

6

Fats and Oils from Plant Materials

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I. INTRODUCTION

Although “extraction” often describes the mass transfer process between two liquid phases, in the following the term “extraction” refers to the preferential dissolution of one or more constituents of a solid by contact with a liquid solvent. It is one of the oldest and most commonly used unit operations in the food industry. “Leaching” is another term often used to describe the operation, although originally referring only to percolation of a liquid solvent through a fixed bed of the solid. Sometimes the term “washing” is employed, as it is intimately associated with extraction as a complementary step. The fundamental purpose of extraction is the removal of a soluble fraction from an insoluble, permeable solid phase with which it is associated. The soluble fraction may be solid or liquid, and may be physically held within, chemically bound with, adsorbed on, or mechanically held in the pore structure of the insoluble matrix.

Although the mining and metallurgical industries are the largest users of extraction technology, extraction is also a critical unit operation in the food industry. Many important foods and food ingredients are obtained by extraction from materials of life origin, including microbes, plants, and animals. For instance, sugar is extracted from sugar beets with hot water, tannin is dissolved out of various tree barks, and beverages such as tea and coffee are prepared both domestically and industrially by leaching operations. In terms of technological sophistication and production scale, vegetable oils are among the most important products recovered from seeds such as soybeans and rapeseed by extraction; therefore, these are discussed in greater detail in this chapter. Although in some cases mechanical pressing methods can be used, solvent extraction is a more

efficient method for the recovery of oil from oil-bearing materials. It is the only efficient technique to recover oil from seeds or other materials low in oil (1). Since heat treatment can be minimized, oil produced by solvent extraction is of high quality, and thermal damage to meal, the residue after oil removal, is also minimal.

The effectiveness and efficiency of extraction depend on many factors, including the solvent used, solid preparation, extraction temperature, modes of operation, and equipment. The theories of extraction have been well developed and are presented in detail in texts such as Treybal's *Mass Transfer Operations* (2). Commercial processes of edible oil extraction are extensively reviewed in *Bailey's Industrial Oil and Fat Products* (3), while essential oils are reviewed in Guenther's *The Essential Oils* (4).

The choice of solvent for extraction is largely determined by the solubility characteristics of the constituent of concern and the solid. Ideally the smaller component of interest should be highly soluble in the selected solvent, whereas the matrix or other major components should have little or no solubility in it. "Infinite" selectivity is never achieved in practice, and the process must be manipulated to obtain high yield and high purity of the desired components with minimal coextraction of undesired impurities. In addition to solubility, cost and safety are also taken into consideration when a solvent is chosen for extraction. To achieve complete extraction, a combination of several unit operations, such as successive extractions with two or more solvents, may be required.

The pretreatment given to the oil-bearing solid frequently plays a very important role in the efficiency of the extraction process. In many instances of extraction, small particles of the soluble material are completely surrounded by a matrix of insoluble materials. The solvent must then diffuse into the mass, and the resulting solution must diffuse out before a separation can result. Particle size reduction by crushing and grinding of such solids greatly accelerates the extraction action, since the soluble portions are then made more accessible to the solvent. The extraction process must find a suitable compromise between the increased extraction rate obtained by reducing the particle size and increased difficulty in separating the small solid particles from the liquid solvent. Plants, microbes, animals, and their parts are cellular in structure, and the desired components are usually found in the cells. If the cell walls remain intact upon exposure to a solvent, the extraction depends solely on the diffusion of the solute through the cell walls, often controlled by osmotic pressure. Pretreatment techniques can be used to disrupt cell walls chemically or thermally. Alternatively, the aspect ratio is changed in a mechanical process. This allows the reduction of the penetration distance of the solvent while maintaining sufficiently large particle size to permit efficient separation from the solvent. As an example, cellular material may be cut into thin slices before extraction so as to reduce the penetration distance required for the solvent to reach the individual plant

cells. In oil extraction, oilseeds are usually rolled to form flattened flakes with thickness ranging from 0.15 to 0.5 mm, while retaining major dimensions of up to 15 mm. The rolling and flaking evidently crushes some of the cell walls and opens up passageways for penetration of the solvent by capillary action (5, 6). It is impractical and sometimes even undesirable to grind the material small enough to release the contents of individual cells because of the difficulties excessively fine particles may cause in subsequent separation. Seed preparation includes heat and moisture adjustment to facilitate cell disruption and solvent penetration.

It is usually desirable to extract at as high a temperature as possible because higher temperatures result in higher solubility of the solute in the solvent; thus, higher concentrations in the extraction liquor are possible. Moreover, the viscosity of most liquids is lower and the diffusivity greater at higher temperatures, leading to increased rates of extraction. Higher operating temperatures also reduce energy requirements in solvent recovery. However, the solvent selection and temperature must take into account that in some natural products high temperatures may cause deterioration and denaturation.

Extraction operations can be conducted in batch (unsteady state) or continuous (steady state) mode. In each case, both stage-wise and continuous-contact types of equipment can be used. Extraction equipment uses two techniques for solid-liquid contact. The liquid can be sprayed and percolated over the solid, or, alternatively, the solid can be entirely immersed in the solvent. The choice of equipment depends on the physical and chemical characteristics of the matrix, the value of the products, and the desired throughput.

II. THEORIES OF EXTRACTION

A. Rate of Extraction

The performance of an extraction process is governed by both mass transfer and equilibrium phenomena. It can be affected by many physical and chemical factors, some of which are difficult to evaluate quantitatively. It is, therefore, not a simple matter to theoretically predict extraction rates, and quite frequently, such data have to be determined experimentally. If extraction only involves simple washing of a solute from the surface of a solid, it may be very fast, comprising merely the blending of solution and solvent, and its efficiency is thus determined almost entirely by the effectiveness of the mechanical separation of liquid from solid. Extracting a solute from the internal parts of a solid, on the other hand, will be much slower, in which case solids are made of a skeletal structure of insoluble substances with pores impregnated with the solute. Diffusion theory can be used to describe extraction processes that fall into this category. Beginning with Fick's law, the following equation is derived (7):

$$N_A = \frac{N_A}{N_A + N_B} \frac{D_{AB}}{z} \left(\frac{\rho}{M} \right)_{av} \ln \frac{N_A/(N_A + N_B) - x_{A2}}{N_A/(N_A + N_B) - x_{A1}}$$

where N_A and N_B are molar fluxes of components A and B, respectively, D_{AB} is the diffusivity of A in B in solution, ρ and M are the solution density and molecular weight, respectively, x_{A1} and x_{A2} are mole-fraction concentrations of component A at the beginning and end of the diffusion path, respectively, and z is the distance in the direction of diffusion. For most common cases where component A diffuses through nondiffusing B, $N_B = 0$, where

$$N_A = \frac{D_{AB}}{z} \left(\frac{\rho}{M} \right)_{av} (x_{A1} - x_{A2})$$

The diffusivity varies significantly among liquids. In the absence of experimental data, it can be estimated by the following empirical correlation for non-electrolytes:

$$D_{AB} = \frac{(117.3 \times 10^{-18} (\varphi M_B)^{0.5} T)}{\mu v_A^{0.6}}$$

where D_{AB} is diffusivity of A in a very dilute solution in solvent B, M_B the molecular weight of solvent, T the temperature, μ the solution viscosity, v_A the solute molar volume at normal boiling point ($0.0756 \text{ m}^3/\text{kmol}$ for water), and φ the association factor for solvent (2.26 for water, 1.9 for methanol, 1.5 for ethanol, 1.0 for unassociated solvents such as benzene and hexane).

The complexity of the structures of natural products may make the application of these models difficult. In addition to the above attributive factors, the rate of diffusion can also be affected by the degree of cell rupture, the diversity of structures in the matrix, and the rate of dissolution of each constituent. All of these phenomena make it impossible to apply a single simple equation to model extraction. Although methods of dealing with solvent extraction of vegetable oils have been suggested (8, 9), very little has been published on modeling the extraction of other natural products.

In oil extraction, the term "miscella" refers to the mixture of oil and solvent outside seed particles, and "raffinate" the mixture of the two within the particles. The design of large-scale solvent extraction apparatus for oilseeds extraction requires the knowledge of the rate at which equilibrium is attained between the miscella and raffinate. In most oilseeds, oil is stored in small, 1- to 10- μm oil bodies, which are enclosed by protein-embedded membranes. The membrane protein oleosin has high affinity for both oil and water on opposite ends of the molecule. The extraction proceeds first by washing out of free oil, which is held in large intercellular spaces and is not bound to the flake structure; it is followed by a diffusion process. Assuming that the cell walls are broken,

the oil must still diffuse through the oleosin membrane of the oil droplets. The next step is the release of bound oil into the solvent, which may involve the breaking of hydrogen bonds or hydrophobic attractive forces. The solution then must diffuse back out through the solid matrix to the bulk miscella, which involves diffusion first through the solid itself, then through the laminar boundary layer on the surface of the solid. Therefore, oil extraction may be quite slow, particularly when the oil content of the seed is reduced to low levels ($\leq 1.0\%$).

Studies have shown that the oil extraction rate is influenced by a number of factors, including the thickness, size, shape, and internal structure of the seed particles; the intrinsic capacity for diffusion of solvent and oil, which is determined primarily by the viscosities of both; and, especially at low oil levels, the rate of extraction of other substances that are less readily soluble than glycerides, which are the primary components of interest in vegetable oils (1). Among these factors, the effect of the thickness of oilseed flakes is most evident. Othmer and Agarwar (5) correlated the rate of hexane extraction of soybean oil to flake thickness and remaining oil concentration as follows:

$$-\frac{dC}{dt} = kF^{-3.97}C^{3.5}$$

where C is the concentration of oil in the flake, t the time, k the proportionality constant, and F the flake thickness. Since F has an exponent of almost 4, a small increase in flake thickness would result in a great decrease in the oil extraction rate.

When using a homogeneous oil-impregnated material made of thin platelets of uniform thickness, approach of estimation of extraction rate becomes simpler as the application of diffusion theories is possible. The calculation has been thus developed by Boucher et al. (8) as follows:

$$E = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 \left(\frac{\pi}{2}\right)^2 \left(\frac{Dt}{R^2}\right)\right]$$

where E is the fraction of total oil unextracted at the end of time t , R is one-half the platelet thickness, and D is the diffusivity of the oil within the platelets. Except for the initial stage where the free oil is washed out quickly, the above equation can be reduced to:

$$E = \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 Dt}{4R^2}\right)$$

or

$$\log E = -0.091 - 1.07 \frac{Dt}{R^2}$$

Thus, when the extraction proceeds past its initial stage, a plot of $\log E$ against t gives a straight line. The slope is a function of the diffusivity of the oil and the platelet thickness. The turbulence in the solvent, indicated by the Reynolds number, was found to have no significant effect on the extraction rate, showing that the limiting step in extraction is diffusion through the cell wall within the platelets, and the liquid-film resistance to the transfer of oil to the solvent was inconsequential (8, 10). The rapid release of oil during the initial stage of extraction was thought to be caused by the rupture of some oil bodies in slicing the seeds, plus the occurrence of void spaces in the seeds after drying (9). The diffusivity of the oil in the platelets was correlated to the viscosities of both solvent and oil by Boucher et al. (8) under their test conditions:

$$D = 12.96 \times 10^{-6} (\mu_o \mu_s)^{-0.46}$$

where μ_o and μ_s refer to the viscosities of oil and solvent, respectively. The numerical values in the formula are obviously specific to the structure of the platelets and therefore are applicable only to the lot used in their tests.

B. Calculations for Steady-State Operation

In steady-state operation, it is assumed that the solid is contacted with more than enough solvent to dissolve all the soluble solute and there is no preferential adsorption of either solvent or solute by the solid. Adequate contact time permitting, all the solute will be dissolved, and the oil concentration in the miscella will be equal to that in the solvent inside the seed matrix; thus, there is an equilibrium between the effluent solution and the solid. The insoluble solid is then separated by settling, filtration, drainage, or centrifugation. This is usually not achieved in practice as the solute may be incompletely dissolved due to inadequate contact time and some solute is usually adsorbed by the solid. Therefore, without corrections for these effects, the actual stage efficiencies are always lower than the calculated ones.

Similarly to other unit operations, two typical calculations are performed in extraction: characterization and design. In the former case the initial solute content of the solid, and the number and amount of washings are known, and the final amount or concentration of solute in the extract is sought. This yields an estimate of the extent to which an extraction process proceeds. In case of design calculations, the final solute content of the solid is specified, with a known amount and concentration of solute in the solvent; whereas the number of washings, or the number of stages, is calculated in order to design an extraction process.

Steady-state operation can be achieved in either a single-stage or a multi-stage manner. Single-stage extraction involves only one cycle of mixing the solid with the solvent and separating the resulting insoluble solid by physical means. [Figure 1](#) shows all the streams involved in a complete process of single-

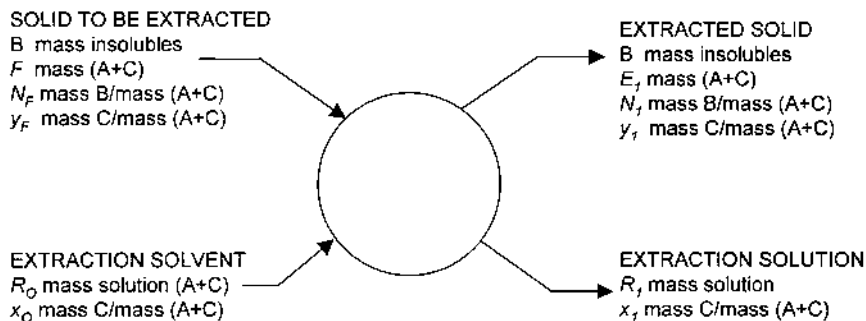


Figure 1 Single-stage extraction (11).

stage extraction. Mass balance is performed for all components in the system to give (11):

$$\begin{aligned}
 F y_F + R_0 x_0 &= E_1 y_1 + R_1 x_1 && \text{for solute C} \\
 F(1 - y_F) + R_0(1 - x_0) &= E_1(1 - y_1) + R_1(1 - x_1) && \text{for solvent A} \\
 F + R_0 &= E_1 + R_1 = M_1 && \text{for solution A + C}
 \end{aligned}$$

M_1 is the mass of the mixture, or the slurry, on an insoluble solid-free basis. The solid and solute concentrations in the slurry are, therefore:

$$\begin{aligned}
 N_{M1} &= \frac{B}{F + R_0} = \frac{B}{M_1} \\
 y_{M1} &= \frac{y_F F + R_0 x_0}{F + R_0}
 \end{aligned}$$

respectively.

By continuously contacting the solids with fresh batches of solvent, more solute can be extracted than a single batch extraction. This is called *multistage cross-current extraction*. All of the above equations are applicable to the calculations for addition stages, in which the already extracted solids from any stage are the feed solids to the next; thus, the procedure for a single stage is repeated with the changes in the subscripts to indicate different stages. Multistage cross-current extraction can be used to extract additional solute from the solids, but a much larger amount of solvent is required for this operation, and as a result, dilute solutions of the solute will inevitably be produced as it proceeds to the last stages of extraction. Although this is uneconomical use of solvent, the procedure allows experimental determination of the performance of countercurrent systems, using simple laboratory equipment.

Countercurrent extraction minimizes solvent use and operating costs. In

this approach, the final solution is withdrawn from contact with the fresh solid and the fresh solvent is mixed with the solid with most of the solute already extracted, keeping the driving force at the highest level throughout the process. A flowsheet of multistage countercurrent extraction is shown in Fig. 2. The process can be operated with any number of extraction and separation steps. An array of these steps is called an *extraction battery*.

Like in single-stage extraction, calculations of multistage cross-current extraction are based on stage-wise mass balance.

The solution (A + C) balance gives:

$$F + R_{N_p+1} = R_1 + E_{N_p} = M$$

The solute (C) balance gives:

$$Fy_F + R_{N_p+1}x_{N_p+1} = R_1x_1 + E_{N_p}y_{N_p} = My_M$$

where M is total mass of the mixture (slurry) on an insoluble solid-free basis. The slurry is produced by mixing the solids and solvent such that:

$$N_M = \frac{B}{F + R_{N_p+1}}$$

$$y_M = \frac{Fy_F + R_{N_p+1}x_{N_p+1}}{F + R_{N_p+1}}$$

where N_M and y_M are, respectively, the concentrations of solid and solute in the slurry on insoluble solid-free basis.

The extraction process can be graphically modeled using a diagram as shown in Fig. 3, to indicate the approach to equilibrium obtained theoretically or experimentally, and the number of theoretical stages required for the extraction. The number of stages is dependent on the average stage efficiencies, which are affected by the mass transfer properties of each stage. In the special case where there is a constant value of N for slurry of all stages, the system approximates a constant R/E . When, in addition, the equilibrium between the solute concentration in the effluent solution, x , and that in the solid (insoluble solid-free basis), y , is of a linear relationship, i.e., $m = y/x = \text{constant}$, the final concentration in the solid, y_{N_p} can be calculated by the following equation:

$$\frac{y_F - y_{N_p}}{y_F - mx_{N_p+1}} = \frac{\left(\frac{R}{mE}\right)^{N_p+1} - \frac{R}{mE}}{\left(\frac{R}{mE}\right)^{N_p+1} - 1}$$

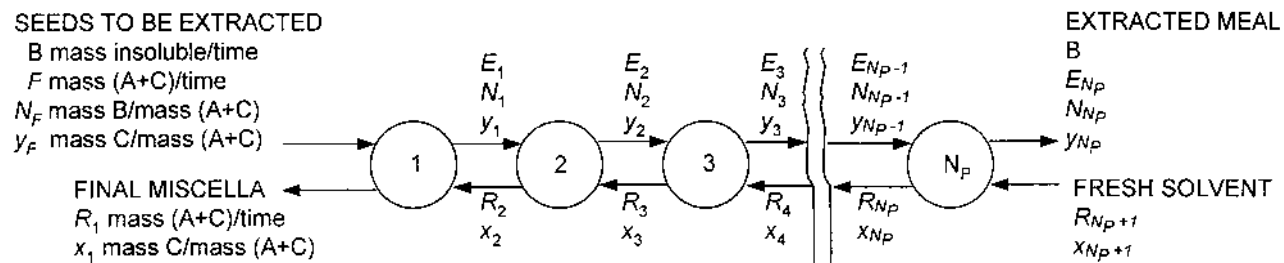


Figure 2 Multistage countercurrent extraction (11).

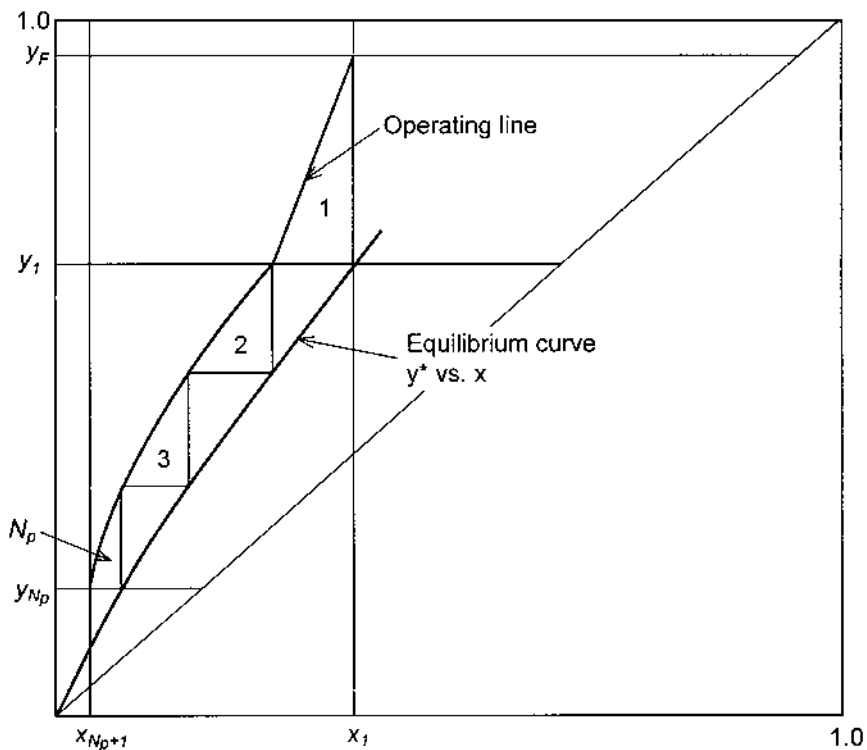


Figure 3 Stage construction diagram (11).

Similarly, the number of stages, N_p , can be estimated when the final concentration is specified. If no preferential adsorption of the solute occurs, the solute concentration is the same in both the solution and the solid, so that $m = 1$.

To calculate the steady-state performance of a multistage countercurrent extraction, the concentrations in the intermediate stages can be experimentally estimated through batch simulation, using cross-current procedure as indicated earlier. The scheme for such a simulation was proposed by Scheibel (12) and Treybal (13). Fig. 4 shows an example of batch simulation of two-stage countercurrent extraction. Each circle in the figure represents a batch extraction. Starting from stage A, F amount of feed solid is contacted with S amount of fresh solvent. The mixture is then separated into a clear solution R' and a solid E_A . At stage B, the solid from stage A, E_A , is again contacted with the same amount of solvent S before the separation to yield a solid E' . The whole simulation process is followed through as illustrated in Fig. 3. It consists of several runs.

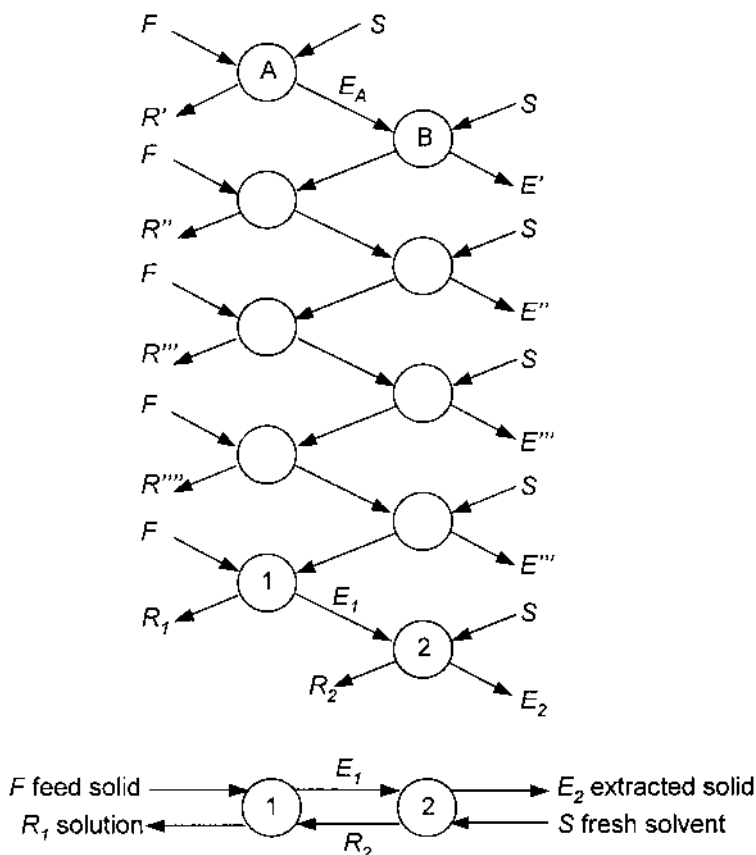


Figure 4 Batch simulation of a countercurrent cascade (13).

From each run R amount of solution and E amount of solid are produced. Although R and E at the beginning are clearly different in solute concentration from those produced by a countercurrent extraction, after several runs in this manner, they approach very closely the values obtained in a truly continuous multistage countercurrent extraction.

III. SOLVENTS FOR EXTRACTION

For oil extraction, nonpolar solvents are usually used, as triglyceride-based oils are typically miscible with these solvents. The most common solvents in solvent

extraction of oil are light paraffinic petroleum fractions. Both hexane (bp 66–69°C) and heptane (bp 89–98°C) mixtures are widely used; sometimes cyclic hydrocarbons, such as cyclohexane (bp 71–85°C), are also used (16). While these solvents are efficient in oil extraction, the major disadvantage to their use is their flammability. Strict safety measures must be taken to avoid fire and reduce explosion hazard in the plants where they are used (17). Much effort has been taken to find alternative solvents, particularly since the Clean Air Act of 1990 designated hexane as a hazardous air pollutant. A methylpentane-type naphtha (bp 55–61°C) is now commercially available (18). Trichloroethylene (bp 86.7°C), due to its nonflammability, is a much safer solvent to handle in terms of prevention of fires and explosions (19, 20), but all chlorinated organic solvents are increasingly perceived as too toxic to be used in the production of food materials. There is pressure on the industry to switch to solvents that are perceived to be more benign: alcohols and even aqueous solutions. Both isopropanol (21) and ethanol (22, 23) have been used commercially to extract soybean and cottonseed oil. Recently, high-concentration isopropanol (~96%), recovered by pervaporation techniques, has been used instead of the commonly distilled azeotropic isopropanol (87.8%) for oil extraction in order to increase the oil solubility (24). Both cottonseed and soybean oils thus extracted, after refining, bleaching, and deodorization, well met commercial standards. However, although improving the flavor, the alcohols tend to lower functionality of soybean protein products, and due to low oil solubility and higher latent heat than hexane, they require significantly more energy for solvent recovery. Supercritical fluids have been tested for oil extraction (25, 26), but due to the extremely high pressures required, most equipment has low capacity, which currently limits the application of this technology to the production of high-value products such as coffee, hops, and flavor concentrates.

IV. SOLVENT EXTRACTORS

Two types of commercial units are currently used for extraction: immersion and percolation. In the immersion type of extractor, solids to be extracted are conveyed through a pool of solvent. The particle size of the solid material must be reduced as much as possible to facilitate maximal contact between the solvent and the solid. However, in this method the separation of fine particles and the miscella is difficult, thus limiting its use to low-volume operations. Most large-volume units are percolation-type extractors that are considerably more efficient in terms of energy consumption and space requirements.

In the percolation unit, the solid material (flakes or prepressed cake) forms a fixed bed, and the solvent is pumped and sprayed over the material, and drained through the bed, washing the oil down with it. Clearly the flakes or

pieces of prepressed cake should be large enough to permit a reasonable flow rate of solvent through the solid material. Fine material can prevent the drainage, causing the bed to be flooded with solvent and resulting in improper washing and poor extraction.

One of the first designs based on percolation was the basket-type extractor (Fig. 5), wherein the seed flakes are carried in baskets supported on endless chains. The baskets are loaded at the top of the descending leg, and the flakes are sprayed with half miscella that percolate through the beds of the flakes in these baskets as they go down. The miscella collected at bottom on the descending side is full miscella and thus is removed for oil and solvent recovery. On the ascent, the flakes are contacted with another stream of liquid that starts as pure solvent; thus, oil in the flakes is extracted in a countercurrent manner as the baskets move up. A short drainage time is provided at the top before the baskets are automatically flipped to unload the extracted and drained flakes into a discharging hopper, and they are then conveyed to the desolventizer.

This early type of solvent extractor is bulky and requires intensive maintenance due to frequent chain breakdown. It has been largely superseded by rotary and horizontal extractors. A rotary extractor is, in fact, a vertical cylindrical shell with radially divided chambers called baskets or cells, either rotating or stationary, around a central shaft. Figure 6 shows a cut-away view of a rotary extractor manufactured by De Smet Process and Technology, Inc., the reflex extractor. Its liquid spraying nozzles and flakes hopper are fixed while the baskets in the shell rotate. The material is mixed with miscella as it enters the extractor and is thus slurry-fed to the rotating baskets. The miscella leaves the basket through the perforated bottom, and is collected and pumped to the previous basket. Thus, a countercurrent flow is set up between the moving seed beds and the stationary miscella or solvent headers. The most exhausted meal is contacted with fresh solvent, while the fresh seed is first contacted with nearly oil-saturated miscella. The totally sealed basket dividers ensure that each miscella stage flows vertically through the basket of material, and these dividers also allow the entire bed of material in the extraction zone to be thoroughly soaked in miscella. It is claimed that, since the miscella has more contact time to penetrate the flakes than in shallow-bed designs, even thicker flakes can be used to achieve desired residual oil content. After the extraction process is complete, a basket passes over an open portion of the screen, allowing the material to discharge into the dump hopper at the base of the extractor by gravity. A number of similar designs were developed based on the earlier Rotocel extractor by the Dravo Engineers and Contractors. Another variant of this design, developed by the French Oil Mill Machinery Company, called the stationary basket extractor, maintains the seed-holding baskets or cells immobile while rotating the solvent headers and bottom connector systems.

Horizontal extractors feature the horizontal movement of the baskets while

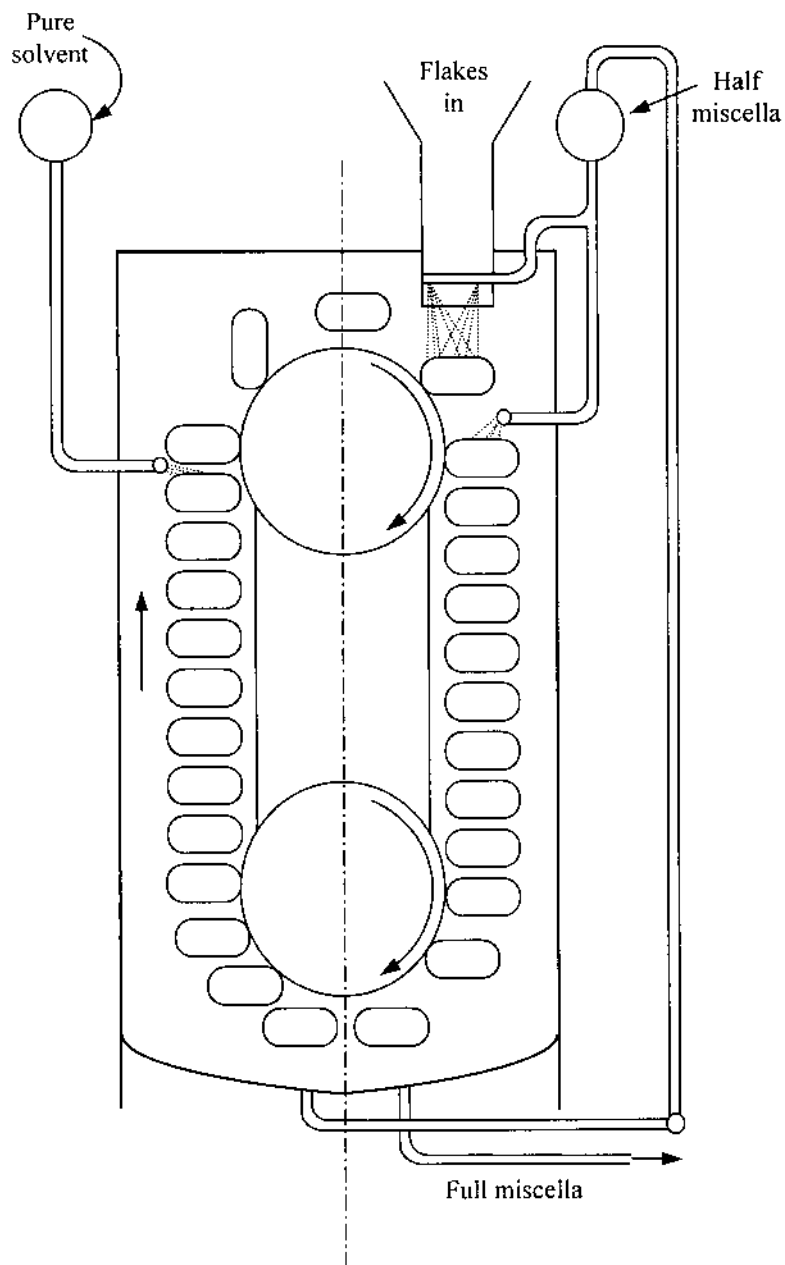


Figure 5 Basket solvent extractor (1).

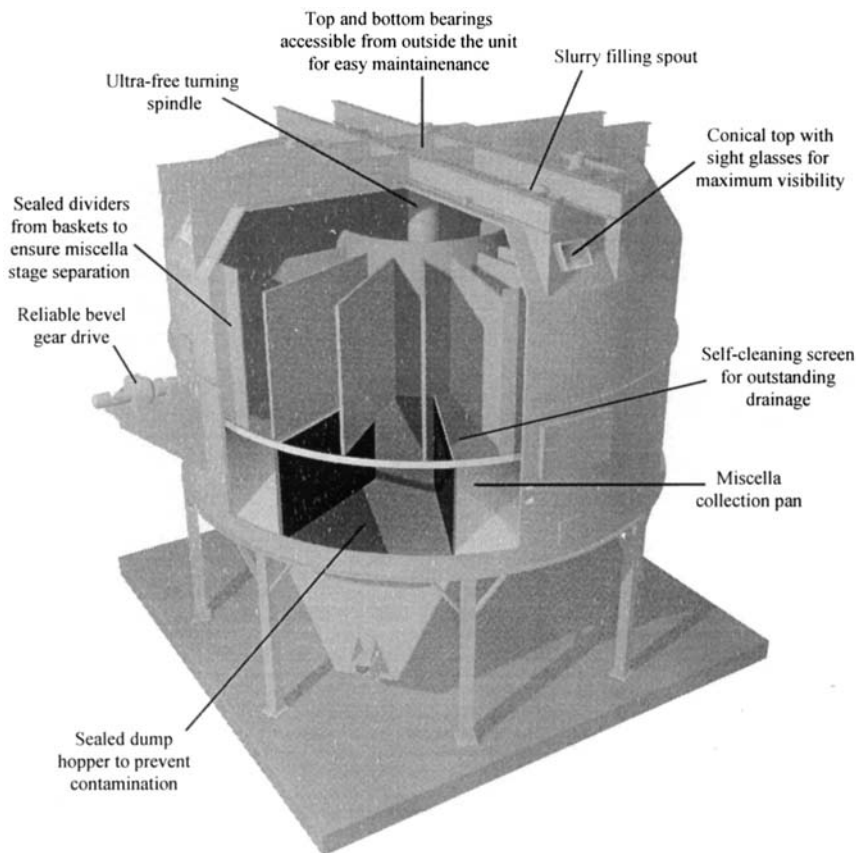


Figure 6 Reflex solvent extractor. (Courtesy of De Smet Process & Technology, Inc.)

the solvent is percolated through the moving seed bed. One typical example of this type is the Crown Model III continuous loop extractor made by the Crown Iron Works Company (Fig. 7), in which the solid material is deposited on vee-bar screen as a shallow bed (0.8 m) and travels a distance about 50 times the bed depth in a closed chamber shaped like a loop. The fresh material is fed to the extractor through an inlet hopper on the top, and moves through four stages on the upper level and another three on the lower level. In the first stage on the upper level it is washed with already concentrated miscella. The solids then move to the second stage concurrent to the miscella. The rich miscella drained from the second stage is pumped through a hydrocyclone before leaving the extractor as full miscella containing approximately 25% oil. The next five stages

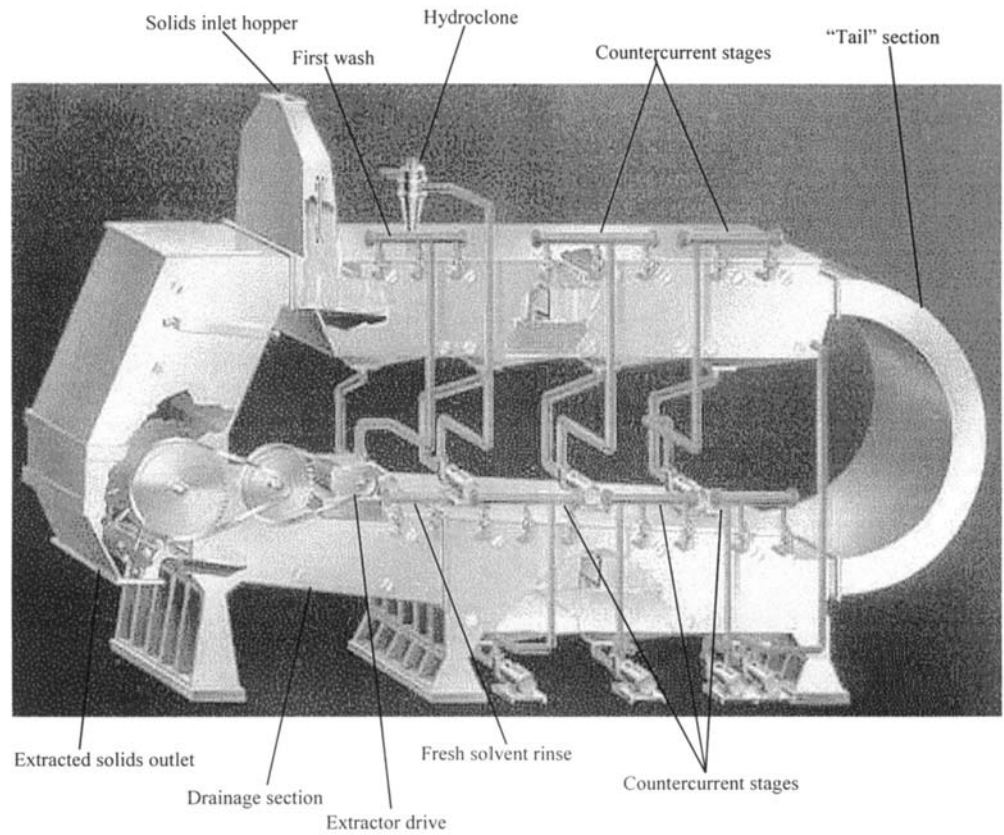


Figure 7 Crown loop extractor Model III. (Courtesy of Crown Iron Works Company.)

are all operated in countercurrent manner. As the solids move from the upper level to the lower level between stages 4 and 5, the bed is completely turned over in the “tail” section so that both sides of the solids are washed with the miscella. Before being discharged, the extracted solids are drained of residual miscella in a drainage section. The mechanical features of this type of extractor promote solvent contact, rapid drainage, and complete extraction with a variety of products and allow utilization of fragile flakes with high content of fines. Extractors with capacities of 50–4000 t/d are in commercial service.

Crown Iron Works Company also developed a Model IV extractor for countercurrent extraction of granular materials that are heavier than solvent (Fig. 8). The material is carried through a pool of solvent by a series of inclined drag conveyors. The solids pulled out of the solvent pool by the last conveyor is sprayed with fresh solvent and then are drained of residual miscella before being discharged. Full miscella is drawn off where solids are fed to the extractor. During the transfer of solids from one conveyor to another, the beds are completely turned over, thus ensuring good solvent–product contact.

V. EXTRACTION OF OILSEEDS

The recovery of oil from oil-bearing plant materials has been a vital industry for thousands of years. Hence, its technology evolved from primitive manual operations in the early times to continuous processing by automated machinery in the modern days. This evolution was obviously driven by the need to maximize the oil yields, improve the oil quality, and produce a valuable residue after oil extraction. Oils from plants are usually contained in seeds, such as soybeans, sunflower seed, cottonseed, and rapeseed/canola, or fruits such as palm (Table 1). They contain 15–50% of oil and are the major source of vegetable oils for human consumption (Table 2). The oil extraction process is often followed by further processing to yield more refined oil products.

Many processes have been developed to recover oil from oilseeds, but the most common ones are hydraulic pressing, expeller pressing, and solvent extraction. Developed in late 1700s, hydraulic pressing, also known as batch pressing, applies pressure using a hydraulic ram to batches of oilseeds confined in a barrel that allows oil to escape while retaining solids. Because it is a labor-intensive, batch operation, its industrial use is uneconomical and thus declined drastically over the last two decades. Currently continuous expellers or screw presses are used for the mechanical extraction of oilseeds. These machines are able to create the pressures generated by a hydraulic press ram but require minimal labor because they operate continuously. The reduced labor cost and increased throughput and yield more than make up for their higher power requirement and maintenance cost (27).

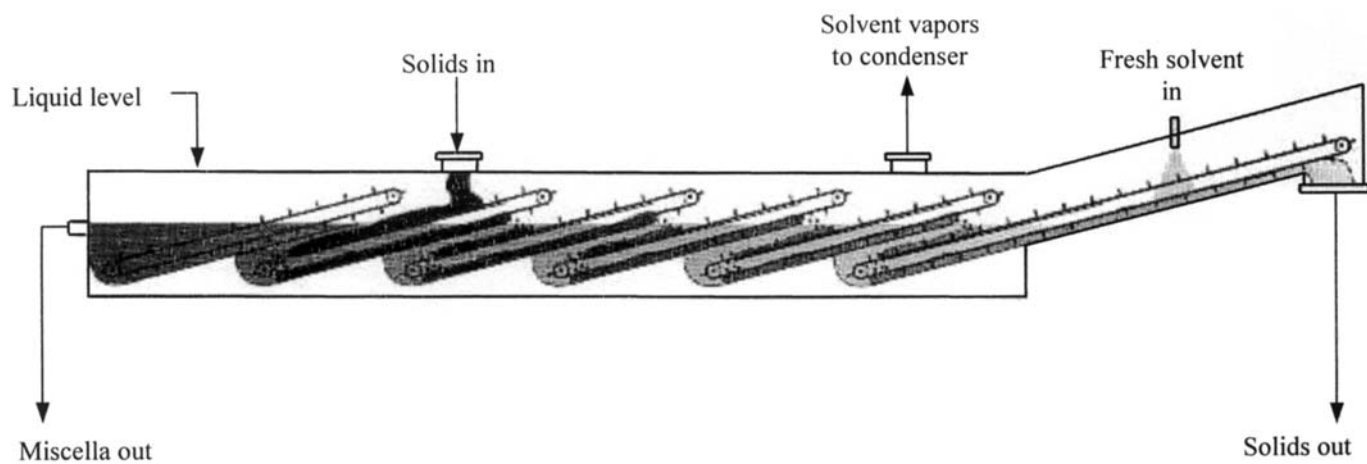


Figure 8 Model IV Extractor. (Courtesy of Crown Iron Works Company.)

Table 1 World Production of Major Oil-Bearing Seeds, Legumes, and Fruits in 1998–1999 Crop Year (in 10⁶t)

Soybeans	154.70
Rapeseed/canola	35.78
Cottonseed	33.63
Sunflower seed	27.26
Groundnuts, shelled	20.88
Palm	16.71
Linseed	2.62
Sesame seed	2.59

Source: Ref. 14.

It is impossible to obtain complete oil removal by mechanical pressing, since the solids retain significant quantities of oil inside the matrix. In addition, as the oil content is reduced, the friction between particles escalates rapidly, and the heat generated by expeller causes very high temperatures that can degrade both the oil and the residual meal. To recover the last 20% of the oil, solvent extraction is the preferred operation. Solvent extraction as a batch process first appeared in 1870. Continuous solvent extraction was developed shortly after World War I. Since then, its use has expanded rapidly in oilseeds processing due to its high efficiency in oil removal and recovery. As solvent extraction is energy intensive, in oilseeds with high oil contents much of the easily removable oil is recovered by expelling prior to solvent extraction. Thus sunflower, rapeseed, and cottonseed are processed by a two-stage technique consisting of a prepress followed by solvent extraction, resulting in more complete removal of oil with a lower usage of solvent.

Table 2 Oil Content of a Number of Oil-Bearing Vegetable Materials

Cottonseed	18–20
Palm kernels	45–50
Peanuts	45–50
Rapeseed/canola	45–50
Sesame seed	50–55
Soybeans	18–20
Sunflower seed	35–45

Source: Ref. 15.

A. Canola (Rapeseed)

The technology to process canola or rapeseed is typical of high-oil-content seed processing. Although expeller pressing or direct solvent extraction may be used, these techniques either leave a fairly high residual oil content in the meal or are not energy efficient. The prevailing process in developed countries is prepress-solvent extraction, which is a combination of mechanical and solvent extraction, with the final portion of oil being removed with a solvent, usually hexane. In this process, much less residual oil is left in the meal.

1. Pretreatment and Prepressing of Oilseeds

A typical oil extraction process begins with seed preparation (Fig. 9). The seeds usually carry foreign materials such as unwanted seeds, sticks, leaves, and even metal shreds. They are typically cleaned by passing through a magnetic separator and seed cleaners using a combination of air aspiration, agitation, and screens.

In rapeseed, the enzyme myrosinase catalyzes hydrolysis of glucosinolates. Among the hydrolysis products are undesirable isothiocyanates, oxazolidinethiones, and nitriles (28), which are soluble in oil. In order to maintain the oil quality, it is necessary to keep the glucosinolates intact by rapidly inactivating myrosinase by “cooking” in a multistage cooker. The seed is first cracked to increase the area available for heat transfer. To achieve rapid myrosinase destruction and to minimize the time spent at the active temperatures of the enzyme (40–65°C), the cracked seed is contacted with live steam, which quickly raises the temperature by releasing the latent heat, and also adds water to aid in the denaturation of myrosinase. The excess water is removed by indirect heating in subsequent stages of the cooker employing stacked steam-jacketed trays with bottoms heated by steam. Since canola has much lower levels of glucosinolates than conventional rapeseed varieties, the cooking temperature for canola has been decreased from ~120°C to less than 100°C.

The cooked seeds are then immediately pressed to separate oil by screw presses. A typical screw press consists of a hard-surfaced, horizontal worm shaft within a barrel composed of cages containing spaced lining bars. As the worm shaft rotates inside the cage assembly, it moves the seed through and out. Pressure on the seed increases as it moves through the barrel, expelling the oil between the lining bars. The pressure at the discharge end of the shaft forms the partially extracted seed into a cake. Important operating factors in prepressing are the speed of shaft rotation, the shaft assembly configuration, and setting of the choking mechanism at the discharge.

Pressing cannot remove all of the oil without significant thermal damage to the meal. Typical residual oil content in fully pressed cake is 6–10%, which

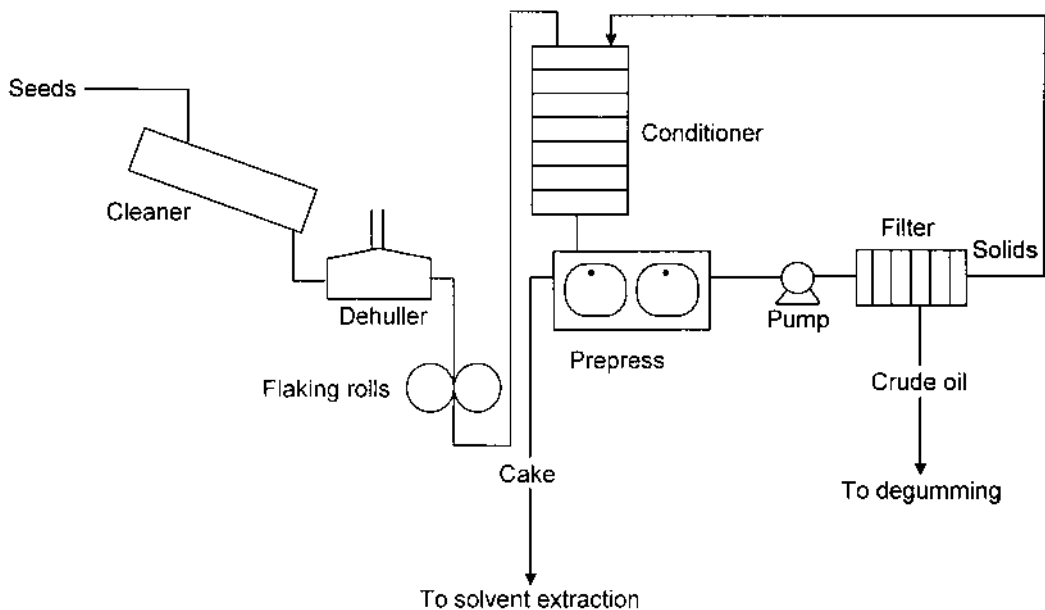


Figure 9 Preparation and prepressing of canola.

makes this approach noncompetitive. Thus, in modern plants seeds are pressed only to the point where the meal protein is not seriously damaged, leaving 15–22% oil in the prepressed material. This removes two-thirds of the oil, uses much lower pressures and considerably less energy than the equivalent full-press operation, and results in better oil and meal quality. As the oil in the seed is contained in structures shaped like fibrous capillaries, application of too high pressures may seal these channels again and make further extraction difficult. Too much pressure may also cause the cake to become hard and impermeable to the solvent. It is, therefore, critical to control the pressure in the press and limit the amount of oil removed from the cake.

To further free the oil, and to stabilize and strengthen the seed, another thermal step, usually referred to as “conditioning,” is required after prepressing. Conditioning involves heating the seed to reduce the viscosity of the oil and to make it easier for the oil to separate from the ruptured seed cell. As the seed is heated by the expeller, external heating may not be needed for this step. During conditioning, it is important to control the moisture content of the seed, as well as the temperature, because once the seed is crushed and flaked, microbial deterioration can take place rapidly, particularly if the material has a high moisture content or is of poor quality. Therefore, it is crucial to have a continuous and rapid flow of material from one piece of equipment to another. The flaked seeds are usually conditioned to a moisture content of 10–12% at a temperature of 80–90°C.

As indicated earlier, oilseeds consist of oil bodies that contain liquid oil enclosed by a protein membrane. A typical oil body is 2–10 μm in diameter. The walls of oil bodies are essentially nonpermeable; therefore, for subsequent solvent extraction these walls must be broken to free the oil and facilitate the penetration of solvent into the cells. This is usually accomplished by flaking the prepressed seed in a roller mill after carefully adjusting the temperature and humidity. Flakes of 0.15–0.5 mm in thickness and up to 10 mm in diameter allow rapid solvent penetration with high bed permeability.

2. Solvent Extraction

A simplified flow sheet of a typical solvent extraction process is shown in [Fig. 10](#). The seed flakes after preparation or the cakes from prepressing are conveyed to the solvent extractor. As described in detail in the section II.D, every extractor performs two primary functions. First, it must provide retention time required to allow large volumes of solvent to penetrate and wash the solid material (flakes or cake). Second, it must separate the solids from the miscella to minimize solvent carry-over in the solids to the next phase of the operation, which is desolventizing of the extracted solid material.

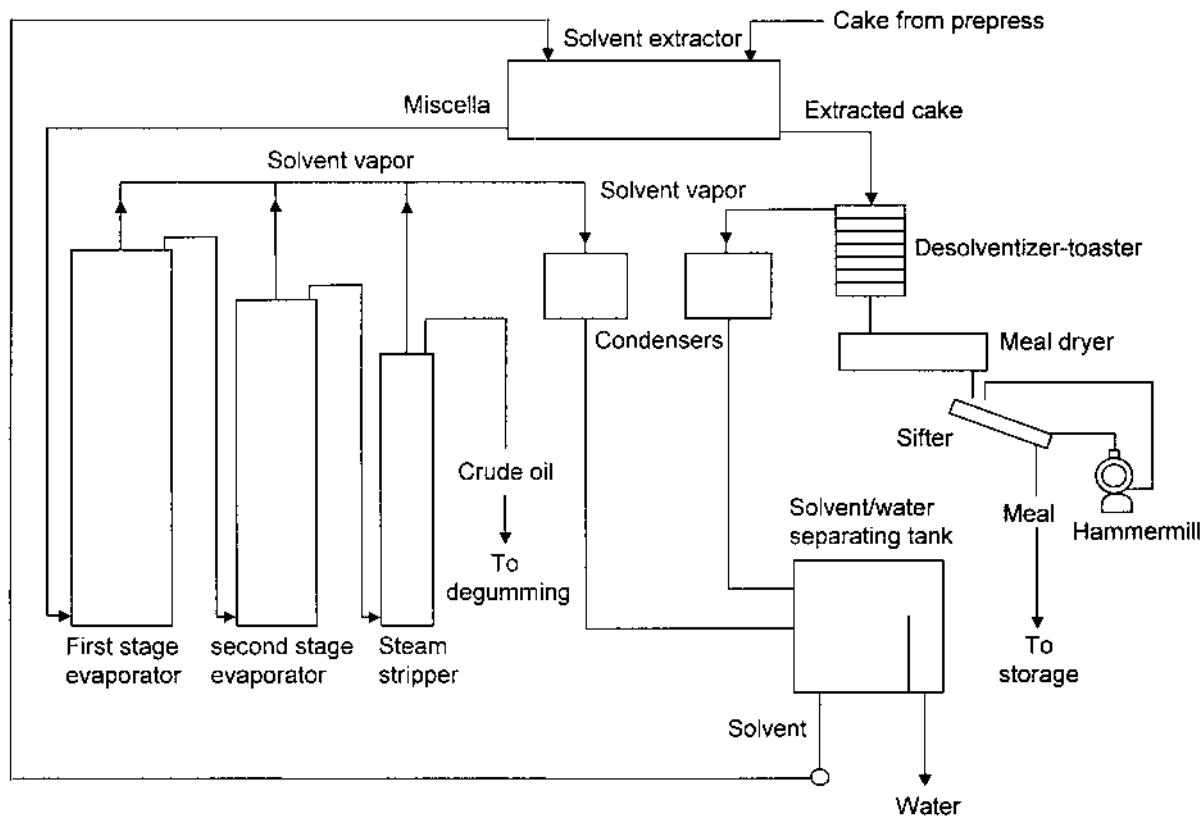


Figure 10 Solvent extraction of prepressed canola.

3. Posttreatment

After oil extraction, the solid material (meal) is transported in a closed conveyer system to the desolventizer-toaster (DT), where the residual solvent is removed by heating the meal enough to evaporate the solvent, but not so much as to deteriorate its nutritional value (Fig. 11). This unit is made of steam-heated trays mounted, one on top of the other, with a vertical shaft and sweep arms attached to move the meal around and down to the level through automatic openings in the trays. The top four trays make up the desolventizer and the bottom two trays

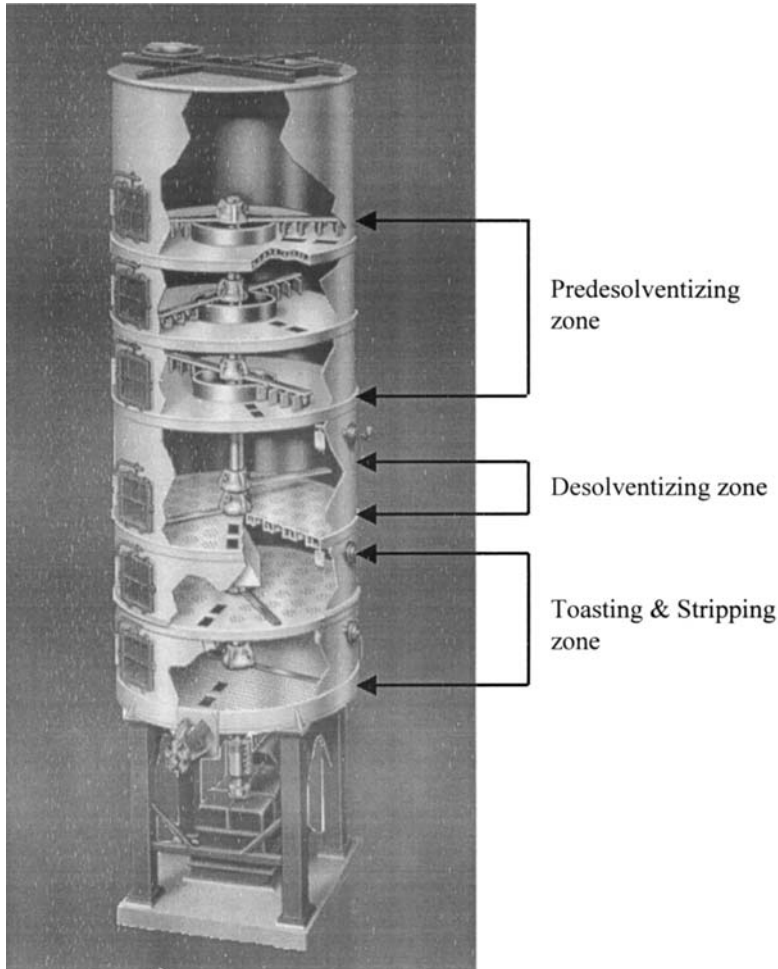


Figure 11 Desolventizer-toaster. (Courtesy of De Smet Process & Technology, Inc.)

the toaster. The desolventizer may be divided into a pre-desolventizing and a desolventizing zone. By the time the meal reaches the toaster, most of the solvent has been evaporated and moved out the top of the desolventizer. Some moisture addition through steam injection is required to facilitate further evaporation by dissociation of bonding between the meal protein and hexane through hydrophobic interactions. The meal discharged from the DT may contain considerable moisture; thus, it must be further dried for final moisture adjustment and cooled. In some cases, all of these steps are accomplished in a single unit, dubbed DTDC for desolventizer-toaster-dryer-cooler. The hot solvent vapor from the desolventizer is used in most instances to heat other evaporation equipment before being condensed and sent back to the solvent tank for reuse. Fine-meal dust is recovered prior to condensation and solvent recovery.

To recover the crude oil from miscella, the solvent must be stripped from the oil in typical distillation columns. As mentioned above, the hot desolventized vapor is used to indirectly heat the vessel to evaporate some of the solvent. An additional stripping unit indirectly heated by steam is used to remove most of the remaining solvent and water. The final traces of solvent are removed by direct steam injection. The solvent vapors are then condensed in either water-cooled or air-cooled condensers. During solvent extraction, all equipment is maintained under slightly negative pressure to minimize solvent losses. The air leaked into the system is passed through a vent condenser and a mineral oil absorption column before being vented to the atmosphere, both for explosion safety and solvent economy.

After the solvent is stripped from miscella, the crude oil can be further processed before storage, to remove entrained compounds such as phospholipids or gums.

B. Sunflower Seed

Sunflower seed processing is similar to that of other high oil content oilseeds including canola and rapeseed. Therefore, this section, concentrates on differences in the operations.

1. Dehulling

Sunflower seed contains 23–25% fibrous hull, which can interfere with the extraction process. Thus, the processor must decide whether to dehull prior to processing, which in turn determines the nature of the meal produced. Processing with the hulls produces a meal with a fiber level of about 18–20% and protein content of 28–30%. Removal of about 75% of the hulls produces a meal with a fiber level of 11–13% and a protein level of 40–42%. The market determines if dehulling is required.

However, if the hulls are not removed, they tend to reduce the total yield of oil by absorbing and retaining oil in the press cake. To accommodate the additional volume of the hulls, larger equipment is required to process the extra tonnage. Moreover, wear on the prepress lining bars and worm shafts is increased, thus increasing the cost of the already expensive prepressing operation. Therefore, dehulling is often desirable. Two types of dehulling equipment are usually used: knife and impact, although a disk type is also available. Such machines break the hull fraction away from the seed, and the mixture is then separated using shaking screens and aspiration. The dehulling process must be finely tuned to leave a minimum of meats in the hull fraction to minimize oil losses.

2. Preparation

The preparation of sunflower seed is similar to that of other high oil content seeds such as rapeseed. The seeds, or meats, are rolled to rupture and expose the oil cells. They are then conditioned, by heating, to reduce the viscosity of the oil and to make it easier to separate the oil from the meats or seeds. Proper temperature and moisture adjustments are critical to maximize the effectiveness of the prepressing stage that follows. This adjustment is usually termed as “tempering.” Cooking at high temperature is not required for sunflower seed.

3. Prepressing and Solvent Extraction

These steps vary little from canola and rapeseed processing except for the adjustments made on the prepressing equipment including the shaft arrangement, spacing of the bars in the cage surrounding the shaft, the rotation speed, and the choking mechanism. After prepressing, the cake containing 16–18% oil is broken and granulated. To make sure that the residual oil content is less than 2% after solvent extraction, some manufacturers condition and flake the broken cake pieces again before conveying them to the solvent extractor. Others simply convey the material directly to the solvent extraction process. In both cases, production of fine particles must be minimized because large amounts of fine material may cause the solvent to flood the extractor bed instead of percolating through the material for proper extraction.

C. Soybean

Oil removal from soybeans is normally carried out by solvent extraction alone since soybeans have a relatively low oil content of 18–20%, as compared with that of rapeseed or sunflower seed. The clean, dry, and tempered beans are broken into four to eight pieces in cracking mills, usually composed of two pairs

of fluted rolls turning at different speeds, cutting beans as they are fed through the two passes. The hulls of the dry beans are then easily separated by aspiration.

The cracked and dehulled beans are conditioned by raising their temperature to 65°C and adjusting their moisture content using live steam. Conditioners are normally rotating drums with an internal steam coil. Conditioning enhances the performance of the subsequent flaking and extraction operations. The conditioned beans are fed to flaking mills to produce consistent flakes with an ideal thickness of 0.3 mm. Good flaking is essential to maximize oil extraction in the solvent extractor.

Extruders are becoming the preferred means of pretreating soybeans. Water is added to the cracked seed, which is then heated and pressurized in the extruder. As the pressure is released at the exit, the absorbed water is rapidly vaporized, resulting in an expanded, porous structure where many of the cells are ruptured. This porous microstructure improves oil and solvent mobility.

The solvent extraction of soybean oil is similar to that of other seeds (Fig. 12). During the process, the heat reduces the natural trypsin inhibitor levels in soybeans, thus increasing the nutritive value of the meal.

D. Corn

Since the corn kernel contains only about 5% oil, it is uneconomical to process corn simply to obtain the oil. Corn oil is obtained by processing the corn germ, which is a byproduct of the wet or dry milling of corn, a major industry. Corn germ contains about 50% oil. This oil is recovered by expelling or direct solvent extraction (dry-milled germ), or by their combination in prepress-solvent extraction (wet-milled germ). The actual processes involved are almost identical to those described above for other oilseeds.

VI. EXTRACTION OF ESSENTIAL OILS

While edible oils are triglyceride-based oils mainly from oilseeds, essential oils are the volatile chemical components from various parts of plants, which are responsible for the characteristic aromas of these plants. To name a few, oils extracted from bitter almond, lemon and orange peels, rose and jasmine flowers, peppermint, and lovage roots are all essential oils. Although lipid-soluble, essential oils do not contain triglycerides, and they are complex mixtures of compounds that usually fall into the following four classes (29):

1. Terpenes
2. Straight-chain hydrocarbons and their oxygen derivatives

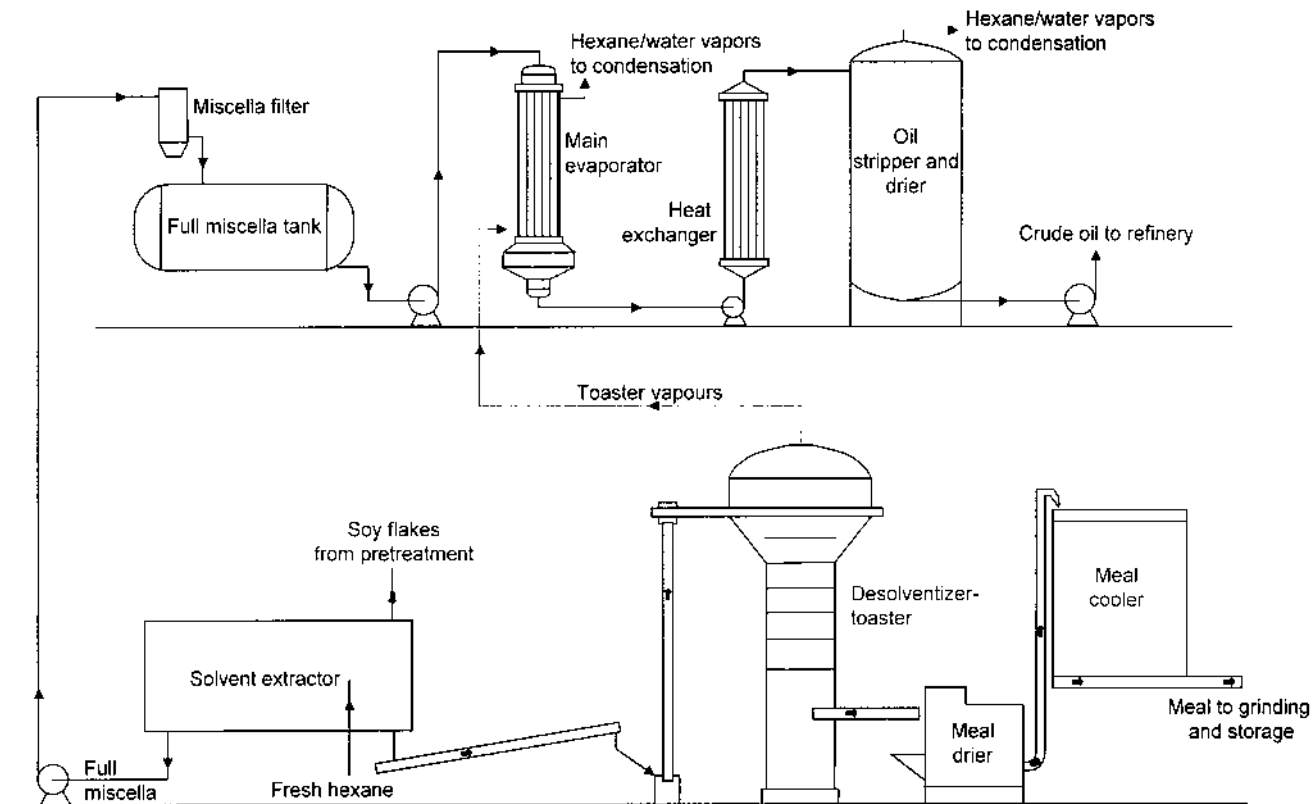


Figure 12 Solvent extraction of soybean oil.

3. Benzene derivatives
4. Volatile sulfur and nitrogen compounds

Essential oils are widely used in the food and fragrance industries. Their active components contribute a significant portion of the flavor or aroma of a spice. They are often diluted with oil or emulsified to make them dispersible before addition to a flavor or fragrance system.

To recover essential oils, distillation has always been most commonly used to take advantage of their volatility (30). The components in essential oils, however, have much higher boiling points than water; therefore, they are actually codistilled with steam or water to avoid thermal damage. Codistillation with water or steam distillation takes advantage of the fact that in the vapor phase the oil, water, and air do not interact. The composition of the vapor phase is directly proportional to the vapor pressures of the vapor components, i.e., water/steam and the volatile oils. The steam acts as a carrier and removes the oil vapors, which have been evaporated well below their boiling point. This is especially important because many of the essential oil components have high boiling points and would break down thermally well below their normal boiling points. After condensation, the oils and water are immiscible and thus are easily separated.

Like oilseeds processing, the production of essential oils also begins with the size reduction of the raw material, the comminution of the plant parts. As the essential oils are enclosed in "oil glands" or "oil cells" of the plant, the rate of oil vaporization will be entirely determined by the rate of hydrodiffusion if the plant parts are left intact, which is obviously a very slow process. Consequently, the plant material must be cut to some extent to rupture enough oil glands and meanwhile reduce the thickness of the material for the steam to diffuse, thus increasing the vaporization rate of the essential oils. The extent of comminution required varies with different plant parts. Seeds or fruits must be thoroughly crushed in order to disrupt as many of the cell wall as possible so as to make the oil directly accessible to the steam. This can be achieved by passing them through a roller as in oilseeds processing. Root, stalks, and all woody materials should be cut into small pieces to expose a large number of oil glands. They can be processed by a hay or ensilage cutter, which reduces the long natural parts of the plant to short lengths to be more easily handled for distillation. On the other hand, flowers, leaves, and other thin parts of the plant can be distilled without comminution since the structures in these parts are thin and permeable enough to allow rapid evaporation of the oil.

The crushed or chopped material is ready for distillation. Three types of hydrodistillation are used in the essential oil industry: water distillation, water and steam distillation, and direct steam distillation. In water distillation, the material makes direct contact with boiling water by floating on the water or

being immersed. The water can be brought to boil by fire, steam jacket, or coil, or even perforated steam coil. Some plant materials, such as almonds and rose flowers, can only be distilled in this manner since upon direct contact with steam they tend to agglomerate and form compact lumps, making it hard for the steam to penetrate. In water and steam distillation, the plant material is supported on a perforated screen placed above the boiling water, so that it is contacted by the steam instead of water. The steam remains saturated in this system (Fig. 13). In steam distillation, live steam (saturated or superheated) is applied through open or perforated steam coil. The choice among these distillation meth-

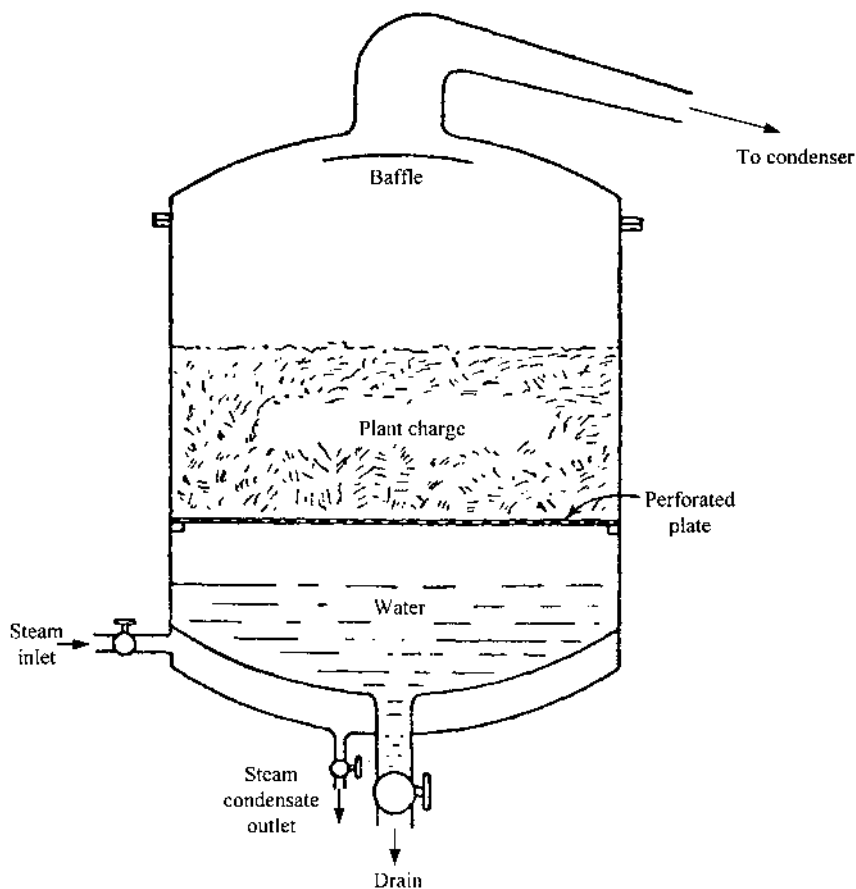


Figure 13 Retort for water and steam distillation of essential oils (30).

ods is usually based on both their efficiency and their effect on the essential oils. Although higher steam pressures result in increased vaporization rate of the oils, the higher temperatures of the pressurized steam may cause thermal decomposition of the oils.

The equipment for distillation of essential oils consists of three parts: the retort, the condenser, and the oil separator. The retort serves as a vessel where the steam or boiling water contacts the plant material to vaporize its essential oils. It can be as simple as a cylindrical container with a removable cover that can be clamped on the cylindrical section. A pipe is attached to the top of the retort to lead the vapor to the condenser. In the case of steam distillation, trays are placed close to the bottom of the container, and the steam is introduced through a open steam line. In multitray retorts, each tray is only filled with a relatively shallow layer of the material to ensure a uniform distribution of both the material and the steam. The height of a typical retort is 1.5–1.8 m. It is insulated to minimize heat loss.

The oil vapor is converted to liquid and cooled down using a condenser. The most common condensers, used in the production of essential oils are coil condensers with the oil vapor and the steam passing inside the coil while cold water enters from the bottom of the condenser and flows outside the coil against the steam and oil vapor as shown in [Fig. 14](#).

The third important part of the distillation equipment is the oil separator, which, as indicated by its name, separates the essential oil from the condensed water. Many separators are built based on the principle of the ancient Florentine flask ([Fig. 15](#)). The condensate flows from the condenser into the separator where the water and the oil separate into two layers since they are immiscible and different in specific gravity. The oil is usually lighter and floats on top of the water. Both layers are then removed continuously from the separator through outlets at different levels.

In addition to distillation, essential oils can also be processed by extraction. Extraction with cold fat is practiced with jasmine and tuberose flowers for their essential oils. Although this method gives a much greater yield than other methods, it is a lengthy and labor-intensive process. Extraction with volatile solvents is considered as the most technically advanced process, producing concentrates and alcohol soluble “absolutes,” the aromas of which truly represent the oils in their natural forms. Citrus oils, for instance, are often extracted with alcohol, from which two layers are obtained: one hydrophobic layer containing the terpene hydrocarbons and one aqueous alcohol layer with the polar compounds. They are separated and the polar compounds recovered.

The essential oils may be used as collected or subjected to further purification, concentration, or separation. Vacuum distillation is the preferred method for refining most essential oils. With this technique the oil components can be

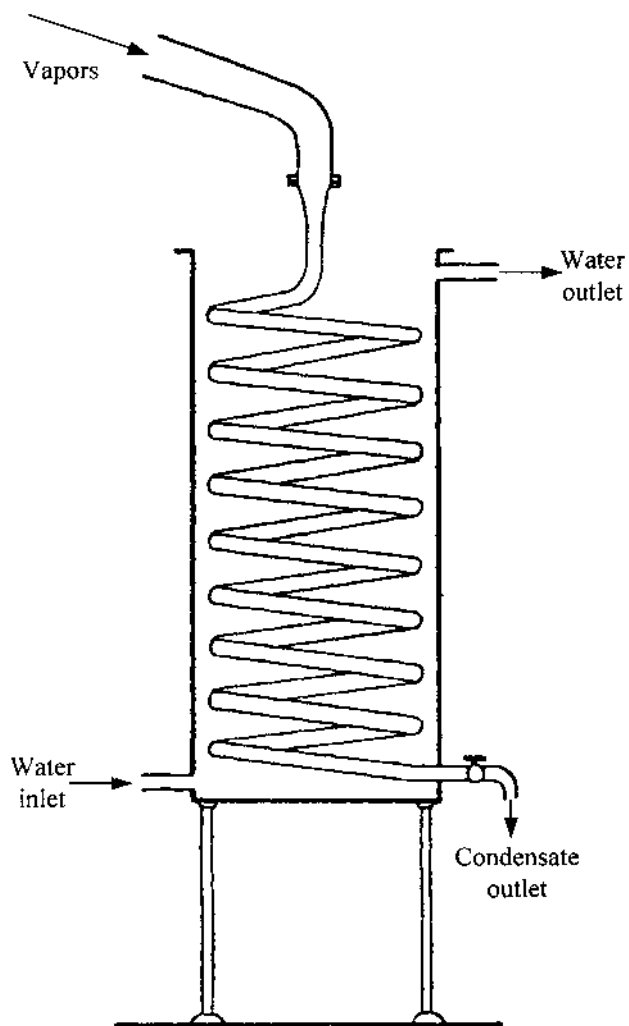


Figure 14 Coil condenser (30).

fractionated according to their boiling points. *Rectified, folded*, and terpeneless oils are made through the selection of the various fractions obtained from redistillation.

Extraction with supercritical carbon dioxide or propane is now practiced on small scales for highly valued components of plants in order to produce either flavor or aroma concentrates in the form of oils or resins.

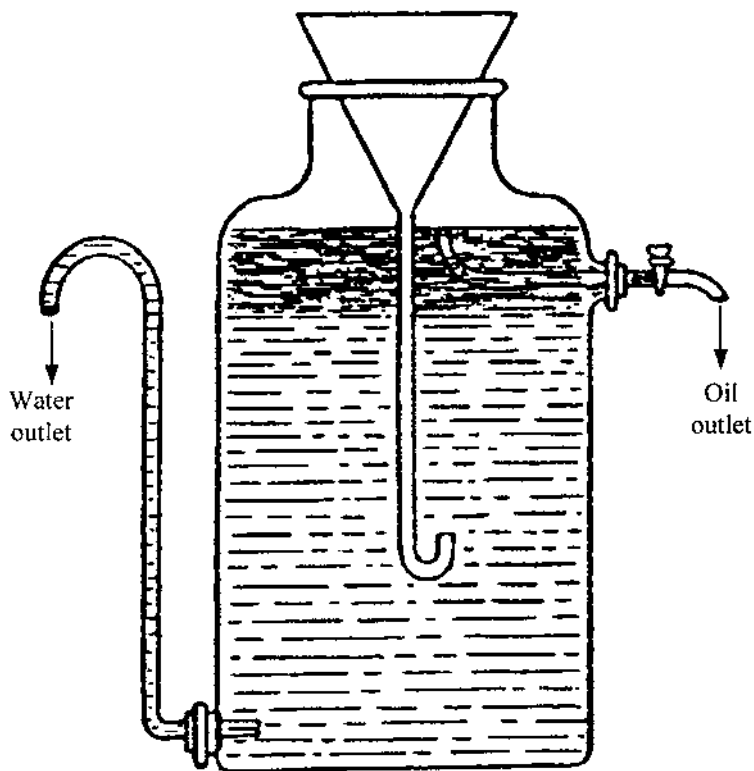


Figure 15 Florentine flask for oils lighter than water (30).

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