# 4
# Extraction Systems

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This chapter deals with different methods and equipment used for solvent extraction of food components from natural sources. A main distinction is made between systems using common liquid solvents that are industrially applied at greater scale since the first decades of the 20th century and an alternative extraction method using compressed gases, which is called supercritical fluid extraction (SFE). SFE started gaining importance in the mid-1970s, especially as a result of rising consciousness with respect to environmental aspects and the recent development of appropriate high-pressure equipment. In the first section, conventional extraction systems using liquid solvents are discussed, including equipment necessary for pretreatment and solvent recovery. The second section is concerned with selection and design of equipment required for SFE.

## I. CONVENTIONAL EXTRACTION SYSTEMS

Design of extraction systems and detailed selection of suitable equipment depends on the objective of the process and physical properties of the material to be extracted as well as of the obtained product. The solubilizing ability and selectivity of liquid solvents that are mainly based on water, hydrocarbons like hexane, or alcohol are used to leach or extract certain desired components from the applied source material, which is a naturally obtained solid in this case. This section first focuses on the extraction process itself describing different processing principles and giving an overview of the required equipment. Product quality and extraction efficiency depend very much on conditioning of the solid feed material ahead of solvent extraction, which will also be discussed. Posterior to

extraction, the solvent has to be recovered from the product and the exhausted meal, taking care of the product quality and increasing environmental demands. Finally, an example of a complete plant used for hops extraction by alcohol is described.

## A. Classification

In the past, extraction or leaching was often divided into percolation and immersion methods, referring to whether the solid is completely submerged or the solvent is just trickled through a solid bed (1). In general, classification has become clearer since technical development has concentrated on a few different types of extractors, most of them working continuously as percolators (2). On the other hand, immersion leaching of solid-solvent slurries using agitators or screws has largely lost industrial relevance. Even though many of the former extractor types (3) have nearly disappeared, they are still worth mentioning because older equipment may still be perfect for certain applications. Therefore, it is useful to start out by listing all possible operation modes and the relative working principles in order to document technical improvements in the past decades but finally focusing on the actual state of the art.

### 1. Operation Mode

*Batch Extraction.* Within batch processing, extraction is carried out in vessels that are filled with the solid matter to be extracted. Afterward solvent is either percolated through the solid bed or added to the vessel until the solid is completely submerged. In the latter case, the solvent-solid mixture may be stirred so as to enhance mass transfer. After a designated holding time, the solvent-extract mixture, called miscella, is drawn from the vessel and the solid matter is discharged. This way of processing has almost completely disappeared because of the required interruptions of the operation for charging and discharging and high amounts of required solvent. Only for some special applications with small product rates, such as extraction of flavors, is batch extraction still used (e.g., extraction of lavender).

Operating several batch extractors in parallel with cross-current solvent flow allows achievement of higher product rates but does not make use of the entire solvent capacity.

*Quasi-continuous Extraction.* In order to increase extractor efficiency, several batch extractors can be operated in series using the solvent that is loaded in one extractor for passing it through another solid bed that still contains higher amounts of extractable substances. In this way, solute concentration is enhanced, gradually approaching the total solvent capacity. One or two extractors are always off-stream for discharging and charging. After a certain interval, input and

output ports are changed so that the solid bed extracted to the highest extent is shut off for discharging and a freshly charged extractor is switched in-line. Usually, extraction is performed countercurrently for maintaining continuously a sufficient concentration gradient of the solute in the solid matter and the solvent. Therefore, the freshly entering solvent is contacted with the solid extracted to the highest extent. Afterward, the solvent is passed through the extractors in the order of decreasing bed age until the solvent is almost completely loaded and is brought into contact with the latest charged solid.

*Continuous Extraction.* For complete continuous operation, the solid matter has to be charged and discharged continuously to and from the extractor. Different types of conveying systems exist depending on whether percolation or immersion extraction is applied. These are presented in the following. In the case of extraction performed under conditions other than atmospheric pressure, either adequate sluice systems for the solid matter are required or quasi-continuous operation must be applied. If, for instance, proper extraction temperatures are above boiling temperature at atmospheric pressure, extraction is to be performed at elevated pressures. With the use of flammable organic solvents their escape through leakages can be prevented by operating under slight vacuum. Table 1 gives an overview of different types of extractor systems, including their field of application with some specific examples.

## 2. Working Principle

*Single-Stage Extraction.* The simplest apparatus for liquid solvent extraction is a single-stage vessel used for immersion extraction. In order to confine the extraction period, the vessel may be stirred. Therefore, the solvent-solid mixture should form a flowable slurry. The extraction time has to be optimized because after a while extraction kinetics becomes quite slow and additional leaching becomes time consuming. The loaded solvent is retrieved and replaced by fresh solvent. This procedure is repeated several times until the solid matter is extracted to an acceptable extent.

*Multistage Extraction.* In multistage static-bed extraction using a countercurrent operation mode, the fresh solvent enters the vessel containing the most exhausted solid. The extract being retrieved from this vessel is successively passed through a battery of extractors until arriving at the vessel most recently loaded. The extract retrieved from this one is discharged for further processing, i.e., desolventizing. The purpose of this operation is to increase the solute load of the solvent to a maximal value for posterior product separation and for solvent recovery to be as economical as possible. This method of quasi-continuous processing can be carried out with immersed solid as well as a solid bed exposed to percolating solvent. A typical application is the extraction of

**Table 1** Extraction Systems: Characteristics and Applications

| Operation | Working principle | Extraction system | Field of application | Examples |
|---|---|---|---|---|
| Batch | Immersion extraction | Stirred vessel | Pharmacy | Alkaloids |
| | Static bed percolation | Single-stage percolator | Spices | Pepper |
| | Static bed cross-current percolation | Multi-stage percolator | | |
| Quasi-continuous | Stationary bed, countercurrent percolation | Multistage percolator battery | Instant material, sugar | Instant coffee, sugar from beets |
| Continuous | Rotating cells, countercurrent percolation | Rotocel | Vegetable oil | |
| | Rotating bed, countercurrent percolation, stationary sieve tray bottom | Carrousel | Vegetable oil, spices, instant material | Soybean oil, paprika, pepper, hops |
| | Stationary bed, countercurrent percolation, rotating feed/discharging locations | Stationary basket | Vegetable oil, spices | Wheat germ, paprika |
| | Horiz. moving bed, countercurrent percolation | Sieve tray belt; sliding cell | Sugar | Sugar from beets/cane |
| | Horiz. moving bed, co-/countercurrent percolation | Crown loop extractor | Sugar, vegetable oil | Sugar cane, soybean oil |
| | Vert. moving bed, co-/countercurrent percolation | Basket elevator | Vegetable oil | Flaked oil seeds |
| | Moving bed, countercurrent, immersion | Screw conveyer | Sugar | Sugar beets |

coffee for instant coffee production by a battery of percolators. At temperatures of up to 180°C and pressures of up to 20 atm, around 40–60% of water-soluble material is extracted from coffee grounds by water in an upstream or downstream fashion. At temperatures above 140°C hydrolysis of polysaccharides takes place enhancing their solubility, which increases the total extraction yield. These sugars are also capable of retaining flavors. A series of four to eight percolators allows the establishment of temperature gradients along the extraction line for taking influence on product yield and quality due to differing solubilities of the various substances present in roasted coffee (4). Figure 1 shows a battery of percolators for instant-coffee extraction. Vessel diameters range from 0.25 to 0.75 m. Typical capacities are around 1 t resulting in bed heights of 4.5–6 m. Applying vacuum to the vessel facilitates loading of the percolators. The ball valve at the top is opened and the grinded coffee enters the vessel. Grind sizes range from 3 to 5 mm, the result of a compromise between favoring mass transfer and limiting pressure drop. After being sufficiently leached, the spent coffee ground is discharged by "shooting" through the ball valve at the bottom of the vessel. Holdup is maintained at 30–35 min showing a tendency to shorter times.

An extractor system developed by NIRO (Denmark) for coffee extraction, called FIC (fast instant coffee), comprises seven percolators arranged in a circle as a compact unit (Fig. 2). The percolators themselves are about half the size of conventional percolators reducing residence time to half. By their relatively compact design, high liquid velocities are reached that enhance mass transfer from the ground coffee particles. Operation is carried out in two steps based on water temperatures of 100°C for aroma extraction and 180°C for hydrolysis of polysaccharides. The process works with high efficiency although concentration of the produced liquid extract is somewhat lower than in the case of normal percolators. The complete extraction cycle takes about 1.5 h from the fresh water entering the unit to withdrawing the concentrated coffee solution.

For extraction of sugar from sugar beets 10–16 columns are used, each having a diameter of around 1.6 m and a height of 2.6–3.2 m, resulting in volumes of 3–4 $m^3$. The scalded beets (cossettes), resembling shoestring potatoes of 3–7 mm width and 5–8 cm length, are loaded to the vessel by means of hinged covers. Extraction is carried out using water at 40–75°C. Holdup is kept between 50 and 120 min. Different apparatus alternatives also exist such as versatile, chain belt, and ring extractors.

*Moving-Bed Extraction.* Extractors with continuously moving beds are distinguished according to the mechanism of transporting the solid matter and contacting the solvent. Moving-bed extractors can be divided into percolators and immersion extractors. In percolation extraction, the solvent phase is passed through the solid bed, which is mainly stationary with respect to the solid-

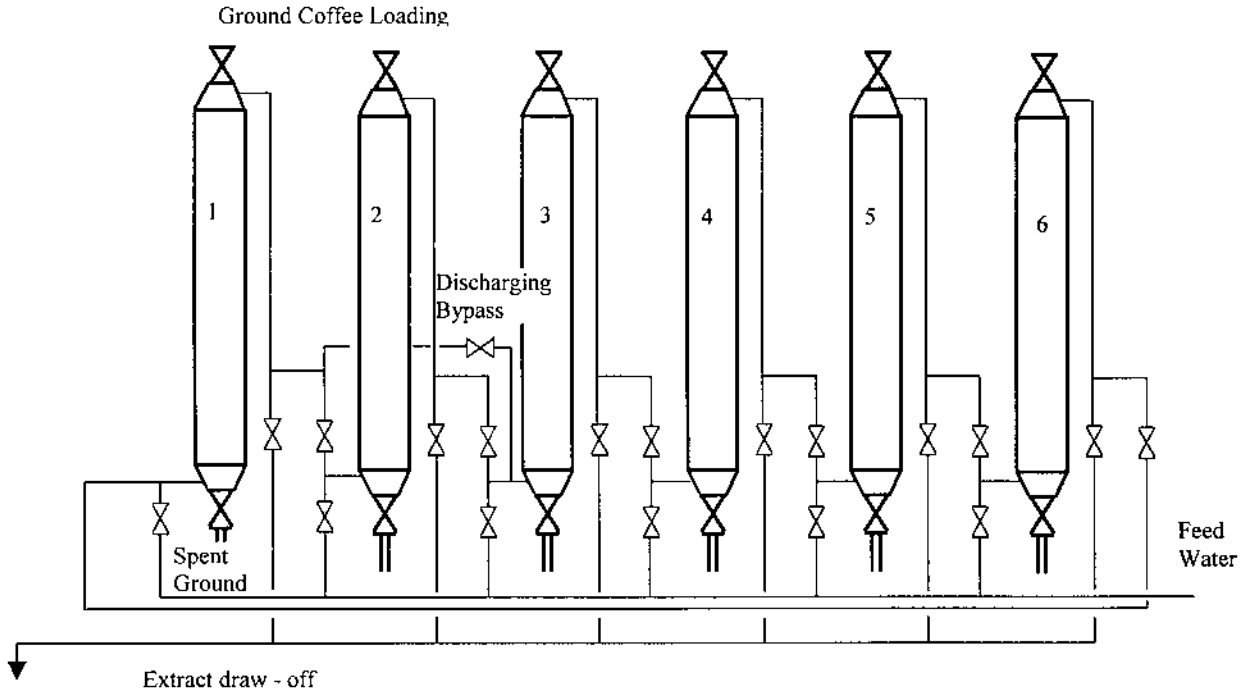


**Figure 1** Schematic of a percolator battery. Each percolator can be bypassed for discharging/charging as indicated only in the case of the second percolator.

**Figure 2** FIC extractor for instant-coffee production. (Courtesy of Niro, Denmark.)

containing cell. Most extractors that make use of the percolation principle have conveyer elements such as conveyer belts, frames, cells, or baskets that carry the solid matter through the extractor. Depending on the actual position, either fresh solvent or miscella is sprayed on the solid passing by. Commonly, fresh solvent is sprayed on the most exhausted solid. The miscella leaving here is recirculated and used for extraction of freshly entering solid. Recirculation is also used for enhancing contact time by submerging the bed to a greater extent. As much as possible countercurrent flow of solid with respect to solvent must

be achieved. Accounting for the flow direction of the draining miscella, the general flow pattern is a cross-countercurrent flow. Nevertheless, when making use of gravity for miscella flow, as in basket elevators or loop extractors, some places of cocurrent flow are unavoidable. If the static solid bed is mixed up at least once during extraction, e.g., by dumping the content of one basket into another, a slightly higher yield may be achieved. To a certain extent, solid mixing already occurs in loop extractors. Cross-current operation of a moving bed means that fresh solvent is used throughout the entire extractor, resulting in rapid leaching of the solid but also causing a high consumption of solvent.

An intensive solid–liquid contact, which includes continuous mixing of the solid, is carried out in immersion extraction using screws for conveying the solid through the extractor that is filled with solvent. The extractor may even consist of several different compartments dividing zones of different miscella concentrations. In this case, solid transport is achieved by screws from one trough to the other throughout the whole extractor. The solid is submerged partly within the solvent realizing countercurrent flow between the solid and the solvent. Immersion extraction is keener in facilitating entrainment of small particles than percolation where there is always some sort of self-filtration. Thus, solid content in the miscella after immersion extraction may easily rise to 1–10%, whereas there are only several parts per million after percolation.

## B. Industrial Extractors

Some general trends concerning efforts for improving extraction efficiency and performance can be observed. Development of an extractor implies a compromise between simplicity with respect to the number of moving parts and transporting systems, such as solvent pumps and solid-conveying systems, and efficiency of recirculation pattern for the miscella. Extractors containing compartments, as opposed to simple conveyer belts, facilitate submersion of the solid, which usually leads to higher extraction efficiencies. Shallow beds that are not divided into separated stages are in danger of forming lakes of solvent freely flowing on the bed surface and mixing miscella of different concentrations. Instead, in deep beds the absolute residence time is often enhanced so that the liquid (miscella or solvent) is sprayed on such a moving bed and dissolving solute on its way, then is drained from the solid in a subsequent section that does not correspond to its solute concentration. For example, full miscella drained from the descending leg of a basket elevator might be collected in the half-miscella tank below the rising leg.

In the following, different types of extractors working with a moving bed are presented. Most of these extractor types have existed for several decades. Technical improvements are mostly confined to some details concerning the position of inlet/outlet streams and recirculation of miscella. The extractors are

subdivided into those containing rotating parts and those in which longitudinal movements are carried out. The latter machines make use of conveying elements such as conveyor belts or chains. In general, capital costs are lower than in case of the rotating principle. Moreover, they can be delivered preassembled to a great extent. Since they mostly work with a shallow bed, extraction results may differ from the previously mentioned rotating deep-bed extractors depending on the material being extracted. In general, the range of application of shallow-bed extractors is somewhat confined due to the extractability and permeability of the meal.

The *Rotocel* extractor is a well-established extraction system developed by Blonox in the early 1960s (5). Then the successor Dravo closed down and fusion of licensees Krupp and Extraktionstechnik in 1990 resulted in production of the *Carrousel* extractor. The Rotocel consists of up to 18 cells located in a circle, each of them containing perforated bottoms that are periodically opened when the cells pass the discharging section during their rotation. One rotation lasts more than 1 h depending on the extractability of the solid. The rotational energy requirement is fairly low because in spite of large diameters there is little frictional force to be overcome. The Rotocel is a so-called "deep-bed" extractor, with a bed height of 1.8–3 m. The flakes, which may also be introduced as a slurry using miscella, are not moved relative to their neighbors. In this way fragile solid structures can be handled, but there is no additional mixing effect that otherwise could enhance extraction yields. Miscella drawn from the bottom of the cells is collected and used for leaching solid of less bed age. This recirculation system consists of up to 10 miscella pumps.

The Carrousel extractor is similar to the Rotocel, except that only the frame of the extraction compartments rotates atop a static sieve tray, the structure of which is shown in Fig. 3. In this way, friction of particles scrapping along the sieve tray bottom needs to be overcome; but on the other hand, particles are kept in movement relative to each other, which enhances mass transfer.

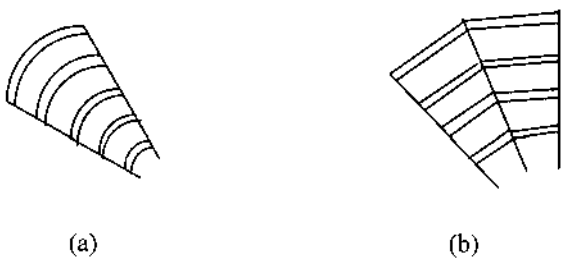


**Figure 3** Segment of the sieve tray bottom of a carrousel extractor. Original (concentric) (a) and actual (b) orientation of sieve gaps.

One rotation takes about 1 h, which means that at a diameter of 8 m the highest relative velocities of particles with respect to the sieve tray bottom do not exceed 7 mm/s. After being exposed to different extraction stages during one cycle, each compartment arrives at the solid outlet position where the complete solid bed of the respective compartment is discharged through the open bottom. The separation walls of the compartments have a conical cross-section (Fig. 4) that helps in discharging the exhausted meal downward.

Carrousel extractors have diameters of up to 15.3 m. At a bed height of 2 m an extractor of 8 m in diameter has a capacity of 75 $m^3$. Double-deck carrousels containing diameters of up to 8 m are also in use (Fig. 4). After passing one cycle in the upper deck, the solid drops onto the lower level for extraction during another rotational period. Such an extractor is capable of extracting oil from 2000 t/d soybeans containing 18% of oil using hexane; the residual oil content amounts to 0.8%. Triple-deck carrousels have also been constructed, but poor accessibility to the middle deck for cleaning and repairing is a disadvantage. Figure 5 gives an overview of solid and liquid flow, also indicating the respective extract concentrations in countercurrent extractors like the Carrousel extractor.

The weight of rotating parts can be reduced by using a stationary basket extractor originally fabricated by French Oil Mill Machinery Co. In such an extractor, the compartments filled with solid are stationary and only feed spouts and the positions of the solid discharging facility and draw-off of miscella rotate. Usually, 12–20 cells are applied, each of them 1.8–3 m deep. In the meantime, the French Company switched from the stationary basket principle to carrousel-type extractors.

Next to rotating extractors also the conveyer belt principle is applied to oil extraction. DeSmet uses sieve tray belts for transporting the meal in their *belt extractor*. Either fresh solvent or miscella provided by a system of miscella recirculation is sprayed onto the shallow solid bed usually containing heights lower than 0.6 m. The solvent containing the freshly extracted solute drops from the belt into collecting trays. Before leaving the extractor, the solid is treated once more with pure solvent (benzene). A slight vacuum within the extractor is obtained by Venturi nozzles. Belt extractors have the advantage of low apparatus costs and fairly uncomplicated installation. Extraction results depend on a precise adjustment of transporting velocity, amount of liquid sprayed on the solid, and solid bed permeability. Following efforts to submerge the solid bed to the highest extent possible, lakes may be formed on top of the solid moving bed freely flowing to all sides and mixing half and full miscella with one another.

Similar to rotational extraction systems, horizontal/vertical working extractors offer different ways of moving the solid for passing it through different stages of extraction. In general, recent development is leaning toward stationary screen plates or sieve trays on which the solid is pushed by cells or frames fixed

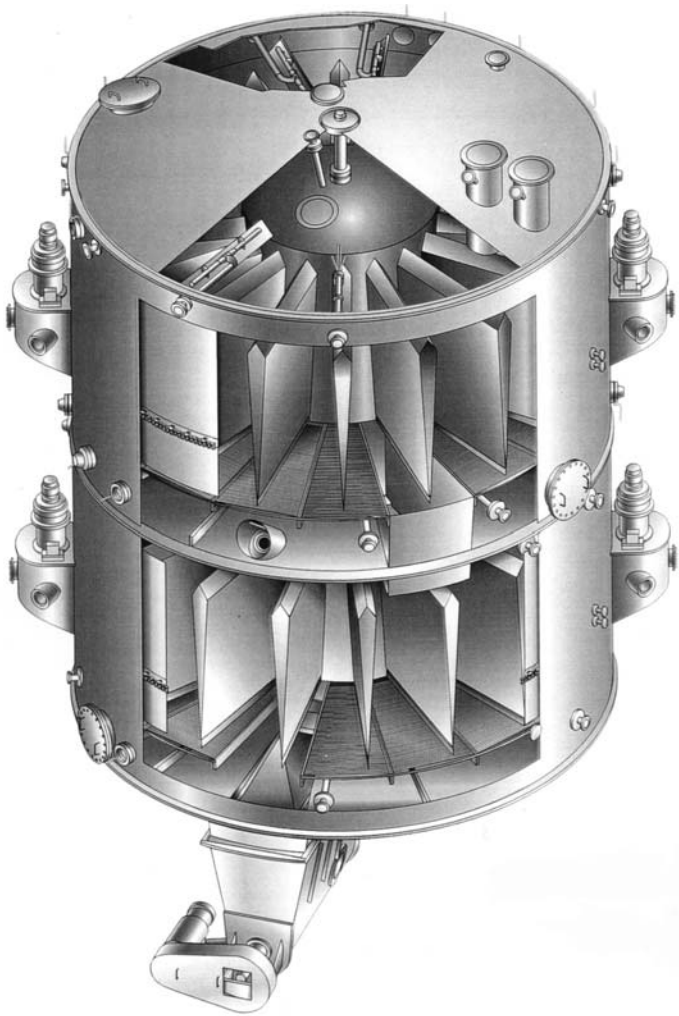

**Figure 4** Interior of a double floor carrousel extractor. (Courtesy of Krupp, Hamburg.)

to chain conveyors, as in the case of the *Crown loop extractor* (Fig. 6). The loop extractor is quite compact with one cocurrent and two countercurrent extraction zones.

In the *sliding cell extractor* from Lurgi (Fig. 7), U-shaped cells run on roller tracks pushing the solid material over stationary screen plates. The screen plates consist of rods aligned in a flow direction. The cross-section of the rods

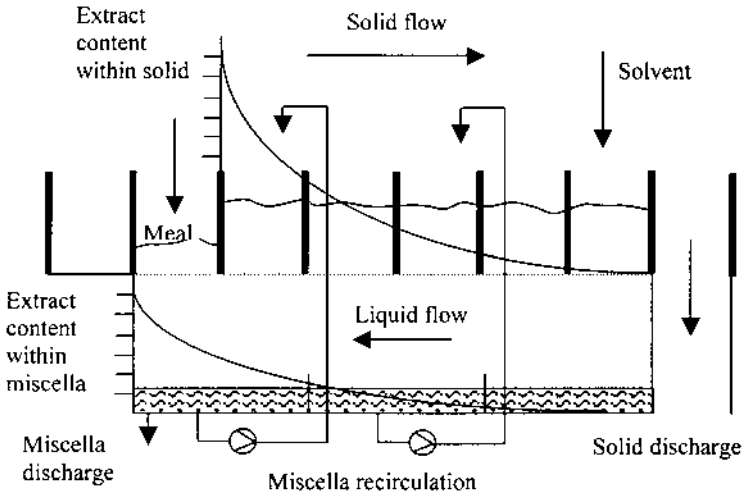


**Figure 5** Concentration profiles of countercurrent extraction, e.g., Carrousel extractor.

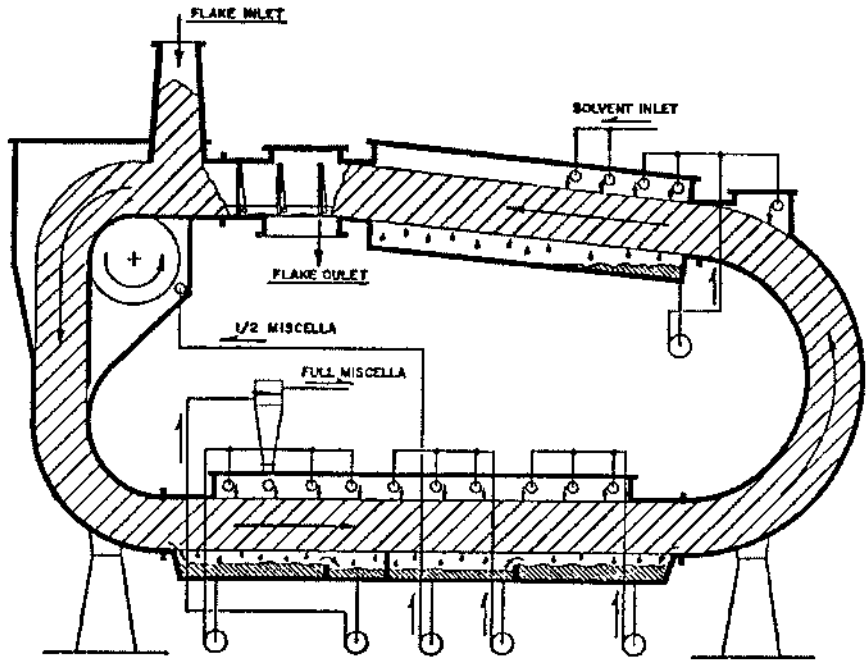


**Figure 6** Crown loop extractor.

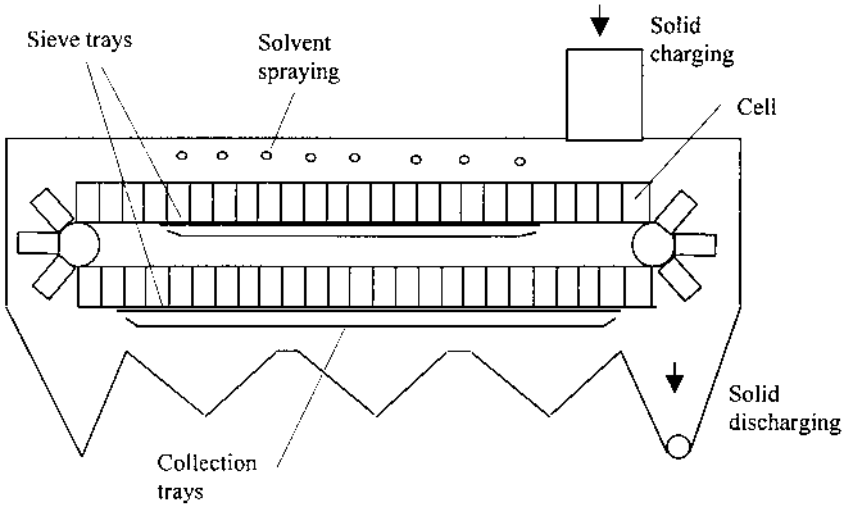


**Figure 7** Lurgi sliding cell extractor.

is V shaped to prevent clogging. The feed material is introduced into the cells of the upper belt by a filling device. After approximately half of the extraction time, the screen plate ends and the feed is dumped through the open cell bottom into the cell, just arriving at the lower screen plate in the feed transfer stage, as indicated in Fig. 7. Before being discharged, the feed is passed through a final drainage zone. The solvent passes through the feed material countercurrently by spraying the collected miscella onto feed at a previous position; it becomes enriched with extract until finally leaving the extractor.

Recently, a *sliding bed extractor* was developed by Krupp containing a chain-frame conveying system on top of a static sieve tray passing two levels (Fig. 8). Miscella collection is also divided into two levels with a sophisticated recycling system. Full miscella is liberated from fines by integrated hydrocyclones. Bed height is adjusted at 0.5–1.3 m.

Baskets fixed to a conveyer belt allow either for construction of tall extractors that take little floor space or for horizontal extractors in case one-floor operation is required. A variety of methods concerning collection and recirculation of the miscella and solvent-solid feed positions exist, always intending to maximize the number of regions of countercurrent flow while confining the number of pumps required. The *basket elevator* (Fig. 9), also known as the Bollman extractor (6), contains a rising and a descending leg, each of which contains around 15 baskets that continuously descend and rise undergoing different stages of charging/discharging of solid, fresh solvent, and circulated ex-

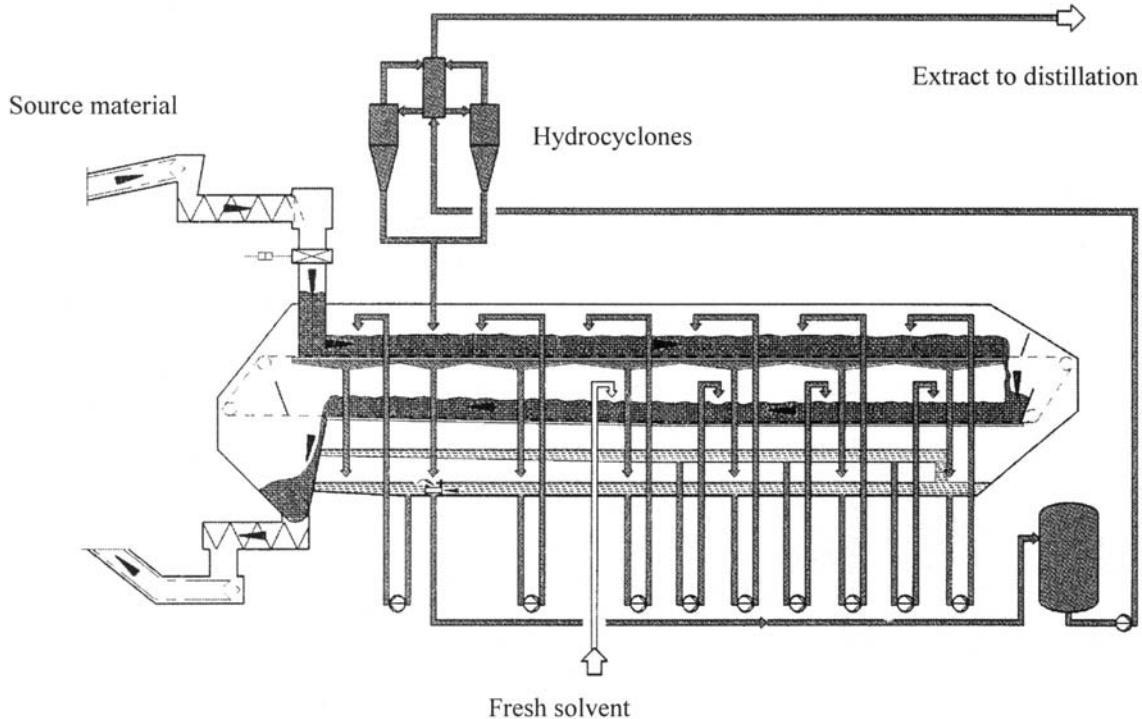


**Figure 8** Sliding bed extractor. (Courtesy of Krupp, Hamburg.)

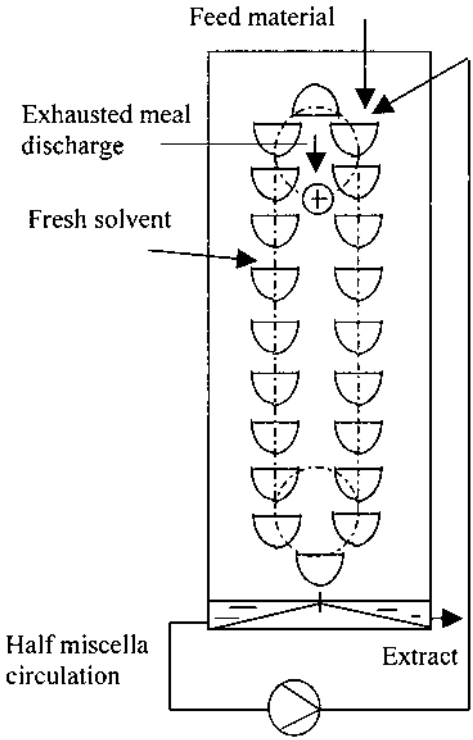


**Figure 9** Basket elevator.

tract. The solid bed formed in the baskets is rather shallow taking heights between 0.5 and 0.7 m. The solid is fed to the top basket of the descending leg. At this place, half miscella originating from drainage through the more exhausted solid beds of the rising leg is introduced draining downward through the descending baskets in a cocurrent fashion. The miscella draining from the bottom basket of the descending leg is collected in a sump and drawn off for further processing. Fresh solvent is sprayed on the top basket of the rising leg draining downward through the rising baskets in a countercurrent fashion, while extract concentration is enhanced resulting in the formerly mentioned half miscella, which is collected in a sump at the bottom. After arriving at the top and being contacted to fresh solvent, the exhausted solid is discharged by inverting the basket.

A couple of extractor types make use of the screw transporting principle, such as the vertical screw tower from Buckau Wolf, Germany, the Hildebrandt extractor formerly applied to soybeans, and the horizontal helix from Raffinerie

Tirlemontoise used for sugar beets, all of which have not been in operation to a great extent (5). Two helicoidal screws transport the solid through the double-screw conveyor called *Contex*, offered at present by Niro, Denmark. The extraction liquid flows through the solids as a submerged stream by means of gravity due to a slight inclination of the vessel. Complications during operation are caused by disintegration of solid particles and flow conditions that depend on solid compacting.

Multiplate tower extractors like the *Bonotto* extractor make use of rotating plates or paddles for transporting oilseed flakes until they fall through openings in the plates to the floor below. Solvent and miscella are transported upward in a countercurrent fashion. Such problems as bypassing, fines entrainment, and back mixing of miscella inhibited commercial application.

## C. Safety Aspects

Working with volatile and flammable solvents implies risks. During normal operation, a number of measures, such as the use of explosion-protected equipment, working at slight vacuum and continuous control of escaping gases by ignition detectors can for the most part guarantee safe handling. Thus, most accidents involving ignition of solvents or even explosions occur as a result of equipment failure (7). When the plant is shut down and vessels are opened for repair, strict safety guidelines might be missing and residual solvent vapors might come into contact with air, producing flammable mixtures. The U.S. National Fire Protection Association has formed a committee dedicated to safety of solvent extraction plants, which issued the following statement given in part:

> NFPA 36 Committee on Solvent Extraction Plants:
>
> Par. 5–8.3: Extractors, Desolventizers, Toasters, Dryers, Spent Flake Conveyers shall be of a design that minimizes the possibility of ignition of product deposits. Such equipment shall be protected by extinguishing systems using inert gas, steam, or a combination of the two, controlled from a safe remote location.
>
> Par. 5–8.1.7: The extractor shall be provided with means to remove solvent vapors so that the concentration of vapors inside the unit in the area where work is required can be maintained at or below 25% of the lower flammable limit, e.g., by a purge fan sized so that it changes the empty air volume of the vessel once every 3 min.

## D. Conditioning

### 1. Mechanical Pretreatment

Extraction efficiency is highly contingent on preparation of the solid matter that undergoes extraction. Small particles are advantageous to small diffusion

resistance within the particles. On the other hand, powders of very small particle size require great efforts of milling or grinding. While preparing the solid bed, reagglomeration may even occur and during operation as a trickle bed extractor channels might be formed, resulting in insufficient extraction yields. If the bed's permeability decreases pressure drop might increase and lakes may be formed on top of the solid bed. Drainage is retarded, which may result in undesired back mixing in case the solid bed is moved through successive extraction zones within the extractor. Furthermore, the so-called fines of very small particle sizes are at risk of being entrained. In general, the content of particles of diameter below 0.5 mm should not exceed 5–10%.

Oilseed processing preparation methods may be distinguished depending on whether they are combined with mechanical deoiling or are applied for obtaining solid material of defined size and structure. In the case of oil content above 25 wt%, mechanical deoiling by expression is suitable for economical reasons. Rapeseeds and sunflower seeds both containing more than 40% and corn germs with about 50% oil always undergo previous pressing. Cottonseeds containing about 25% are the limiting case for previous mechanical deoiling. Corn and soy, containing less oil, are usually directly extracted after conditioning. Mechanical deoiling implies changed characteristics of the feed material for extraction, e.g., moisture and cell structures differ from their natural state due to high pressing temperatures. Even agglomerates may be formed that have to be crushed prior to further processing. Furthermore, different equipment for mechanical pretreatment exist due to the type of force applied. The fluted rolling mill (Fig. 10) mainly cuts larger particles into pieces. A hammer mill (Fig. 11) inserts kinetic energy in particles, which is converted to surface energy by increasing surface area during impact with the agitator or the wall. In this case, the fines content is higher than that of the formerly described cutting principle.

A roller mill works by pressing two cylinders against each other. In case there is no differential circumferential speed, the seeds are flaked only by com-

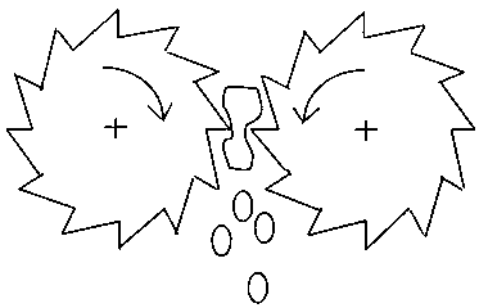

**Figure 10** Working principle of a fluted breaker rolling mill.

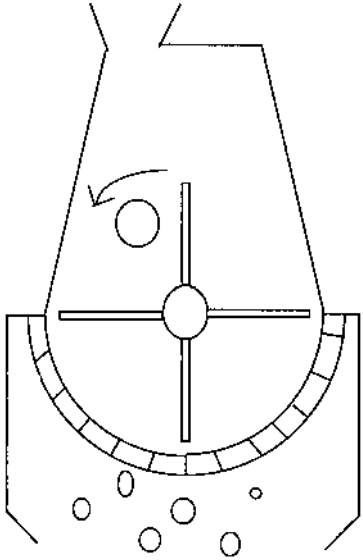

**Figure 11** Working principle of a hammer mill.

pressing. A slight differential speed gives rise to shear forces, and seeds may also be ruptured. Extruders being high-shear devices are also capable of rupturing oil cells prior to solvent extraction or mechanical pressing. For processing of high oil content material the extruder may be provided with a drainage cage similar to those used for screw presses described below. In order to obtain particles of defined size, pelletizing or granulating may be applied by pressing, cutting, or adding moisture. The adequate pretreatment depends on the individual feed material and must be determined by experience.

As already mentioned, if the content of extractable substances is fairly high, prepressing is carried out prior to extraction. Commonly, the screw presses used easily reduce the oil content in solids to 10% or less. Following solvent extraction requires less solvent because of the reduced amount of extractable substances. In addition, cell structures are destroyed, mechanically liberating enclosed substances. Using a pressure measurement technique described by Eggers et al. (8), the screw geometry may be adjusted to obtain an adequate pressure profile for achieving an optimal pressing result. Presses of the EP series manufactured by Krupp contain a shaft with a rising outer diameter in flow direction at a constant inner diameter of the strainer cage (Fig. 12) in order to achieve adequate compacting. Recent developments tend to obtain the complete final product only by mechanical treatment (full or final pressing; see section

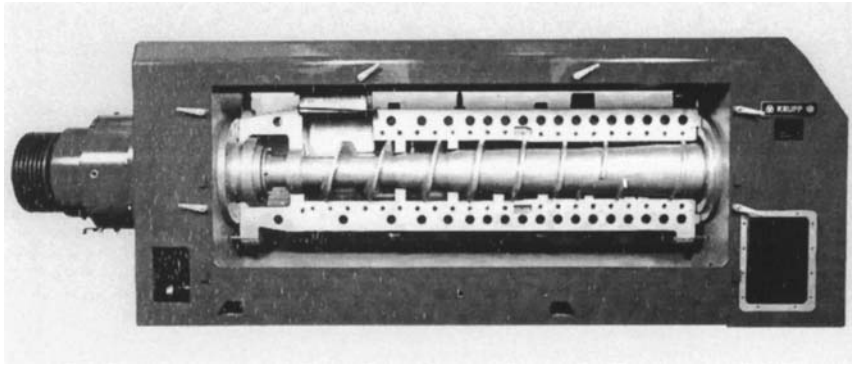

**Figure 12** Screw press. (Courtesy of Krupp, Hamburg.)

below). Therefore, different steps of pressing according to different operating temperatures may be applied for obtaining products of specified quality and quantity. Usually, elevated operating temperatures result from frictional forces. In order to avoid temperature rising, cooling of the press is needed. On the other hand, rising solid temperature before feeding may help performance and enhance product yield. A press recently developed by Krupp contains different temperature zones within one machine. Here prepressing is carried out at lower temperatures resulting in higher product quality but low yield. Final pressing at elevated temperatures has the objective of enhancing the product yield. Monforts has developed a compact double-acting screw press called *Komet* having a broad range of applicable source material (9) but without any special facility for cooling. Screws of various slopes are used for solids of different hardness, but the shafts always have the same constant outer diameter. Compacting is additionally regulated by use of different nozzles at the cake discharge spout. Very hard solids should be broken or crushed before being fed to the press. If the residual press cake still contains a considerable amount of extractable substances, solvent extraction follows pressing but the compacted solid cake should pass through a cake breaker first.

Presses manufactured by Anderson International under the name *Expeller* are in use for prepressing and full pressing of a variety of oil containing material such as cottonseed, peanuts, corn germ, and sesame seed. After conditioning for careful adjustment of its temperature, the feed material enters the downspout where it receives a first pressing by a vertical screw (Fig. 13). Leaving this section, the solid arrives at the horizontal barrel containing a second screw for final pressing. The compacting pressure of the solid cake is regulated by a hydraulic cone choke at the position of solid discharge. A couple of different

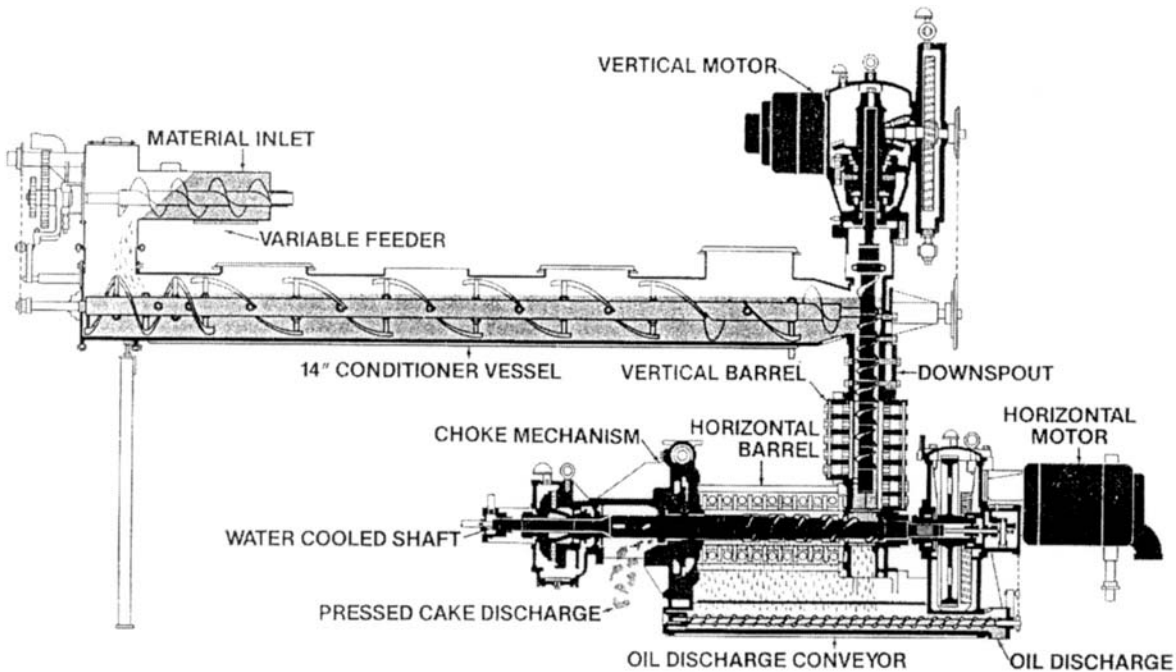


**Figure 13** Pressing by Anderson Expeller. (Courtesy of Anderson International Corp.)

Expeller types are offered to meet specific demands. The Expeller 33 prepress leaves 15% residual oil content in the cake for further solvent extraction working at rates of up to 90 t/d feed material. The 33 duplex press was developed to handle especially hard fibrous and high oil content materials such as copra and palm kernels. The residual solid contains about 7% oil. The high-capacity Model 55 allows processing of more than 25 t/d with residual oil contents of 4–5%. Commonly, Anderson expellers are combined with thermal conditioning like cooking and drying of the feed prior to pressing.

### 2. Thermal Pretreatment

Materials that are destined for oil production and contain a large amount of proteins, such as cottonseeds, soybeans, flaxseeds, sesame seeds, and peanuts, must be cooked prior to pressing in order to coagulate proteins and allow efficient recovery of the liberated oil. Therefore, the raw material is maintained for about 20 min at a moisture content of around 10% and temperatures of 90–95°C. Afterward the material must be dried in a separate step to approximately 3% moisture before entering mechanical pressing so as to stiffen the particles. Materials containing small amounts of proteins only undergo the drying procedure. Drying time strongly depends on the physical properties of the solid particles, e.g., size, moisture, and porosity.

Cooking of proteins and starches is combined to adjustment of moisture and porosity by the expander technology. Vapor is introduced into the solid structure during extrusion in a screw press–like device containing steam inlet nozzles at the circumference (Fig. 14). The solid-vapor mixture is expanded at the outlet gap resulting in increased porosity due to explosive-like evaporation from the solid cells. Amandus Kahl offers a ring gap expander disposing of an adjustable ring-formed gap that keeps a defined pressure of the solid moving bed. The resulting material is homogeneous having a high porosity at an increased bed density (compacting). Penetration of liquid in posterior solvent extraction is facilitated while the resulting homogeneous structure and high density facilitate enhanced solid throughput and safe performance of percolators. The expander-extruder-cooker fabricated by Anderson also allows blending of water into the feed material for cooking at a prescribed moisture level.

An alternative method of preparing source material for extraction is so-called electropermeabilization. High-intensity electric field pulses cause cell damage and release of liquid contained in the cells (10). Because of its high viscosity, oil cannot be obtained by this technique but it may be applied to fruit juice extraction.

## E. Solvent Recovery

The extracted cake and the product need to be liberated from any solvent residuals by stripping or distillation procedures. Therefore, the miscella leaving the

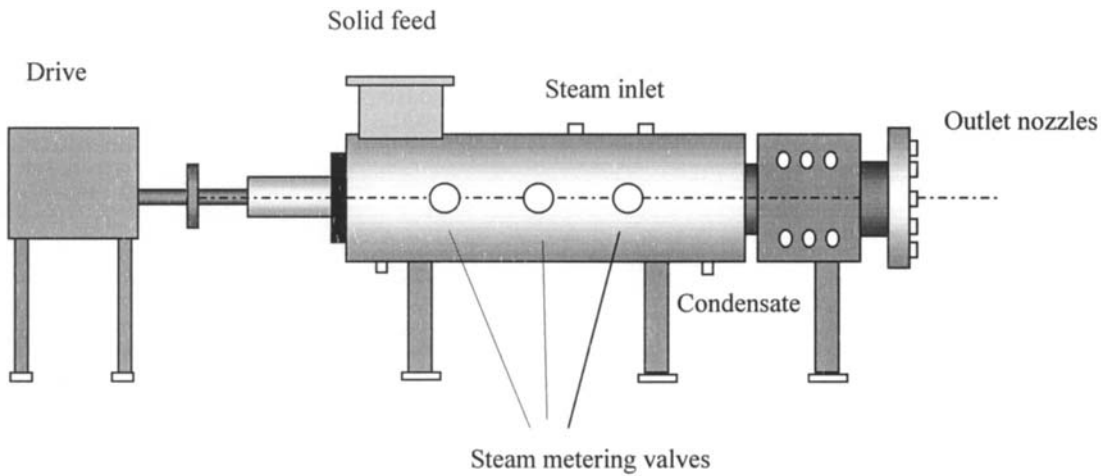


**Figure 14** Schematic of an expander.

extractor is passed through a distillation step for stripping the solvent and obtaining a solvent-free product. This product is ready for further treatment, such as liquid extraction of undesired components, enrichment of desired ones, or chemical modification.

The exhausted meal is discharged from the extractor and transported to the desolventizing step by conveyer belts or screws. Here the solvent is evaporated in order to obtain a solvent-free solid residual that can be used, e.g., as animal food. Usually, the desolventized meal is toasted to increase its nutritional value as food material. Desolventizing and toasting is usually carried out in two separate steps. Lurgi offers a toaster including so-called pre-desolventizer stages at the top end of the same tower. Steam is passed from below through vapor duct trays holding the meal at various heights of the tower. Double-arm agitators move the meal atop these trays until it drops through outlet holes to the tray below. Within the trays there are also steam-heated sections for indirect heating. Using solvents that are partly miscible with water (e.g., alcohol, acetone), steam cannot be applied in view of posterior separation and solvent recovery. In this case, the so-called flash desolventizing process can be applied contacting the meal with superheated solvent.

If volatile flammable organic solvents are used, operation of extraction, distillation, and desolventizing is carried out at slight vacuum to prevent the risk of explosion in case of leakage. If less volatile solvents are used, e.g., water, high temperatures must be applied, e.g., in spray drying of the extract-solvent mixture. Often, high temperatures are disadvantageous with respect to valuable compounds such as flavors and fragrances. Since the 1930s freeze drying is increasingly applied in order to evaporate water, e.g., from the extracted solubles of coffee. Here temperatures of 60–85°C are applied for sublimation of water at 50 Pa from coffee that is frozen at temperatures below −30°C. The highly concentrated frozen coffee is either filled into trays that are moved onto heated plates through a vacuum tunnel or directly scrapped over heated plates by agitators. In the former case, heat transfer is worse but the latter method leads to abrasion of the solid particles.

In general, environmental protection and consumer demands afford development of solvent recovery systems that provide adequate cleaning of exhaust air and careful treatment of conserving valuable product components.

## F. Final Pressing Systems

For production of small amounts of edible oil, mere mechanical pressing may be suitable. Physical limits of the minimal residual oil content exist due to strong adhesive forces. In case of rapeseed, a content of 7% of oil remaining in the solid matrix can be achieved only by pressing. Further treatment using solvents is not economic. Accounting for the loss in residual oil compared with a content

of 1.5% after combined prepressing and solvent extraction and high costs of maintenance in the case of full pressing, production costs of oil coming from either process are usually equal at production rates above 500 t/a.

Fruit juices are commonly produced only by mechanical treatment. Belt filter presses, e.g., manufactured by Flottweg or Zentrifuges from Westphalia, both in Germany, are used to mechanically extract juice, such as from apples and cherries. In processing of citrus juice, crushing of the fruit must be avoided since oil and bitter compounds originating from the peel have to be kept low in the juice. The FoodTech Extractor System from FMC, Florida, extracts juice and oil simultaneously by scratching off the peel using two approaching cups while the peeled fruit moves into a strainer tube. Here the juice is separated from the seeds and the rest of the fruit. In general, around half of the weight remains as solid residue subsequently processed to cattle feed supplement. Furthermore, about 0.4% is formed by citrus oil situated in the peel. Next to pressing of the peel, water is used for rinsing the oil, which on its turn requires separation of the obtained emulsion by centrifugation. Quality of peel oil depends on the amount of water used. While the oil obtained directly from pressing may be sold as cold-pressed citrus oil, the oil obtained from a subsequent aroma recovery step using multistage evaporation and distillation, and thus lower in quality is applied for production of soaps and detergents. Within the juice extractor offered by Brown International Corp., the peel oil is obtained before juice extraction. The peel is cut and rinsed with water. Centrifuges carry out separation of the resulting emulsion.

### G. Complete Extraction Plants

Figure 15 shows a flow diagram of a hop extraction plant using ethanol as solvent. Cone hops is fed to a double-deck Rotocel extractor with 16 compartments after being dried. The miscella drawn from the extractor is concentrated by passing a four-stage vacuum evaporator at gentle temperatures. Complete elimination of the alcohol is carried out in a posterior separation step. The spent hops discharged from the extractor is desolventized in a dryer and subsequently pelletized for animal feed application. Recovered ethanol-water mixture is adjusted to the desired composition by rectification and recycled. Compared to alternative $CO_2$ extraction (discussed in the next section), ethanol possesses little selectivity resulting in a product that contains almost the natural composition of extractables given by the feed material.

## II. SUPERCRITICAL FLUID EXTRACTION (SFE)

Extraction from solid material using supercritical fluid extraction (SFE), especially carbon dioxide ($CO_2$) extraction, is established on an industrial scale for

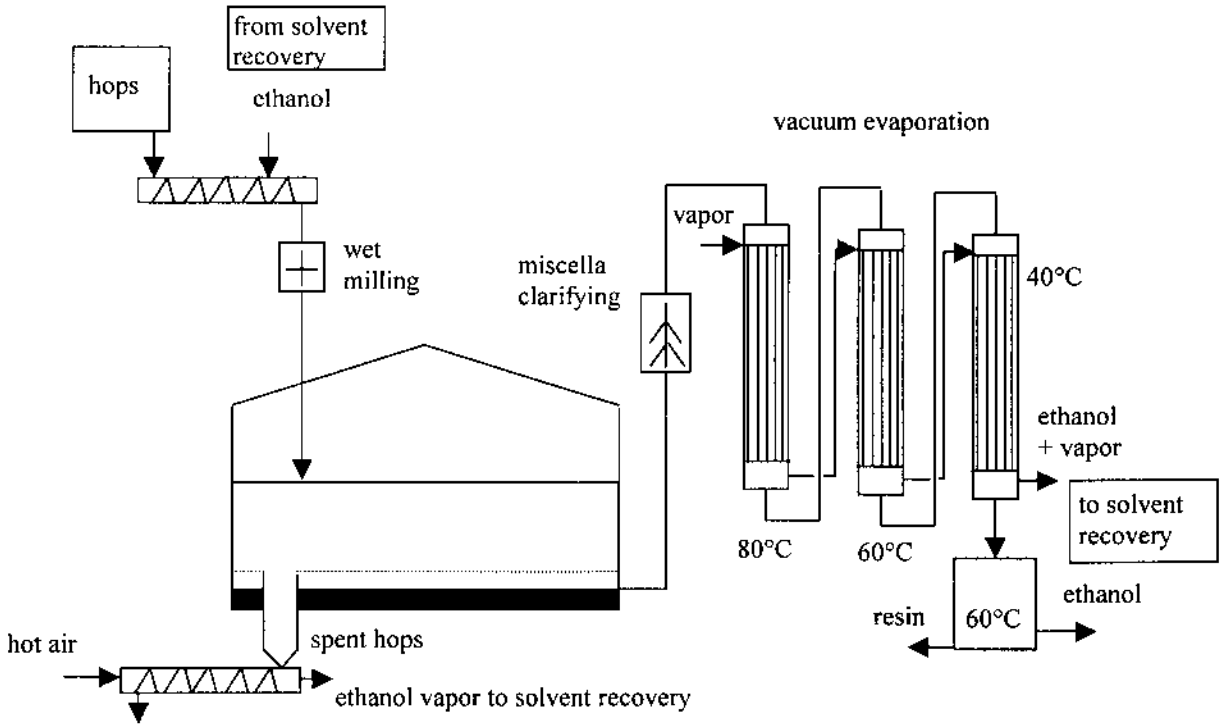


**Figure 15** Flow diagram of a hops extraction plant using ethanol as solvent. (Courtesy of Hallertaler Hopfenveredelungsgesellschaft.)

a wide range of applications. Besides some large plants used for industrial production of decaffeinated coffee and hops extract, there are a number of smaller multipurpose plants that obtain extracts from a variety of natural materials, such as spices, herbs, and valuable vegetable/essential oils (11).

## A. Extraction System

In Fig. 16 a general flow sheet of a supercritical fluid extraction is shown. Such a processing line mainly consists of a pressurizing device, a pressure vessel for extraction, one for separation (i.e., solvent recovery), and a couple of heat exchangers.

If separation is performed in the most common way by pressure release, the fluid must be vented through a butterfly valve before entering the separator. Separation is carried out at lower pressure than extraction. The type of pressurizing device used to recirculate the fluid by rising pressure back to extraction conditions depends on the state of the solvent fluid coming from the separator. If the pressure in the separator is high enough for the fluid to be liquified by chilling in a reasonable temperature range, piston pumps may be applied. On the other hand, gas compressors working with much lower volumetric efficiencies are needed if the fluid at the pump inlet is in a gaseous state. Nevertheless, the corresponding low separation pressures might be of interest for highly volatile components that are well solubilized by the compressed fluid. Pressure must be reduced considerably for precipitating these solutes. Alternative methods of solvent recovery also exist for a complete isobaric solvent cycle. The solute can

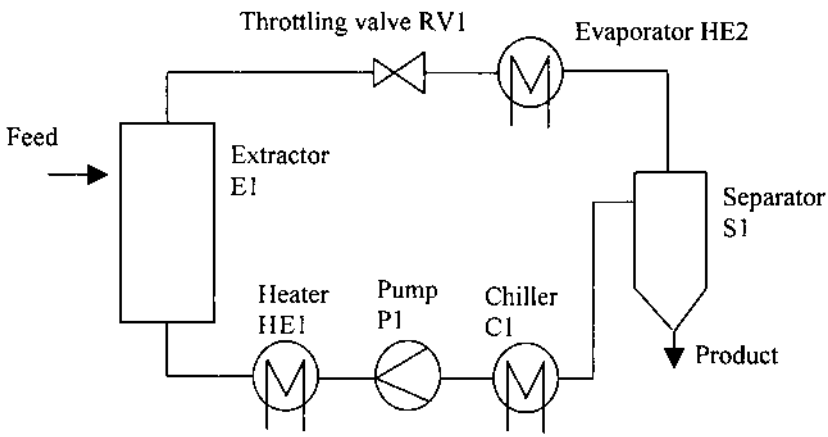


**Figure 16** General flow sheet of supercritical fluid extraction.

either be absorbed by an additional liquid, e.g., water, or adsorbed on a fixed bed, e.g., of activated carbon. Therefore, the pump is just needed for maintaining fluid flow and overcoming relatively low-pressure drops along the processing line. For arriving at the operating pressure and compensating solvent losses, a relatively small additional pump has to be installed. The solvent cycle is commonly represented by a T-S diagram from which energy balances may be drawn that are needed for heat exchanger design. For a usual SC-carbon dioxide ($CO_2$) extraction with liquid $CO_2$ at the pump inlet, Fig. 17 shows this clockwise turning cycle in such a T-S diagram.

After being liquified in the chiller C1 the fluid is compressed by the pump P1. Pressure increase is supposed to take place nearly reversibly (isentropically). HE1 heats up the fluid to extraction temperature. Adiabatic expansion (no significant change in enthalpy) occurs in the butterfly valve RV1. Due to the Joule-Thompson effect, the carbon dioxide is cooled down arriving at saturation conditions. For better separation, the loaded fluid is completely evaporated just before entering the separator in HE2.

Besides some large-scale plants for extraction of α-acids from hops (12), there are quite a number of smaller, multipurpose plants for obtaining extracts of a variety of natural materials such as spices, herbs, and solids containing flavors or fragrances, all of them using similar setups as depicted in Fig. 16 (13). For

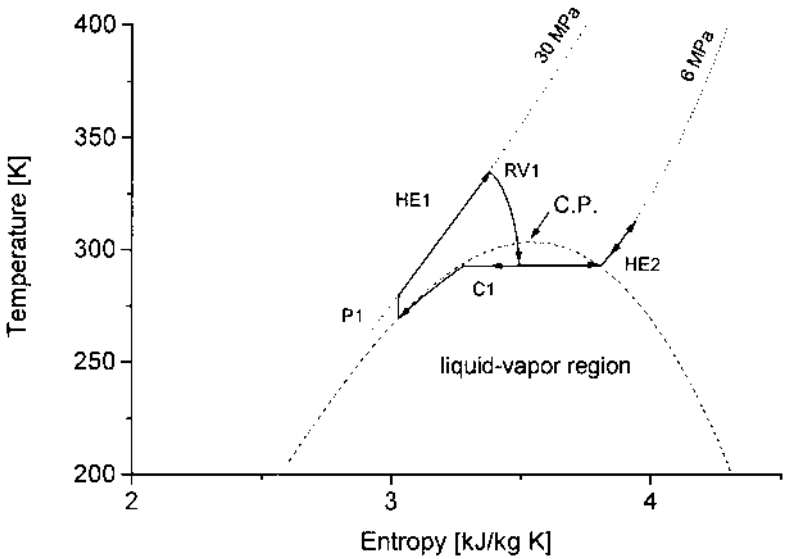


**Figure 17** $CO_2$ cycle, depicted in a T-S diagram.

decaffeination of green coffee beans, either the beans are moistened or moist carbon dioxide is used (14). Separation and regeneration of the supercritical solvent after decaffeination is usually performed by isobaric adsorption on activated carbon or absorption by water (15). In a similar way, caffeine-free tea can be produced (16). An alternative procedure has been proposed by Buse GmbH for decaffeination of green coffee beans using water saturated with carbon dioxide at pressures of up to 30 MPa (17).

## B. Batch and Continuous Processing

Up to now, supercritical extraction of solids at industrial scale is mostly performed in a discontinuous manner due to the lack of reliable sluice systems for continuous inflow and outflow of solids to and from high-pressure vessels. In order to save expensive operation time, two to four extractors are often operated in turns. Figure 18 schematically shows a plant for solid extraction containing two extractors and an optional second separator in case stepwise pressure reduction is necessary. Figure 19 shows a time schedule of discontinuous supercritical extraction including charging and discharging of four vessels in turns. One vessel is always off-line for depressurizing, discharging, charging, purging, and pressurizing.

Different methods have recently been proposed to achieve continuous charging and discharging of solids to and from high-pressure vessels. By using screw conveyers or extruders, the solid is compacted entering into the extractor (18, 19). The resulting pressure drop along the moving solid bed prevents pressure loss while charging the extractor. An alternative multistage sluice system containing various compartments on an axially moving frame has problems of scaling up due to lack of appropriate sealing systems. In case a slurry is formed, continuous processing can be carried out using common piston and membrane pumps (20). The solid–liquid dispersion is introduced into rather tall and thin extractors or columns where the supercritical fluid is directed either co- or countercurrently with respect to the liquid flow. Anyway, using a liquid "carrier" enhances mass transfer resistance from the solid particles into the supercritical fluid phase, which can partly be overcome by finely dispersing the liquid within the supercritical solvent.

Finally, discharging of solid powders formed inside the extractor by dissolving the original carrier phase completely within the supercritical fluid may be realized by simply opening a discharge valve at the bottom and blowing out the solid particles together with the supercritical solvent. For pressure release of vessels containing, for example, pressurized carbon dioxide, one must also take into account temperature drops toward the vapor–liquid line or even surpassing the triple point that is situated at a slightly elevated pressure. As a consequence, outflow from the vessel partly takes place as a two-phase flow and blocking by

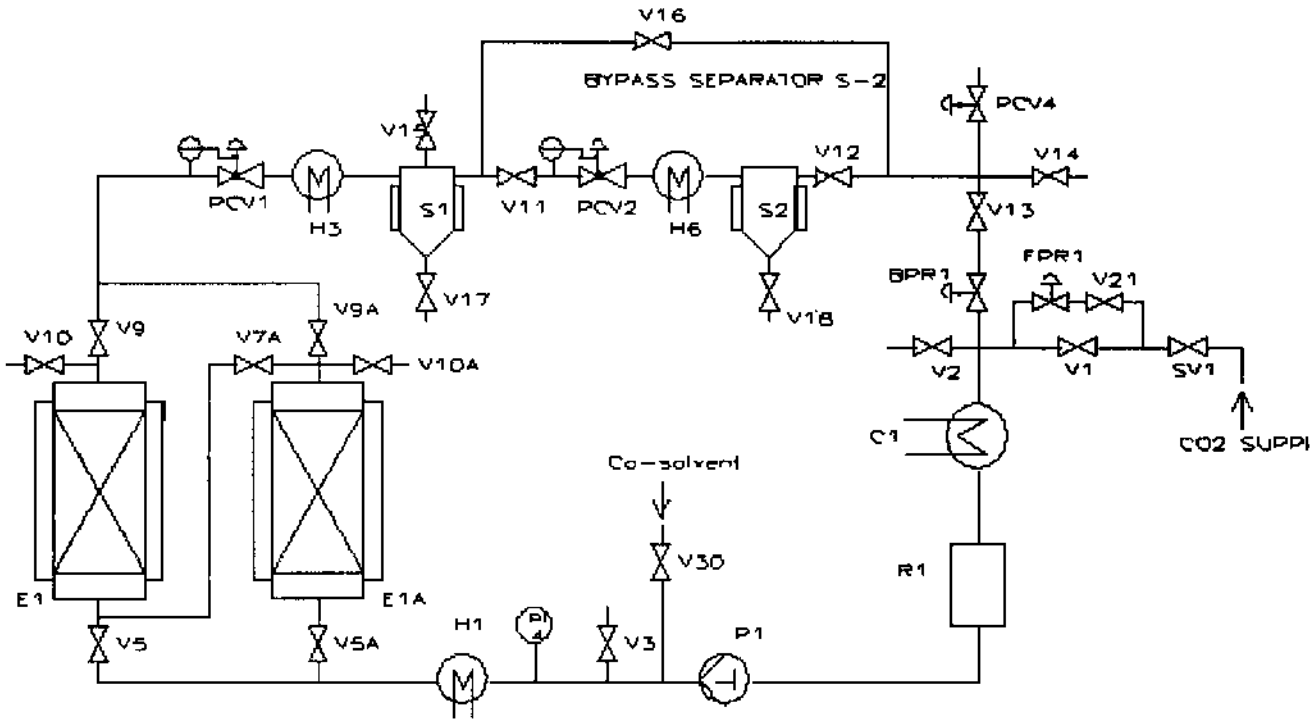


**Figure 18** Flow diagram of an extraction plant with two extractors and fractionated separation.

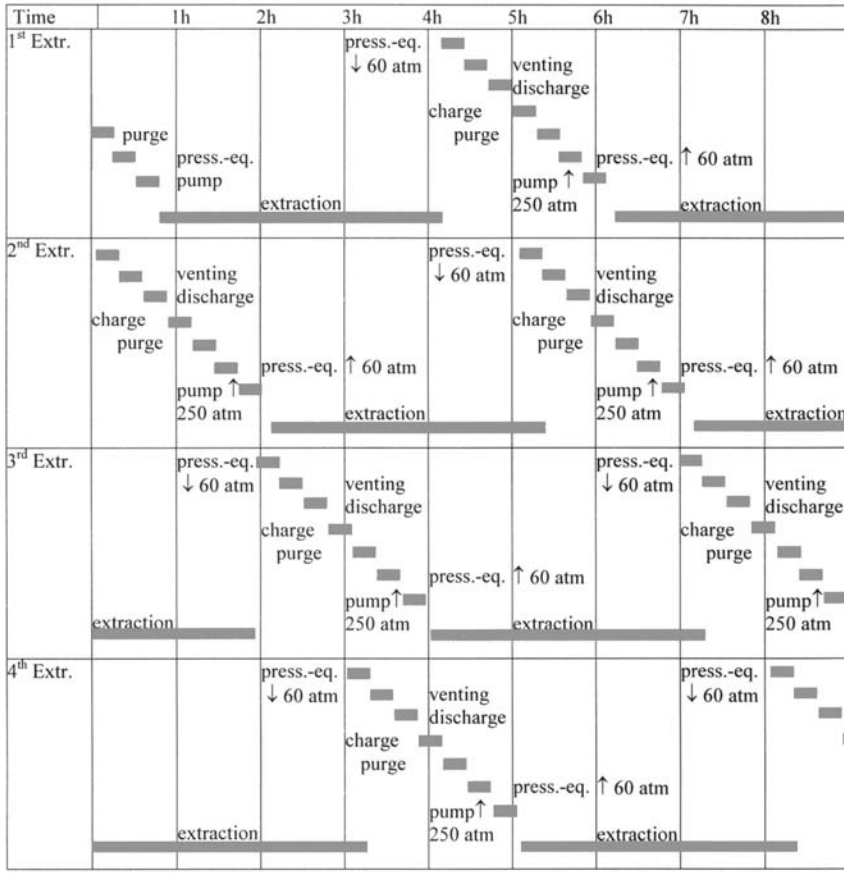


**Figure 19** Time schedule of supercritical–solid batch extraction using four extraction vessels in turns, 120 kg per batch, 1200 kg $CO_2$/h at 250 atm.

dry ice (solidified carbon dioxide) may occur (21). The interior of the vessel is easily cooled down to −30°C (Fig. 20).

## C. Recovery Systems

As mentioned above, different principles of solvent (supercritical fluid) recovery have been proposed that are also applied at industrial scale. Next to the energy-consuming method of depressurizing the supercritical solvent, adsorption and absorption methods are used especially in case high amounts of supercritical

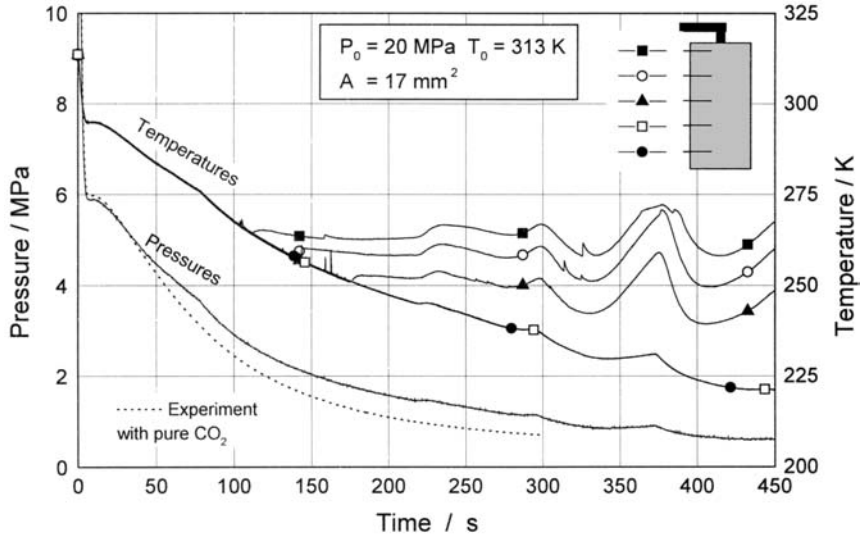


**Figure 20** Pressure and temperature decrease during depressurizing of moist carbon dioxide from a 50-L vessel.

fluid must be circulated and the substances dissolved by this solvent are destined for elimination. If the objective is to obtain a valuable product as the extract phase, separation by pressure reduction is usually most suitable. Nevertheless, caffeine that is dissolved by supercritical carbon dioxide for decaffeination of green coffee beans may be absorbed by water in some type of high-pressure liquid–fluid extraction plant such as a cocurrent spray tower, countercurrent packed column, or mixer-settler (22), concentrating the caffeine in a posterior membrane module and obtaining a product of elevated purity (23). The high-pressure countercurrent principle is described by Jaeger focusing on the wetting behavior of packing materials at elevated pressures (24).

At industrial scale, adsorption of caffeine on activated carbon dominates, but up to now the caffeine is burned for thermal recovery of the adsorbent. Each recovery implies a 10% loss of activated carbon. Recent developments are aimed at obtaining the adsorbate without being destroyed during regeneration. The use of alternative adsorbents, such as ion exchangers (25), is also proposed to enhance processing rates or others with hydrophilic properties in order to facilitate their regeneration by water (26). For dimensioning an adsorber, one has to consider a sufficient length in order to establish plug flow within the adsorbent bed. Therefore, the minimal length-to-diameter ratio is about 10. The required length further depends on the amount of substance to be adsorbed.

Adsorption capacities range between 25 and 80 g/kg adsorbent. Back mixing should be prevented by keeping fluid velocities at values below a few centimeters per second by choosing an adequate inner diameter.

## D. Pretreatment

Similar to conventional liquid extraction, the solid feed material has to be conditioned properly. Mass transfer should be favored by maintaining small particles, eventually removing skins by pealing or dehulling. On the other hand, the structure of the solid bed should be porous and as homogeneous as possible. Large particles result in high void fraction, but at the same time the mass transfer from inside the particles into the bulk fluid is slowed down. Solid particles that tend to stick to each other (e.g., at high moisture content) often form channels by the fluid or even complete blocking. As a consequence, the solid material is extracted heterogeneously and to a low extent. Figure 21 shows the influence of pretreatment on the kinetics of supercritical extraction of sunflower oil. Extraction of dehulled and flaked sunflower seeds proceeds faster. In general, flaking

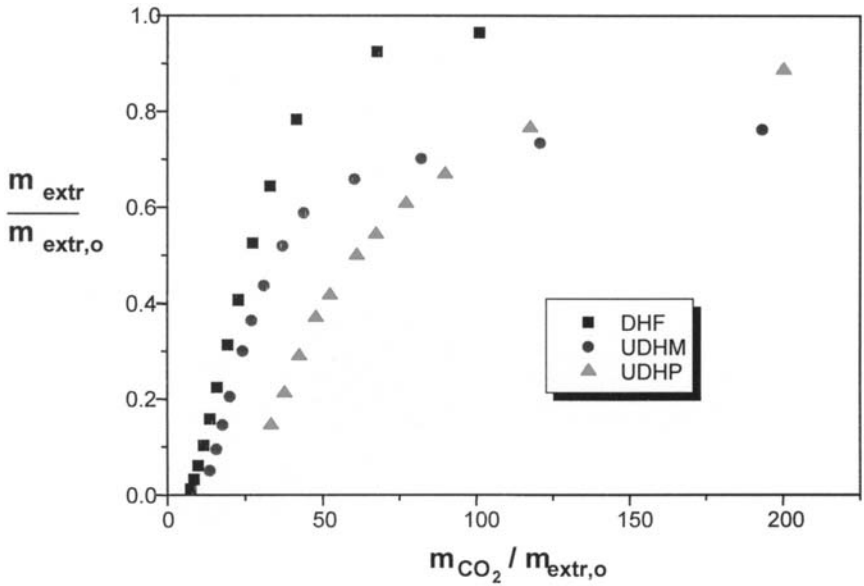


**Figure 21** Kinetics of oil extraction from sunflower seeds at 50 MPa, 60°C. DHF = dehulled, flaked; UDHM = undehulled, milled; UDHP = undehulled, pelletized.

appears to be an appropriate approach to pretreatment since the thin layers minimize transport resistance while leaving a firm and porous structure to the bed.

## E. Vessel Design

In supercritical extraction, pressure vessels are needed for supply and recovery of the solvent, the extraction (loading of the solvent) itself, and a number of heat exchangers. According to their dimensions and way of operation, different types of construction and factoring of these vessels are applied (27). Figure 22 summarizes the most important methods of pressure vessel construction. In general, vessels with solid walls and those containing compound (layered) walls are distinguished. Solid-walled vessels are normally produced as single forgings. Using this method, the diameter is limited to about 1 m and the wall thickness to about 150 mm. Greater heights may be obtained by joining several cylinders by circumferential welding. Wall thickness in excess of 200 mm is achieved by joining two half shells by longitudinal welding.

The technological limitations of weight and size imposed on the mentioned methods for solid-walled vessels are overcome to a large extent by the use of vessels with laminated walls. The presence of such multiple layers while normally beneficial, can produce complications; the insertion of an adapter or a nozzle in a layered wall requires very careful design.

Working with corrosive substances, the multilayer principle has the advantage of separating the corrosion problem from the required pressure resistance. The inner layer is made of a corrosion-resistant material with less tensile strength, whereas the outer layers resist the high pressure. A disadvantage of this type of vessel is reduced thermal conductivity. Usually, contact between the layers is not ideal leaving small gaps that give rise to enhanced thermal resistance. However, at high pressure, this effect is partially reduced due to additional pressing of the layers toward each other. Calculation of wall thickness is carried out according to national codes, such as the Boiler and Pressure Vessel Code of the American Society of Mechanical Engineers (ASME).

Especially for design of extractor vessels, rules concerning some construction principles are based on experience gained in the past two decades of industrial application of SFE. The ratio of inner length to inner diameter influences the performance of extraction and should therefore be carefully chosen. At too low an inner diameter, wall effects become noticeable. Although axial dispersion may be relatively low, back mixing becomes relevant within a tall extractor. On the other hand, high inner diameters may result in heterogeneous extraction with respect to the radial position. In most cases, solid extraction is performed upflow. The fluid enters the bottom of the extractor at its center. The extractor contains a so-called product basket that has a sieve tray bottom or, even better,

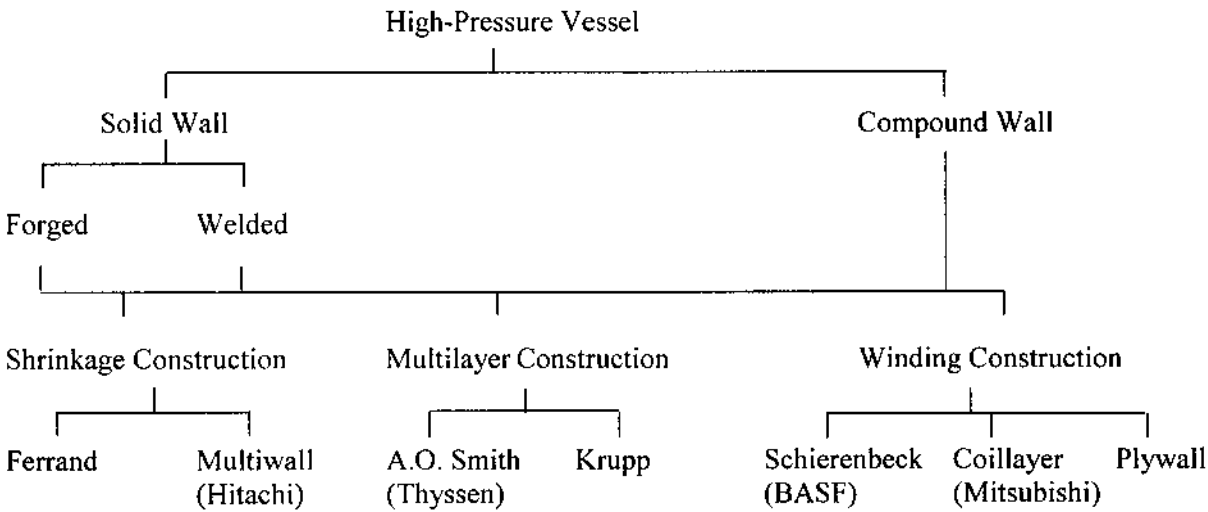


**Figure 22** Methods of pressure vessel construction.

a sinter metal bottom. At its circumference, the basket must be sealed towards the inner wall of the extractor to prevent bypassing of the fluid. Since the basket enters the extractor by opening the extractor top, this top must be removable. Therefore, any fixed tubing at the top would have to be replaced for opening the extractor. Therefore, the outlet is positioned just below the top to one side of the extractor. This has to be considered for a homogeneous flow within the extractor because having the outlet on one side results in asymmetrical flow.

In the case of discontinuous charging and discharging of solids, the vessel must contain quick-acting closures. Furthermore, cleaning must be facilitated if there is a risk of accumulating precipitates.

## F. Heat Exchangers

The specific heat transport properties of the respective supercritical fluid and their variation depending on operating conditions must be taken into account for heat exchanger design. The rate of heat to be transferred within the fluid cycle, e.g., $CO_2$, may be deduced from the T-S diagram taking the respective points of specific enthalpy. Coming from the pump (Fig. 16) the supercritical fluid, e.g., $CO_2$, enters the heater HE1 at, say, 15°C and 30 MPa. The corresponding enthalpy of $CO_2$ amounts to about −284 kJ/kg. Raising the temperature to 100°C, which gives an enthalpy of −116 kJ/kg, 168 kJ/kg of heat needs to be transferred. At a $CO_2$ mass flow of 500 kg/h the transferred heat flux comes out to be 23 kW.

For cleaning purposes, heat exchangers should be constructed as tube bundles or double tubes. In particular, the evaporator following the throttling valve is at risk of being blocked by precipitated extract. Vertical orientation of this heat exchanger helps downflow of precipitating liquid. For the condenser position, different possibilities are discussed leaving some doubts for the best solution. In the course of cooling, a condensate film is formed on the walls increasing heat transfer resistance to the gaseous phase. A diagonal orientation down toward the fluid outlet allows the freshly formed liquid to drop off the tube walls right away, leaving only a thin film of condensate. For laboratory-scale plants, heat exchangers may also be constructed as a coil of high-pressure tube placed in a thermostat bath to keep dimensions small despite relatively high heat transfer area.

## G. Pumps and Compressors

In general, pumps are used to transport liquids through pipes. Every pump has certain operating characteristics due to which mass flow and pressure increase are related for the installed piping. Figure 23 qualitatively shows operating characteristics for centrifugal and piston pumps. Centrifugal pumps that are usually

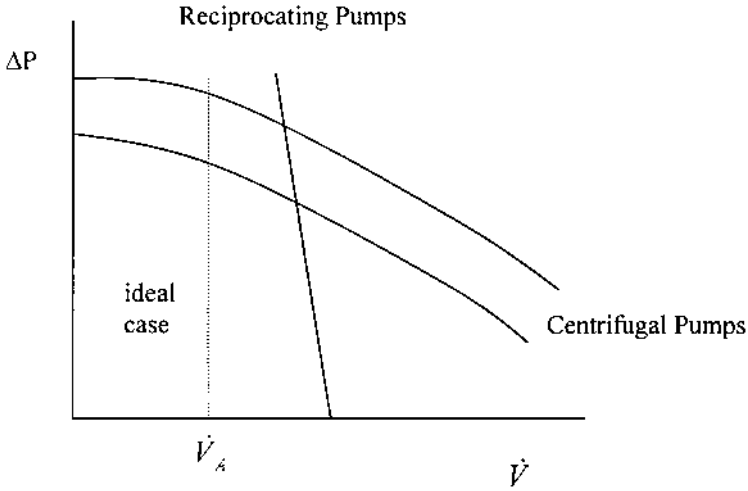


**Figure 23** Characteristic curves of different types of pumps.

not applied to high-pressure technology show a reciprocal behavior of pressure with respect to mass flow: at higher pressure mass flow diminishes. The pump is actually operated at the point of intersection of the operating line and the characteristic line of the piping due to pressure losses caused by friction. On the other hand, piston pumps that are commonly used for high-pressure purposes ideally maintain a constant mass flow no matter the pressure at the outlet, assuming a noncompressible liquid. Cavitations, i.e., evaporation due to pressure loss at the pump inlet, must be avoided in the case of both centrifugal and piston pumps. So-called net pressure suction height (NPSH) is a measure of the minimal inlet pressure that ensures complete liquid pumping, usually based on properties of water.

Since piston pumps have a certain constant volume per stroke, it is very dangerous to shut valves right behind the pump. Pressure will increase until either tubes burst or major damages occurs, e.g., at the pump transmission. Therefore, security devices such as security valves and rupture discs are obligatory.

If the fluid to be circulated is highly compressible and the pressure is to be increased, compressors with multistage working principle need to be used. Pressure is increased stepwise with an intermediate cooling step. In each step pressure may be raised by a factor of 3–4. Compressors have a much lower volumetric efficiency than pumps but can work with almost any suction pressure.

Supercritical fluid extraction works with fluids under conditions ranging from the need of compressors to the possibility of applying pumps. Usually, the

circulating fluid enters the pump at elevated pressure. Whether or not a liquid state can be assured at this point depends on conditions of the previous separation step and the chilling capacity. In the following we will assume that a pump is used. The two main different types of reciprocating pumps used for supercritical fluids are plunger (piston) and membrane pumps. Membrane pumps have certain advantages, especially concerning sealing. While piston pumps need special dynamic sealing packing to guarantee hermetic operation, the membrane itself separates the pressure chamber from the pressure-transmitting liquid and the transmission of the pump (Fig. 24). For food and pharmaceutical applications sealing toward, say, lubricants may be decisive for pump selection. On the other hand, the fact that the efficiency of piston pumps is higher than that of membrane pumps is important for realizing high mass flows.

For circulating fluids on a high-pressure level but relatively small pressure drops in the cycle, canned centrifugal pumps (hermetic) may be applied.

### 1. Pump Efficiency (Volumetric Efficiency)

Multiplying the stroke volume and the pumping frequency gives a theoretical value of the volume flow of the pump. This volume flow is never reached because of various factors that are quantified by using the so-called pump efficiency, $\eta_p$. $\eta_p$ is composed of a systematic efficiency accounting for back flow through valves, fluid losses, and so forth, as well as an elastic efficiency taking into account elasticity of the pumping head, stagnant volumes, and compressibility of the fluid. The elastic efficiency that usually comes close to the total pump efficiency is defined by (28):

$$\eta_E = 1 - (\varepsilon_T \kappa + \lambda_E)\Delta p \frac{H}{h}$$

with $H/h$ denominating the stroke ratio. In case of a nonelastic piston ($\lambda_E = 0$) and a normal stagnant volume ($\varepsilon_T = 1$), the pump efficiency for a single acting piston pump comes out as:

$$\eta_E = 1 - \Delta V/V_0$$

where $\Delta V/V_0$ is the relative compressibility, which can also be defined as $\Delta V/V_0 = \kappa\ \Delta p$, $\kappa$ being the compressibility coefficient. In Fig. 25, the relative compressibility is depicted as a function of pressure for $CO_2$.

The compressibility is not only important to the pump efficiency but also to the pulsation of the pump. The volume flow characteristics of a double-acting plunger pump can be seen in Fig. 26. In the case of incompressible fluids one peak is directly followed by the other. For compressible fluids the first part of the peak is cut away and the flow becomes similar to that of a single-acting pump.

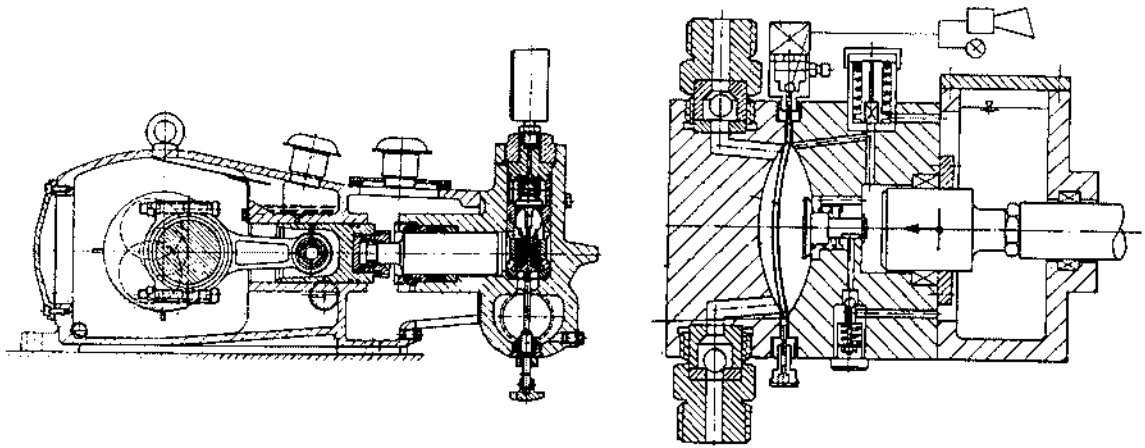


**Figure 24** Schematic of a piston (a) and a membrane (b) pump.

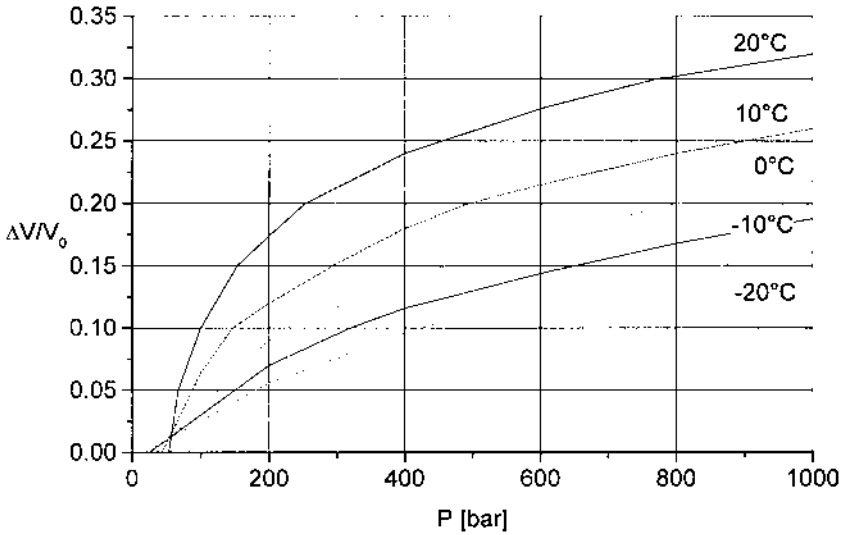


**Figure 25** Relative compressibility of $CO_2$.

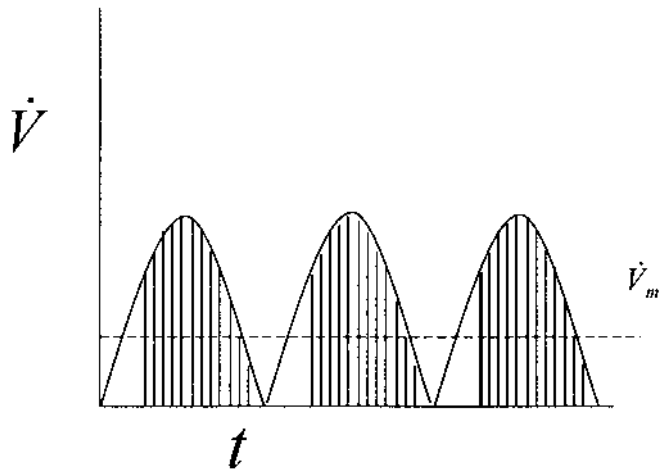


**Figure 26** Volume flow characteristics of a double-acting pump.

### 2. Dimensioning of Pumps

For solid extraction using supercritical $CO_2$, velocity with respect to the empty cross-section of the extractor should amount to a few millimeters per second. In many applications the resulting mass flow (in kilograms per hour) comes out as about 20 times the content of the extractor (in kilograms), of course still depending on the solubilities in detail. Whether or not a sufficient mass flow can be achieved depends strongly on conditions at the pump inlet and on the desired extraction pressure. Taking into account conditions on the suction and the high-pressure side of the pump, an estimation may be carried out using the volumetric efficiency described above.

### 3. Formation of Gas Hydrates

In general, low temperatures are required for assuring liquid state of the fluid at the pump inlet. For many gases, including $CO_2$, there are limits given in case water is present in the cycle. In spite of moist $CO_2$ containing only around 0.02–0.2 wt% water, gas-hydrate crystals may be formed in or near the condenser, growing on the inner walls and possibly blocking tubes and pumps. These hydrates were found to be formed below 10°C and be quite stable, eventually lasting for days after stopping operation (31).

## H. Industrial Plants

In the meantime, several applications for SFE have been established. Two of the most important industrial scale applications are extraction of α acids from hops and caffeine from green coffee beans. The purpose of using supercritical fluids is mainly to obtain a solvent-free product of high quality, carefully treated with respect to temperature and to save costs for environmental protection. A selection of industrial operated plants is shown in Table 2.

The product value depends on whether the objective of the process is to obtain the fluid-soluble extract or the remaining nonsoluble substances. Because of rather low solubilities within supercritical $CO_2$ in most cases, product costs are much higher when aiming for the extract. In detail, the costs depend on the solubility of the desired component in the solvent phase; on the possibilities of continuous, quasi-continuous, or semicontinuous operation; and on the type of regeneration of the solvent. Since the used supercritical solvent may have an increased selectivity in comparison with conventional liquid solvents, the final composition of the extract mostly differs from its natural composition within the solid matrix. This fact has to be taken into account considering product stability since many natural components disintegrate rapidly after being isolated or simply when nonsoluble natural stabilizing agents or antioxidants are absent in the obtained extract.

**Table 2** Industrial Applications of SCF-Extraction

| Company/Country | Capacity (L) | Products |
|---|---|---|
| Yasuma (Japan) | 100 | Spices, pigments, food additives (19) |
| Fuji Flavor (Japan) | 300 | Tobacco, flavors |
| Sago Koryo (Japan) | 300 | Flavors, pharmaceutical compounds (19) |
| Mori Seiya (Japan) | 500 | Flavors, pigments (19) |
| Idemitsu Sekiyu (Japan) | 1000 | Flavors (19) |
| Takeda Seiyaku (Japan) | 1200 | Pharmaceutical compounds (19) |
| Essences (Italy) | 1200 | Essential oils (20) |
| CUB (Australia) | 1000 | Flavors (21) |
| Universal Flavors Ltd. (UK) | 1000 | Flavors (21) |
| HAG (Germany) | 45.000 | Decaffeinated coffee (21) |
| Barth (Germany) | 12.000 | Hops (22) |
| SKW (Germany) | 18.000 | Hops (22) |
| Sumitomo Seika (Japan) | 100 | Coffee extract (19) |

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