconut	Beef Tallow	Lard
4	Butyric	C_3H_7COOH	4.0	—	—	—	—	—	—	—	—	—
5	Caproic	$C_5H_{11}COOH$	2.0	—	—	—	—	—	—	—	—	—
8	Caprylic	$C_7H_{15}COOH$	1.0	—	—	—	—	—	—	—	—	—
10	Capric	$C_9H_{19}COOH$	2.5	—	—	—	—	—	—	8.0	—	—
12	Lauric	$C_{11}H_{23}COOH$	3.0	—	—	—	—	—	—	7.0	—	—
14	Myristic	$C_{13}H_{27}COOH$	10.0	0.6	—	—	—	—	—	48.0	—	—
14	Myristoleic	$C_{13}H_{25}COOH$	—	—	—	—	7.0	8.0	—	17.5	3.0	1.0
16	Palmitic	$C_{15}H_{31}COOH$	25.0	22.9	8.3	7.5	16.0	12.1	—	—	—	0.2
16	Palmitoleic	$C_{15}H_{29}COOH$	—	—	—	—	17.0	15.0	6.5	8.8	28.0	28.0
18	Stearic	$C_{17}H_{35}COOH$	11.0	2.2	5.4	3.5	1.0	2.3	—	—	—	3.0
18	Oleic	$C_{17}H_{33}COOH$	28.5	24.7	24.9	46.3	27.0	33.4	4.5	2.0	25.0	13.0
18	Linoleic	$C_{17}H_{31}COOH$	2.5	49.7	52.7	42.0	—	—	20.9	6.0	42.0	46.0
18	Linolenic	$C_{17}H_{29}COOH$	—	—	7.9	—	—	9.0	17.4	2.5	2.0	6.0
20	Arachidic	$C_{19}H_{39}COOH$	—	—	0.9	0.5	—	—	50.6	—	—	0.7
20	Arachidonic	$C_{19}H_{37}COOH$	—	—	—	—	20.0	—	—	—	—	2.0
22	Clupanodonic	$C_{21}H_{43}COOH$	—	—	—	—	12.0	8.2	0.1	—	—	—
24	Lignoceric	$C_{23}H_{47}COOH$	—	—	—	0.2	—	10.5	—	—	—	—

USES AND ECONOMICS. Fats and oils have always had an essential role as food for human-kind. In addition, however, our modern industrial world has found many important applications for them. The largest consumption of fats for chemical raw materials is in making fatty acids (Chap. 3), which have an estimated tonnage of 813,000 t/year. Oils are saponified, hydrogenated, epoxidized, and sulfonated to a great number of usable products, and fats are isomerized and interesterified, all to produce upgraded and more useful oils and fats. Table 2.2 gives some industrial uses of fats and oils.

There are two broad classifications for fats and oils: edible and inedible. The consumption of fats and oils in edible products represents about 72 percent of all uses of these materials and averages about 24 kg per capita. Various edible oils, cottonseed, olive, soybean, corn, etc., are employed for salad dressings, for other table uses, and for cooking purposes. Hydrogenated fats for cooking and baking, such as Crisco, may include a wide variety of vegetable oils, such as cottonseed, palm, and soybean, since the hydrogenating process *improves* the color, flavor, and odor of the original crude product as well as its keeping factor. Various fish-liver oils are used in the medicinal field for their vitamin content and in the paint industry as drying oils. Castor oil is a well-known cathartic.

In 1980, 28 percent of all oils and fats consumed in the United States was for inedible products, as shown in Fig. 2.1. About 18 percent was used in the soap industry, including tallow, coconut oil, palm oil, and certain greases. Some were slightly hydrogenated to make them suitable for soapmaking. The drying-oil industries (including paints and varnishes) consume 9 percent of all inedible oils, and other consumption of linseed oil, tung, soybean, and castor is in smaller demand. These drying oils are essentially unsaturated and produce films or coatings upon oxidation. They are also employed with synthetic resins and cellulose derivatives to give special types of films. Castor, linseed, soybean, rapeseed, and cottonseed oils are being used to some extent as plasticizers for lacquers and polymers. Other miscellaneous uses include applications in the following industries: oilcloth and linoleum, chemical (for the manufacture of fat and oil derivatives), lubricant and grease manufacturing, printing, and tin plate. A wide variety of oils are included as integral parts of various polishes, creams, and emulsions. Large quantities of sulfonated glycerides and sulfated fatty alcohols and derivatives serve as wetting agents and detergents. Table 2.3 details the statistics of the principal fats and oils, together with some of their important derivatives. It should be compared with Fig. 2.1. *Waxes*, such as carnauba, beeswax, and candelilla, enter into the manufacture of various polishes for floors, shoes, automobiles, and furniture. Other outlets include the making of carbon paper, candles, electrical insulation, waterproof textiles, and phonograph records.

Table 2.2 Industrial Uses of Fats and Waxes

Fat or Oil	Use
Animal fats	Soaps, greases, paints, varnishes, syndets, fatty acids, and plasticizers
Coconut oil	Fatty alcohols, soaps, and detergents
Linseed oil	Paints, varnishes, floor coverings, lubricants, and greases
Soybean oil	Paints, varnishes, floor coverings, lubricants, and greases
Castor oil	Protective coatings, plastics, plasticizers, lubricants, hydraulic fluids
Tung oil	Paints and varnishes
Tall oil	Soaps, leather, paint, emulsifiers, adhesives, ink

Table 2.3 U.S. Production of Fats, Oils, and Derivatives, 1980
(in thousands of metric tons)

Vegetable		Fish	100
Soybean	8115	Derivatives	
Cottonseed	655	Salad oil	2200
Peanut	99	Shortening	1900
Sunflower	607	Margarine	1140
Safflower	36	Soap	423
Corn	373	Animal feed	656
Linseed	69	Paint and varnish	250
Animal		Fatty acids	813
Tallow and grease	3351		
Lard	454		
Butter	445		

SOURCE: *Statistical Abstract of the United States, 1981*, U.S. Dept. of Commerce; *J. Am. Oil Chem. Soc.* 59 (1) 8A (1982).

VEGETABLE OILS

Extraction of Oils

For purposes of discussion of the various technical aspects, the three classical divisions of the general subject of oils, fats, and waxes will be retained: vegetable oils, animal oils and fats, and waxes. Under each of these headings the general methods of manufacture will be discussed for the most important of the illustrative individual members. Table 2.4 indicates the yields of vegetable oils from some of the usual sources. The two general methods employed in obtaining vegetable fats and oils are expression and solvent extraction or a combination of the two. However, solvent extraction is increasing in use.² Solvent extraction has assumed importance in virtually all vegetable-oil recovery plants, alone or in combination with prepressing. For high-oil-content seeds, such as cottonseed and safflower seed, usually both expression and extraction are utilized in the recovery systems for higher yields.³ Obtaining crude vegetable and animal oils involves primarily physical changes or unit operations, but chemical conversions are concerned in the refining and further processing of such oils.

COTTONSEED OIL. Figure 2.2 presents a flowchart for cottonseed and similar oils. The flowchart can be broken down into the following sequences of *unit operations* (hydrogenation will be considered under its own special heading):

²For cottonseed oil, expression by the *expeller*, followed by solvent extraction, has become the most practiced. The solvent extraction upgrades the oil and increases the yield, especially from damaged seed.

³Haines et al., Filtration-Extraction of Cottonseed Oil, *Ind. Eng. Chem.* 49 920 (1957) (flowsheet); Decossas et al., Cost Analysis (of preceding), *Ind. Eng. Chem.* 49 930 (1957); Brennan, Making the Most Out of Cottonseed Processing, *Chem. Eng.* 70 (1) 66 (1963); Tray and Bilbe, Solvent Extraction of Vegetable Oils, *Chem. Eng.* 54 (5) 139 (1947) (pictured flowchart); Witz and Hendrick, New Plant Puts Science into Cottonseed Processing, *Chem. Eng.* 71 (18) 48 (1964) (flowchart).

Table 2.4 Approximate Oil Yields of Certain Vegetable-Oil Materials

Raw Material	%	Raw Material	%
Babassu kernels	63	Palm kernels	45
Castor beans	45	Peanuts in the shell	30-35
Corn kernels	4	Peanuts shelled	45-50
Copra	63	Perilla seed	37
Cottonseed	15	Rapeseed	35
Flaxseed	34	Sesame seed	47
Hempseed	24	Soybeans	18
Kapok seed	18	Tung nuts	50-55

SOURCE: Mostly taken from U.S. Tariff Commission, *Fats, Oils, and Oil-Bearing Materials in the U.S.*, December 15, 1941. (Modified in 1977.)

Cottonseeds are cleaned by screening and aspiration. The lint is removed by passing the seeds through a series of linters (machines similar to cotton gins which operate on the saw-and-rib principle).⁴ Each series of linters removes lint of different length, which is designated first-cut and second-cut lint. The lint cuts are aspirated and air-conveyed to separate lint beaters or cleaners which remove dirt and hull fragments from the lint before it is baled and sold.

The delinted seeds (blackseed) are cut or split in a bar-type huller, freeing the meats from the hulls, which are separated from the meats by screening and aspiration. The hulls thus removed are cleaned of attached meat particles in a beater and sent to storage for eventual consumption as roughage in animal feeds.

The meats are rolled into thin flakes (about 0.25 to 0.35 mm thick) to make them easily permeable to steam in the cooking operation; they are next cooked or conditioned in horizontal cookers at 110°C for 20 min before expression to rupture the oil glands, to precipitate the phosphatides, to detoxify the gossypol, and to coagulate proteins.⁵ In direct solvent extraction, meats are conditioned before flaking.

The horizontal cookers are generally integrated with the expellers (Fig. 2.3); in prepress plants they are supplemented with a stacked cooker for additional heating capacity. The moisture is frequently raised to 12 to 14% and then gradually reduced to 5 to 7% in these units.

Most of the oil from the conditioned cottonseed is prepressed in mechanical screw presses with single or double worm shafts revolving inside a heavy perforated barrel and capable of exerting a pressure of up to 11.7 to 13.8 MPa (Fig. 2.3). (These have largely displaced the hydraulic presses previously used in cottonseed plants.) The oil removed by these presses is screened, cooled, filtered, and stored for refining. About 74 percent of all cottonseed is so

⁴Bailey, *Cottonseed and Cottonseed Products*, Interscience, New York, 1948.

⁵Dunning, Unit Operations in a Mechanical Extraction Mill, *J. Am. Oil Chem. Soc.* 33 (10) 465 (1956).

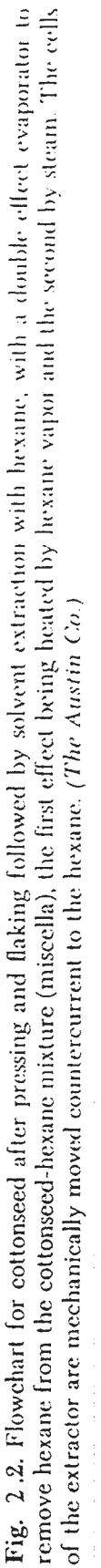


Fig. 2.2. Flowchart for cottonseed after pressing and flaking followed by solvent extraction with hexane, with a double effect evaporator to remove hexane from the cottonseed-hexane mixture (miscella), the first effect being heated by hexane vapor and the second by steam. The cells of the extractor are mechanically moved countercurrent to the hexane. (*The Austin Co.*)

processed; an additional 18 percent is processed by prepressing with solvent extraction and 8 percent by direct solvent extraction.

Solvent extraction recovers up to 98 percent of the cottonseed oil (Fig. 2.2), compared with 90 to 93 percent from screw-press expression alone. The soybean, which has a low oil content, but whose physical structure is particularly suited to solvent extraction (Fig. 2.4), has been responsible for this development. Solvent extraction has assumed importance in virtually all vegetable-oil recovery processes, alone or in combination with prepressing. In Fig.

2.2 the solvent hexane is sprayed onto flakes in buckets moving horizontally in the extractor⁶ countercurrent to the hexane. The hexane dissolving the oil is known as miscella and is pumped to the evaporators, the first of which is heated by hot hexane vapor and steam from the toaster and the second by steam.

Virtually the entire cotton seed-oil production is used by edible-oil processors for shortening, margarine, and salad or cooking oils. The cake is broken or ground and used for cattle feed. The hulls provide roughage for livestock feeding. The linters which contain 70 to 85% α -cellulose are utilized as a cellulose source of high purity for rayon, plastics, lacquer, and explosives.

SOYBEAN OIL. Soybean-seed preparation differs slightly from cottonseed preparation. The weighed and cleaned seeds are first cracked between corrugated rolls, then conditioned without significant change in moisture in a stacked cooker or a rotary steam-tube conditioner, and finally rolled to thin flakes (about 0.25 mm thick). Solvent extraction can recover up to 98 percent of the oil, compared with about 80 to 90 percent from hydraulic or screw-press expression. Because of the efficiency of oil yields (hydraulic press, 14.5 kg/100 kg; screw presses, 15.3 kg/100 kg; solvent extraction, 18.2 kg/100 kg) virtually all new soybean installations today are solvent extractors. When solvent extracted, soybean flakes produce meal with a protein content of 44 to 46%, which can be increased by removing the soybean *hulls* before (front-end dehulling) or after (tail-end dehulling) solvent extraction. Front-end dehulling is accomplished by screening the cracked seed and removing the hull fraction by aspiration. Small meat particles are then separated from the hull stream on specific gravity separators. In the tail-end dehulling system the entire dried-meal stream is passed over specific gravity

⁶The V. D. Anderson Co., Cleveland, horizontal hydraulic basket extractor.

TABLE TO ACCOMPANY FIG. 28.2

LABOR AND UTILITIES				
RAW MATERIALS	SEED HANDLING	SOLVENT EXTRACTION	PRODUCTS	WEIGHT, KG
Cottonseed, kg	1000	1000	Oil	173
Labor, work-h	7.7	1.5	Cake	482
Electricity, MJ	61	56	Hulls	185
Solvent (hexane) loss, L		2	Linters	104
Water, L	125*	250	Loss and trash	56
Steam, kg	288	495	Total	1000

*Recirculating cooling water.

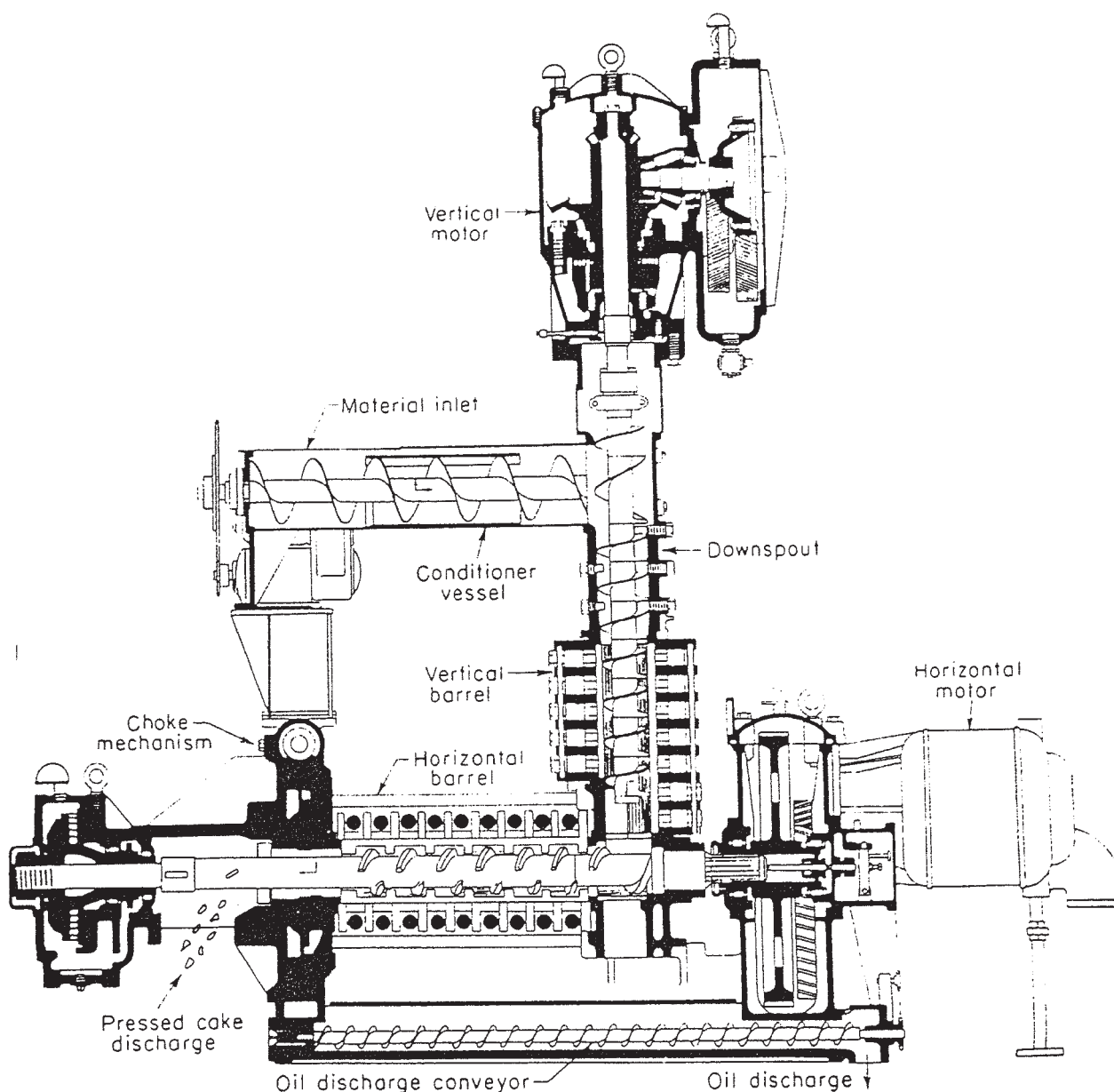
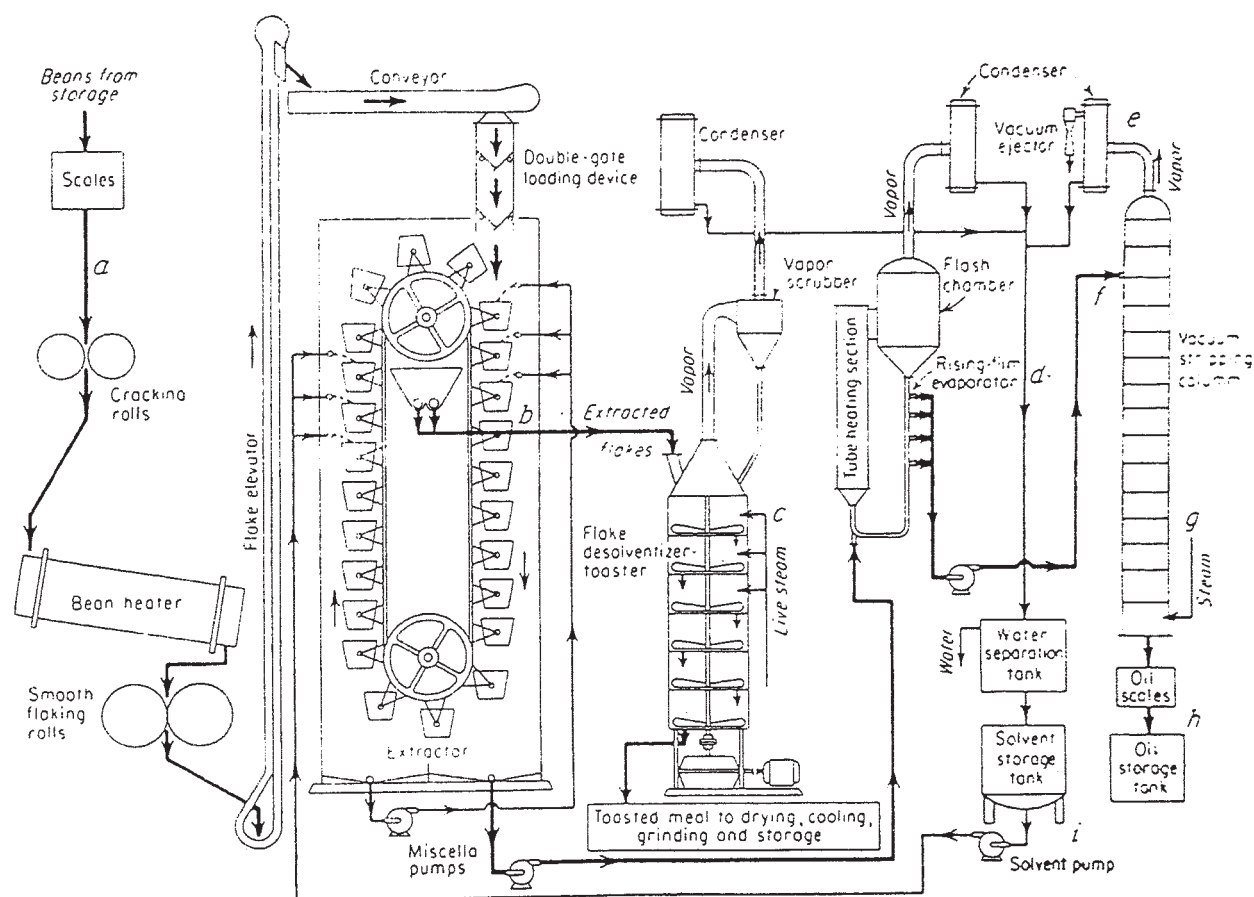


Fig. 2.3. Cutaway section of a twin-motor Superduo expeller. On cottonseed, the capacity is from 45 to 90 t per 24-h day, and for soybean about 24 t per 24-h day. To drive the propeller, 52 kW is required, and up to 4 boiler kW of steam is needed for the conditioner. (V. D. Anderson & Co.)

separators, producing two grades of meal, one containing 41% protein and the other containing 50% protein.

Solvent extraction⁷ is carried out in a continuous countercurrent manner through a series of extraction stages. The extractors most commonly used in this country circulate solvent over the flakes, which are carried, usually in baskets, through the several extraction stages, the baskets moving in a circular, vertical, or horizontal direction. The vertical circular procedure, using hexane as solvent, is illustrated in Fig. 2.4. Although milling releases some of the oil, which is immediately dissolved in the solvent, the greater portion is removed by diffusion of the solvent through the cell walls until equilibrium is reached. By replacing the equilibrium solution with a solvent of lower oil content, the diffusion process is again resumed. The economical limit of this procedure is about 0.5% oil remaining in the seed mass. The rate of diffusion is directly proportional to the surface area of the seed particle and in an (inverse)

⁷Solvent Extraction of Oilseed, Chem. Eng. 58 (1) 127 (1951); Perry, 5th ed., p. 19-42.



UTILITIES, PER HOUR		QUANTITIES, KG/H	
Steam	18,600 kg	In circulation at points marked	
Power	4300 MJ	a.	37,650 beans, 12% moisture
Water (cooling)	378 m ³	b.	29,940 extracted flakes, 18,144 hexane
Labor	3 work-h	c.	4536 steam
Solvent loss	90 kg	d.	6800 oil, 19,500 hexane
		e.	680 hexane at 13.5 kPa abs
		f.	6800 oil, 680 hexane
		g.	272 steam
		h.	6800 oil
		i.	37,650 hexane

Fig. 2.4. Continuous flowchart for solvent extraction of soybeans.

power function of thickness with free circulation of the solvent. After extraction, the meal is toasted to increase its nutritive value. Solvent is usually removed from the miscella phase by passing it through a rising-film evaporator followed by a steam-stripping column. Double-effect, or dual, evaporators are frequently used, with one evaporator operated under vacuum and heated by vapor from the other stage or by vapor from the desolventizing toaster.⁵ Solvent losses are usually minimized by venting the process noncondensables through a refrigerated vent condenser or an oil-absorption unit. The process crude oil produced is then stored for refining or sale. Dried and toasted meal from the solvent-extraction operation is ground to 10- to 12-mesh fines in a rotary pulverizer, screened, and stored for sale as feed.

⁵Milligan and Tandy, Distillation and Solvent Recovery, *J. Am. Oil Chem. Soc.* 51 347 (1974); R&D in Oilseed Routes, *Chem. Eng.* 89 (26) 21 (1982).

OTHER VEGETABLE OILS

Linseed oil. The flaxseed produced in this country is grown largely in the midwest, south Texas, and the far west. Production and refining are carried out by a process similar to that used for cottonseed oil, depicted in Fig. 2.2, and Anderson expellers are first employed. The average oil content of the flaxseed is about 40%, which indicates a yield by expression of about 34 percent based on the weight of the seeds, leaving about 6% oil in the press cake. Newer and improved installations combine screw pressing with solvent extraction, reducing the residual oil in the cake to about 0.75%, as illustrated by Fig. 2.2.

Coconut oil. The raw material for the production of coconut oil⁹ is all imported from various tropical countries, a large part coming from the Philippines. The raw material is brought in as copra, which is coconut kernel that has been shelled, cut up, and heat-dried at the point where grown. This treatment not only avoids the cost of shipping excess moisture, but also prevents deterioration of the oil. Coconuts, as they come from the tree, contain from 30 to 40% oil, and the copra contains from 65 to 70% oil. The copra is expressed in expellers or screw presses. A metric ton of copra yields about 800 kg of oil and 365 kg of cake. The oil is refined and contains from 1 to 12% free fatty acid, depending on the quality of the copra meats. Only oil of low free fatty acid content is employed for edible products, the rest (about 60 percent of the total receipts) being used for the production of soap and alcohols.

Corn oil. The production of corn oil differs from that of some of the other oils in certain respects. After cleaning, the corn is placed in large tanks and steeped in warm water containing SO_2 , thus loosening the hulls from the kernels. The steeped corn is run through *attrition* mills, which break the germ away from the rest of the kernel. The separation of the germ and the kernel is accomplished by running the mixture into a tank of water, where the germ floats, because of its oil content, and is skimmed off. Before going into the ordinary grinding and expelling apparatus, the germ should be washed and thoroughly dried. The crude oil from the expellers (Fig. 2.3) is given the usual purification treatment, such as that described for cottonseed oil. The oil content of the corn kernel, exclusive of the hull, is about 4.5%. This oil is used almost exclusively as a salad oil, with lower grades going into soap manufacture.

Palm oil. Palm oil is prepared from the fruit of the palm tree, which has been cultivated on plantations in Indonesia, the Malay Peninsula, and elsewhere. Palms grow naturally on the west coast of Africa. The fruit is 2.5 to 5.0 mm long and oval-shaped and weighs about 6 to 8 g on the average. The oil content ranges from 40 to 50% of the kernel, or seed. The oil is obtained in two separate procedures. In the first, it is removed from the fruit, and in the second from the kernels, or seeds. The former is done at the place where the fruit is grown. The procedure consists in cooking the fruit in large steam-pressure digesters equipped with agitators. From the steaming the charge goes to basket centrifuges, where a 10-min treatment, accompanied by blowing with live steam, separates the oil. The residual fiber and kernels are dried in a continuous rotary dryer and separated by a screening operation. The nuts, or kernels, are bagged and shipped to the United States, where they are processed by the methods previously described for oil removal. The fibers are burned under the boilers of the first processing plant. In the United States most of this oil goes into soap manufacture.

Peanut oil. Peanut oil is produced by either the hydraulic press or the Anderson expeller, from deskinning peanuts grown in the various southern states. The cold, first expression (about 18 percent) is edible, and some is hydrogenated. The oil is hydrogenated and refined for use in the manufacture of margarine, salad and cooking oils, and some vegetable shortenings.

⁹Copra Refining. *Chem. Met. Eng.* 52 (2) 148 (1944) (pictured flowchart).

Inedible grades of the oil result from additional hot expressions and are consumed by soapmakers.

Tung oil. Tung or China wood oil is obtained from the fruit of the tung tree, which grows extensively in China. Since 1923, large-scale planting has been carried out in Florida, and tung oil production has become one of the prime industries of that state. Because of the large demand for fast-drying finishes and the difficulties in obtaining this oil from China, various modifications of other oils (Chap. 24) for drying purposes are employed. This oil dries in one-third the time required by linseed oil. The oil is obtained by expression, and the cake, unfit for stock feeding, is used as fertilizer because of its high nitrogen and phosphorus content.

Castor oil. This well-known oil is obtained from the seeds, or beans, of the castor plant found in most tropical regions. The beans contain 35 to 55% oil and are expressed or solvent-extracted. The finest grade of oil is reserved for medicinal purposes. The lower grades are used in the manufacture of transparent soaps, flypaper, and typewriter ink, and as a motor lubricant. Large quantities of the oil are "sulfonated" to produce the familiar turkey-red oil long employed in dyeing cotton fabrics, particularly with alizarin. Dehydrated castor oil is a very important drying oil as described in Chap. 24. This manufactured product compares quite favorably with tung oil, previously imported.

Safflower oil. Safflower oil is the fastest growing of the edible oils, largely because of its high percentage (68%) of the polyunsaturated fatty acid, linoleic acid. The market is for special foods containing unsaturated fats, such as margarine and salad and cooking oils, to which this oil is particularly adapted by reason of its delicate flavor. It also finds use in paints and varnishes. It grows largely in the low-rainfall states of the Great Plains, usually on land diverted from wheat. Oil-free safflower meal is used for cattle food.

Processing of Oils¹⁰

REFINING.¹¹ The usual processing of vegetable oils involves degumming and/or steam refining, adsorptive bleaching, hydrogenation, and deodorization. These steps are usually batch operations, although a few continuous processes are in operation.

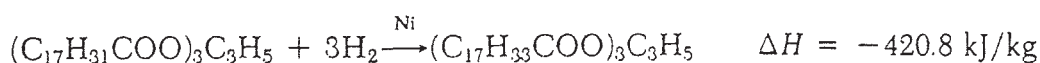
The oils are degummed by coagulation with a small amount (0.05%) of concentrated phosphoric acid. In the alkali refining methods, the free fatty acids are neutralized with an excess of 0.1% sodium hydroxide solution and the mixture heated to about 75°C to break any emulsions formed. The gums and soaps are removed by centrifugation, and the fatty acids are recovered by acidulation. Steam refining involves degumming, bleaching if necessary, and treatment with sparging steam under high vacuum so that the fatty acids are removed by distillation.

BLEACHING. Bleaching is accomplished by the use of adsorptive bentonite clays for edible oils, and alternatively by chemical reactions for nonedible ones. The bleached oil, if it is to be used for salad oil, is then subjected to a *winterizing* treatment which removes any materials that will solidify out at refrigerator temperatures. This is accomplished by cooling to about 5°C and filtering out any solidified material.

¹⁰Gillies, *Shortenings, Margarines, and Food Oils*, Noyes, Park Ridge, N.J., 1974; Erickson, et al., *Handbook of Soy Oil Processing and Utilization*, Am. Oil Chem. Soc., 1980: ECT, 3d ed., vol. 9, 1980, pp. 795-831; Food Plant of the Future, *Food Eng.* **54** (3) 61 (1982).

¹¹Wiederman, Degumming, Refining and Bleaching Soybean Oil, *J. Am. Oil Chem. Soc.* **59** (3) 159 (1981).

HYDROGENATION.¹² Hydrogenation or hardening, as applied to fats and oils, may be defined as the conversion of various unsaturated radicals of fatty glycerides into more highly or completely saturated glycerides by the addition of hydrogen in the presence of a catalyst. Various fats and oils, such as soybean, cottonseed, fish, whale, and peanut, are converted by partial hydrogenation into fats of a composition more suitable for shortenings, margarine, and other edible purposes, as well as for soapmaking and numerous other industrial uses. The object of the hydrogenation is not only to raise the melting point but to greatly improve the keeping qualities, taste, and odor for many oils. It is frequently accompanied by isomerization with a significant increase in melting point, caused, for example, by oleic (cis) isomerizing to elaidic (trans) acid. As the reaction itself is exothermic, the chief energy requirements are in the production of hydrogen, warming of the oil, pumping, and filtering. The reaction may be generalized:



Manufacture of hydrogenated oils requires hydrogen-generating equipment, catalyst equipment, equipment for refining the oil prior to hydrogenation, a converter for the actual hydrogenation, and equipment for posthydrogenation treatment of the fat. One type of continuous converter is pictured in Fig. 28.6 but usually the process is a batch operation.¹³

The hydrogen needed may be manufactured by a number of methods, but the hydrocarbon-steam process is the most widely used. Since gaseous sulfur compounds (H_2S , SO_2 , etc.) are strong catalyst poisons even in trace amounts, as is carbon monoxide, but to a lesser degree, it is essential that the hydrogen be completely free of these poisons, as well as of taste-producing substances. The amount of hydrogen necessary is a function of the degree of reduction of unsaturation required, as measured by the decrease in the iodine number of the oil during hydrogenation. The theoretical quantity needed to reduce the iodine number one unit is about 0.95 m^3 of hydrogen per metric ton of oil. The catalyst¹⁴ used commercially is nickel. It is generally manufactured by the liquid, or wet-reduced, process.

The catalyst and unsaturated oil are introduced into a specially designed tall, cylindrical closed vessel equipped for accurate temperature control. The charge is heated as quickly as possible to as high as 240°C , but 190°C is a more common temperature. Normal operating pressures are 200 to 700 kPa gage. At about 150°C the nickel formate begins the reduction:



The charge is held at the maximum temperature for about 1 h and then cooled. During the reduction and cooling period, hydrogen is bubbled through the oil solely to sweep decomposition products from the oil. Upon completion of the reduction, the charge may be pumped directly to the converter or formed into blocks, flakes, or granules for later use.

The degree of hydrogenation is followed and controlled by refractometer readings to indicate the physical properties (saturation and melting point). The catalyst is filtered off and reused. As the hydrogenation is exothermic, the heat must be removed by an interchanger.

¹²Allen, Hydrogenation, *J. Am. Oil Chem. Soc.* 58 (3) 166 (1981); Albright, Theory and Chemistry for the Hydrogenation of Fatty Oils, *Chem. Eng.* 74 (19) 197 (1967); Commercial Processes for Hydrogenating Fatty Oils, *Chem. Eng.* 74 (21) 249 (1967).

¹³See Chap. 7 for details of these various processes.

¹⁴Burke, Catalysts, *Chem. Week* 111 (19) 35 (1972).

Selective, or directed, hydrogenation can also be used, wherein polyunsaturated fatty acids can be largely converted to monounsaturated acids before there is significant conversion of the monounsaturated fatty acids to saturated fatty acids. Also, conditions can be changed to permit hydrogenation of both mono- and polyunsaturated fatty acids simultaneously.

DEODORIZATION. Deodorization is accomplished by blowing superheated steam through the oil (if hydrogenated, while it is still hot and in the liquid stage) under a high vacuum of 138 to 800 Pa and 210 to 275°C. This removes most of the odor-causing compounds and also destroys many of the color-producing pigments present. Final packaging is often done under a nitrogen atmosphere to prevent any deleterious oxidation.¹⁵

ANIMAL FATS AND OILS

Much chemical processing, started early by hydrogenation and now intensified by interesterification and isomerization, has improved the quality of animal fats and oils.

Neat's-foot oil. The skin, bones, and feet of cattle (exclusive of the hoofs) are cooked or rendered in water for 10 h to separate the fat. This is skimmed off the top of the water and, after filtering through cloth, heated in a kettle to 121°C for several hours. The kettle is cooled, and the contents are settled; the oil is then drawn off, filtered through flannel bags, and sent to the refinery. Here the oil is *grained*, which requires about 2 weeks at 1°C. The product is pressed once, yielding pure neat's-foot oil. The stearin from the first pressing is re-pressed to yield a second grade oil. The pure variety is used for oiling watches and other fine machinery, and the latter in the textile and leather industries. The stearin from the second pressing is consumed in soap manufacture.

Whale oil. This oil is now obtained from modern floating factory ships which catch, butcher, and process the mammals at the scene of the catch. To prepare the oil, the blubber is stripped from the flesh and boiled in open digesters. The finest grade of oil separates first. It is practically odorless, very pale in color, and contains very little free fatty acid. Upon continued boiling, a second grade is obtained and, if the residue from this operation is cooked under pressure, a third grade is made available. All grades are centrifuged to clarify and dry them further before they are placed in storage. The oils obtained are used in the manufacture of lard substitutes and in soapmaking.¹⁶ Both fish and whale oil contain unsaturated fatty acids of 14 to 20 carbon atoms, and as many as six double bonds.

Cod-liver oil. This oil, whose value was known long before the discovery of vitamins, was originally prepared by storing fish in barrels and allowing them to rot until the oil floated to the top. It is now rendered fresh by live steam cooking of cod and halibut livers (and other parts) until a white scum floats to the top. This usually requires about 30 min, after which the mass is settled for 5 min, decanted, and strained. The oil desired for medicinal purposes is filtered, bleached, and winterized. It is rich in vitamins A and D. Lower grades are employed in leather dressing and for poultry feed.

Shark-liver oil. Recent investigations have shown that the oil obtained from the liver of the shark *Galeorhinus zyopterus* contains more vitamins A and D than cod- or halibut-liver

¹⁵Gavin, Deodorization and Finished Oil Handling, *J. Am. Oil Chem. Soc.* 59 (3) 175 (1981).

¹⁶Industrial Use of Whale Oil, *CHEMTECH* 6 (5) 322 (1976).