Distillation and Other Industrial Separations

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Foreword by Henry Z. Kister

American Institute of Chemical Engineers

Practical Engineering Perspectives
Distillation and
Other Industrial Separations

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PREFACE

This book is a compendium of recent articles of interest to practitioners. It is aimed at chemical engineers and other technical professionals in the chemical process industries who must contend with and try to improve the performance of separation operations in their processes.

Such separation operations are critical to the successful functioning of most process plants. After all, the reactions that produce desired products also yield byproducts or leave residual raw materials. So, achieving desired product purity invariably requires some separation technology. Likewise, meeting environmental regulations frequently demands the removal of specific contaminants to some defined level from waste streams.

Indeed, the lead article in this collection, "Separation Processes: Playing a Critical Role," by Jimmy L. Humphrey, clearly underscores that plants could not survive without cost-effective separation operations.

There are numerous separation technologies in the chemical engineer's arsenal, and no modestly sized book such as this can possibly cover anything more than a fraction of them. So, this volume instead highspots a number of the more industrially important options.

After the overview article already cited, the various sections are arranged according to the type of separation technology. The first such section and, indeed, the main emphasis of this compendium is on distillation. As the article "Distillation: Still Towering Over Other Options" by John G. Kunesh, Henry Z. Kister, Michael J. Lockett, and James R. Fair points up, distillation is by far the most popular separation technique and promises to remain so. A number of articles address key issues in the design and selection of appropriate distillation hardware, including choosing between trays and packings, and special considerations for high-pressure and severe services. Other articles offer practical advice for minimizing operating problems, for instance, in dealing with trapped minor components, vibration, solids, and fouling, as well as on control-system design. Troubleshooting insights and tools also are covered.

While distillation accounts for a majority of the content of this volume, other sections are devoted to adsorption, centrifugation, and membranes, all important industrial separation techniques. The final section covers a variety of other techniques, including phase separators, cyclones, crystallizers, electro-separators, and liquid/liquid extractors.

Articles have been selected based on their usefulness to practitioners, and their emphasis on practical and generic guidance. The roster of authors includes many of the world's foremost authorities in the field—and represents a mix of individuals who work for operating, engineering/construction, and equipment companies, as well as research organizations, and academia.

All the articles have been published by the American Institute of Chemical Engineers over the past three years. One article was drawn from the Institute's ongoing Symposium Series. All the others appeared originally in *Chemical Engineering Progress*, the broad-based monthly magazine of AIChE.

Mark Rosenzweig
Editor-in-Chief
Chemical Engineering Progress

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Gail F. Nalven
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Separation Processes: Playing a Critical Role

Plants could not survive without cost-effective processes to purify products and remove wastes.

Jimmy L. Humphrey,
J. L. Humphrey & Associates

Separation processes are the main cog in the manufacturing wheel of the chemical process industries (CPI). They are used for such essential chores as removal of contaminants from raw materials, recovery and purification of primary products, and elimination of contaminants from effluent water and air streams (see Figure 1). Thus, to maintain or improve the competitiveness of their companies, chemical engineers must stay abreast of new developments in separation processes and technologies.

This article provides an overview of key separation processes, highlights recent commercial developments, and provides insights on expected new developments. It focuses on the core processes for fluid mixture separations — distillation, extraction, adsorption, membranes, and their hybrid systems. Other important processes, such as crystallization and fluid/particle separations, are left for others to cover.

The heart of the separation process is the mass-separating agent *(1)*. In distillation, it is heat; in extraction, the solvent; in adsorption, the adsorbent; and in membrane separation processes, the membrane material. Table 1 lists a number of separation processes, their mass-separating agents, and representative applications. In evaluating the relative economics of separation processes, one approach is to determine what the performance of the mass-separating agents in competing processes must be to compete economically with a baseline process (normally distillation). For instance, Hinchcliffe and Porter used this approach to compare distillation with a membrane process *(2)*.

The two key design and operating parameters for any process are efficiency, which indicates how well it separates components, and capacity, which relates to the hydraulics and the rate at which material can be processed without a loss in efficiency.

Now, let's look at distillation, extraction, adsorption, and membranes in more detail.

DISTILLATION

Distillation separates components of a liquid mixture based on their different boiling points. It is the baseline process for the CPI, with 40,000 columns in operation in the U.S., handling 90–95% of all separations for product recovery and purification. The capital invested in distillation systems in the U.S. alone is at least $8 billion.

The factors that favor distillation are:
- relative volatility is greater than 1.3:1;
- products are thermally stable;
- production rate is 5,000–10,000 lb/d or more; and
- high corrosion rates and explosive reactions do not occur at distillation conditions.

Distillation applications range widely from the separation of bulk petrochemicals like propylene/propane and ethylbenzene/styrene to the cryogenic separation of air into nitrogen and oxygen. Petroleum refiners use distillation to separate large volumes of crude oil into gasoline and other liquid fuels. The distillation process, equipped with heat pumps to increase energy efficiency, produces potable water from salt water. In spacecraft, distillation is used to recover water from the urine of astronauts.

The strengths of distillation are that it has a simple flow sheet, low capital investment (that generally scales by an exponent of 0.6 or less), and is generally low risk. Its
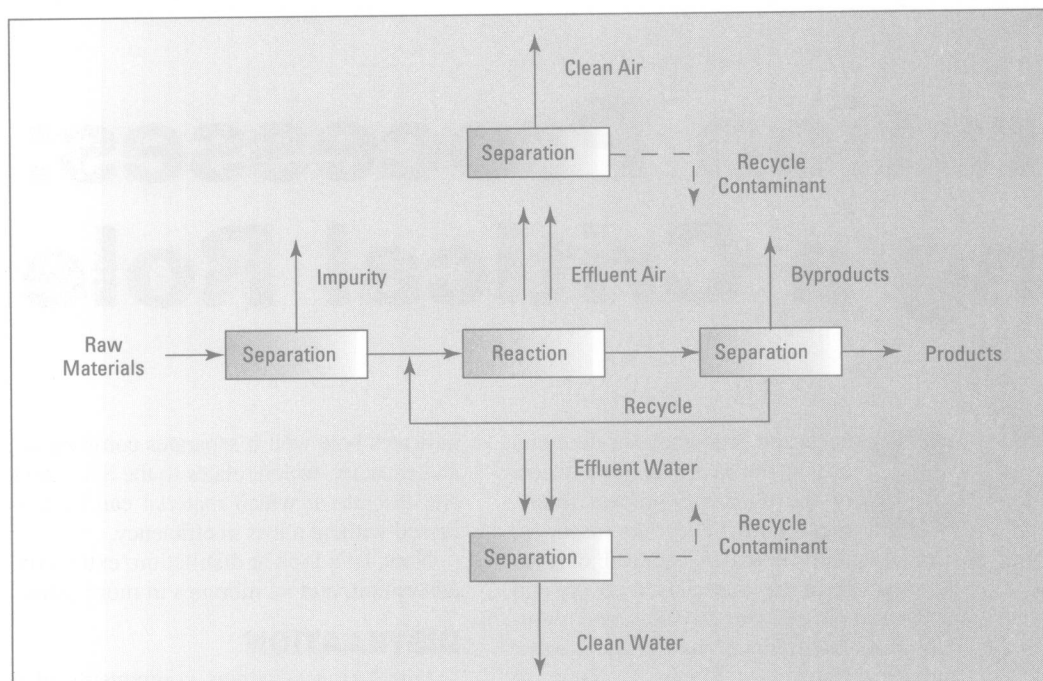
■ *Figure 1. Separation processes play a critical role in the CPI.*

weaknesses are that it is not energy-efficient, cannot separate components having overlapping boiling points or components of an azeotropic mixture, such as ethanol and water, and can degrade thermally sensitive materials.

Because of its high energy use, distillation generally is not employed to separate a small amount of high boil-ing component from a large amount of carrier, such as water. Distillation usu-ally loses its investment advantages at smaller volumes — where the distilla-tion column and its internals contribute less to total system cost than the pe-ripheral valves, pumps, and control systems. The capital cost of a distilla-tion system based on a 6-in.-dia. col-umn is only 20–25% less than a system having a 12-in.-dia. column.

Spurred in part by the increasing costs of feedstocks and energy, distilla-tion has seen new developments in high-efficiency trays and packings, en-hanced process configurations, and hy-brid systems. There also have been sig-nificant developments in design tools,

Table 1. Examples of separation processes.

Process	Mass-separating agent(s)	Representative applications
Absorption	Solvent	Removal of carbon dioxide and hydrogen sulfide from natural gas with amine solvents
Adsorption and ion exchange	Adsorbent/resin	Separation of *meta*- and *para*xylene; air separation; demineralization of water
Chromatography	Adsorbent	Separation of sugars
Crystallization	Heat removal	Production of beverages such as "ice" beers
Distillation	Heat	Propylene/propane separation; production of gasoline from crude oil; air separation
Drying	Heat	Drying of ceramics, plastics, and foods
Electrodialysis	Membrane	Water desalination
Evaporation	Heat	Water desalination; sugar manufacture
Extraction	Solvent	Benzene/toluene/xylenes recovery from gasoline reformate; removal of caffeine from coffee
Membranes	Membrane	Separation of hydrogen from hydrocarbons; concentration of fruit juices; water desalination
Stripping	Stripping gas	Removal of benzene from wastewaters

such as the rate-based design method, and models to predict efficiency and capacity of newer trays and packings.

Newer cross-flow trays are finding important applications, particularly when it is desirable to increase capacity in distillation columns operating at pressures of about 100 psig and higher. Meanwhile, the latest random packings boast thinner walls and occupy less of the volume of the column than traditional packings — freeing up more space for fluid traffic. They have been found to be especially attractive for high-pressure applications. At low pressures, structured packing such as that shown in Figure 2 has become prominent as a device that gives high efficiency at high capacity. (In addition to distillation, structured packings also are finding a number of important applications in high-pressure gas absorption.)

Deciding among the many variants of trays, and random and structured packings depends heavily upon specifics of the application. However, some general guidance on relative performance is provided by Kister, Larson, and Yanagi (3).

Enhanced configurations

Reactive distillation, also called catalytic distillation, provides the advantage of lower capital investment; one reactive distillation column takes the place of a reactor plus a distillation column. For reactive distillation to be feasible, reaction and separation temperatures must overlap, and a reversible reaction must be involved. Removing product as it is formed reduces the rate of the reverse reaction, thereby increasing conversion of feed(s) to product(s). Exothermic heat of reaction is used to provide the heat for the separation. A relatively new commercial device having a configuration similar to structured packing in distillation provides for contact between the reactants and catalyst while allowing space for fluid traffic. Reactive distillation already is being used for the production of methyl tertiary-butyl ether (MTBE) and methyl acetate (4).

The trend towards monoliths

A monolith is a structure composed of individual parts that form an organized whole without joints or seams. Capable of achieving high efficiency at high capacity, the monolith has emerged as an important contacting device in a number of separation processes. Initially used to contact vapor and liquid in distillation, the monolith has spread into catalytic distillation, extraction, adsorption, and membrane separation processes.

Structured packing used to provide vapor/liquid contact in distillation (see Figure 2) is an example of the honeycomb type monolith. In reactive distillation, the catalyst is held by panels of screen wire configured like structured packing used in distillation.

In extraction, structured packing has been installed in over 30 commercial units. The packing provides ordered channels of flow to promote countercurrent contact of the dispersed and continuous phases. The primary advantage is an increase in capacity relative to other devices.

In adsorption, the monolith takes the form of rotary wheels with surfaces coated with hydrophobic molecular sieves or activated carbon to remove organics from air. Rotary wheels find application where concentrations are low, volumes are high, and removal requirements of contaminants are not stringent — about 97% or less.

Ceramic membrane modules, configured as monoliths, are available for ultrafiltration and microfiltration applications, and for filtration of solid particles from gas mixtures.
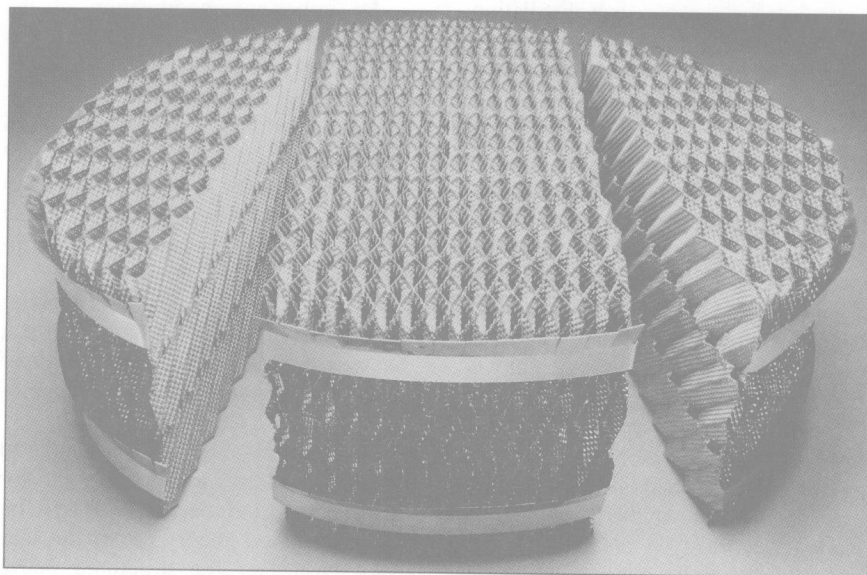
■ *Figure 2. Structured packing for distillation. (Photo courtesy of Norton Co.)*

Thermally coupled columns offer a way to save energy where it is possible to integrate column operation (5,6). Installations have been slowed in recent years in the U.S., though, because of its relatively low cost of energy.

Molecular distillation operates under vacuum and incorporates the condenser within the distillation column. It often is used for high-value products, such as vitamins, that decompose at conventional distillation temperatures.

High-gravity distillation gives both high efficiency and capacity while oc-

cupying a relatively small space. A centrifugal force is achieved with a high-speed (1,100 rpm) rotating bed. The liquid phase is forced to flow radially outward through the bed. Gas is introduced at the outer surface of the rotating bed and is forced countercurrent to the direction of liquid flow. This configuration results in an extremely high rate of mass transfer (7). High-gravity distillation may find future applications where space is limited, such as when distillation must be accomplished within a building or on

offshore platforms. At the present time, there are no commercial units in operation.

Spinning-cone distillation uses a column with alternate rotating and stationary cones whose surfaces are wetted with liquid whose flow is induced by an applied centrifugal force. Developed primarily for the food industry, spinning-cone distillation has advantages of low liquid holdup and short residence time, as well as low pressure drop. It also is said to be tolerant of solids *(8)*.

Hybrid systems

Another separation process sometimes is teamed with distillation to form a hybrid system. For instance, the second process can polish distillation-column product so as to enable a reduction in column reflux, and an increase in column capacity. Examples include the use of adsorption or membrane processes to dehydrate ethanol/water and other crude azeotropic mixtures from distillation columns. When adsorption is used as the polishing process, a pressure swing cycle serves to regenerate the molecular sieve adsorbent. Pervaporation is the more mature of the membrane processes employed commercially to dehydrate azeotropes *(9)*, although vapor permeation also is used commercially *(10)*.

Because European and Japanese energy costs are far higher than those in the U.S., hybrid systems aimed at energy savings find more applications there.

A membrane (or other type of process) also can be employed to concentrate the feed to a distillation column. For example, reverse osmosis (RO) is used commercially to concentrate wastewaters from cogeneration plants prior to evaporation. This offers energy savings *(11)*, but also may reduce capital and operating costs when complex downstream distillation equipment is required.

The separation of carboxylic acids and water often requires complex distillation/extraction systems. Acetic acid, which occurs in dilute concentra-

tions in aqueous streams, frequently is discarded because of high recovery costs. A membrane process could be used to concentrate the acetic acid, thereby reducing the feed volume and size of a complex distillation/extraction system. This hybrid system promises to achieve desired water quality while producing salable acetic acid *(12)*.

Design tools

To convert equilibrium stages to the actual number of distillation trays, it is necessary to use a tray efficiency in the design procedure. Although this approach may be adequate for binary mixtures, there can be serious deficiencies when applied to multicomponent mixtures.

An important modification of the equilibrium-stage design procedure has been developed at Clarkson University *(13)* using a nonequilibrium-stage approach called the Rate-Based Design Method. In this approach, conventional mass and energy balances around a tray are replaced by two balances, one for the vapor phase and one for the liquid phase. Although this requires a knowledge of mass- and heat-transfer correlations, it provides a significant benefit of avoiding the uncertainty of using tray efficiencies in multicomponent mixtures *(14)*.

Several new models are available to predict capacity and efficiency for newer trays and packings. Based on two resistance theory, a model has been published for structured gauze packings *(15)*, and structured packings with metal surfaces *(16)*. Bravo and coworkers *(17)*, and Rocha and coworkers *(18)* presented a general model of structured packings to predict pressure drop and efficiency. This model takes into account the construction material and the degree that the packing surface is wetted. Billet *(19)*, and Billet and Shultes *(20)* provided models applicable to both random and structured packings. Spiegel and Meier *(21)* developed an efficiency correlation for structured gauze and structured sheet-metal packings. They assumed that mass-transfer resistance in the liq-

uid phase is either negligible or can readily be incorporated in the coefficient for the gas phase.

Distillation's prospects

Because it is unlikely that existing distillation columns will be scrapped before the end of their useful lives (usually at least 30 years), replacement of distillation by other processes probably is limited to new plants. But there are plenty of opportunities for good economic returns from improving existing distillation processes. Projects that offer the quickest returns are those where an increase in distillation capacity is needed and can be achieved by merely retrofitting the column with a high-capacity tray or packing. These devices are commercially available and can be installed in a relatively short period of time. As energy costs increase in the future, however, distillation may come under more pressure from more energy-efficient processes. For more details on the status of distillation technology, see "Distillation: Still Towering Over Other Options" on p. 43.

EXTRACTION

Liquid/liquid extraction separates components of a liquid mixture based on their different solubilities in a solvent. Because a solvent is required, extraction is a more complex process than distillation. While in distillation the simplest system is a binary, in extraction it is a ternary. Models to predict efficiency and capacity in extraction are more complex than those for distillation, as is scale-up. While there are 40,000 distillation columns in the U.S., there only are 1,000 or so extractors. Nevertheless, there are many applications where distillation is not suitable and extraction is needed.

The extraction system has three components: *carrier* or nonsolute portion of the feed phase; *solvent*; and *solute* or material being transferred from feed to solvent phase. The terminal streams from the extractor are defined as *extract* and *raffinate*.

There are two requirements for liquid/liquid extraction to work. First,

component(s) to be separated from the feed phase must preferentially distribute themselves in the solvent phase. Second, the feed and solvent must be substantially immiscible.

The factors that favor extraction are:
• azeotropes or low relative volatilities are involved;
• low-to-moderate processing temperatures are needed;
• solvent recovery is easy; and
• energy savings can be realized.

Extraction is used to recover benzene, toluene, and xylene (BTX) from close-boiling paraffins, and lubricating oils from residue using propane as a solvent. Extraction also can be employed to remove oils from sludges, and phenol from wastewater (22). In the food industry, supercritical carbon dioxide is used to extract caffeine from coffee beans.

The strengths of extraction are that it can separate components with overlapping boiling products, and operate at low temperatures (which is important to the food and pharmaceutical industries). In some cases, it also may offer energy-efficiency advantages over distillation, depending upon the ease of solvent recovery. Null (23) has provided an analysis of the energy requirements of extraction vs. distillation.

The weaknesses of extraction stem from its use of a solvent, and the added complexity that this incurs. For example, the solvent must be stored, distributed, recovered, and recycled within the plant. Extraction, because of its more complex nature, is more difficult to model and scale up than distillation.

Hardware options

Contact between the two liquid phases is enhanced by dispersing one phase into the other. Thus, there are dispersed and continuous phases — depending upon relative specific gravities, either may be the light or heavy phase. In the sieve-tray extractor shown in Figure 3, the solvent is the dispersed (light) phase and the feed is the continuous (heavy) phase.

The simplest extractors are spray tower, sieve-tray, and packed-column
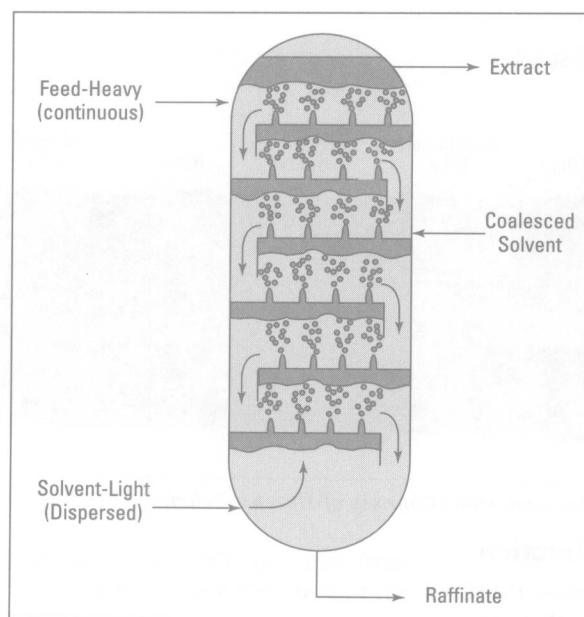
■ *Figure 3. A sieve-tray extraction column.*

Feed-Heavy (continuous)
Extract
Coalesced Solvent
Solvent-Light (Dispersed)
Raffinate

units. A spray tower simply is an empty column, and is used when only one or two equilibrium stages are needed. Tray and packed towers offer more stages. The trays and packings achieve breakage of dispersed-phase drops, reduce backmixing of the continuous phase, and enhance the tortuosity path of dispersed-phase drops. The sieve-tray extractor may have downcomers (as in the unit shown in Figure 3) or upcomers, depending on whether the dispersed phase is the light or heavy phase.

Structured packings offer capacity advantages in extraction in much the same way as in low-pressure distillation (24). There are said to be over 30 commercial extractors equipped with structured packings.

Mechanically-aided extractors can significantly reduce, through mechanical shear, the drop size of the dispersed phase and, thereby, increase the interfacial area between phases. This results in an increase in efficiency. Most mechanical designs are proprietary. Vendors not only provide the equipment but also provide scale-up information (which may not be available in the open literature). Most of these extractors have proven to be reliable and should be considered when a number of equilibrium stages are needed.

A relatively new commercial development is the membrane phase contactor (25), which is illustrated in Figure 4. In membrane extraction, the mass-transfer interface is a liquid film that forms across the individual membrane pores. The solute moves from the carrier to the solvent phase through these interfaces. The membrane phase contactor can be operated at a lower solvent rate than that required in conventional extractors. This is important when an expensive solvent, such as a crown ether (used to extract cesium from radioactive wastewaters), is involved. A lower solvent rate also translates into a reduction in downstream costs for solvent recovery.

The membrane phase contactor also is being used for absorption (for instance, to carbonate beverages), and stripping (for oxygen removal to produce ultrapure water for the microelectronics industry).

Solvent selection is a key decision in the design of the extraction system. Software, based on group-contribution methods, now is commercially available (26). It generates a list of possible solvents for a specified application, and then chooses the best one based on multicomponent equilibria.
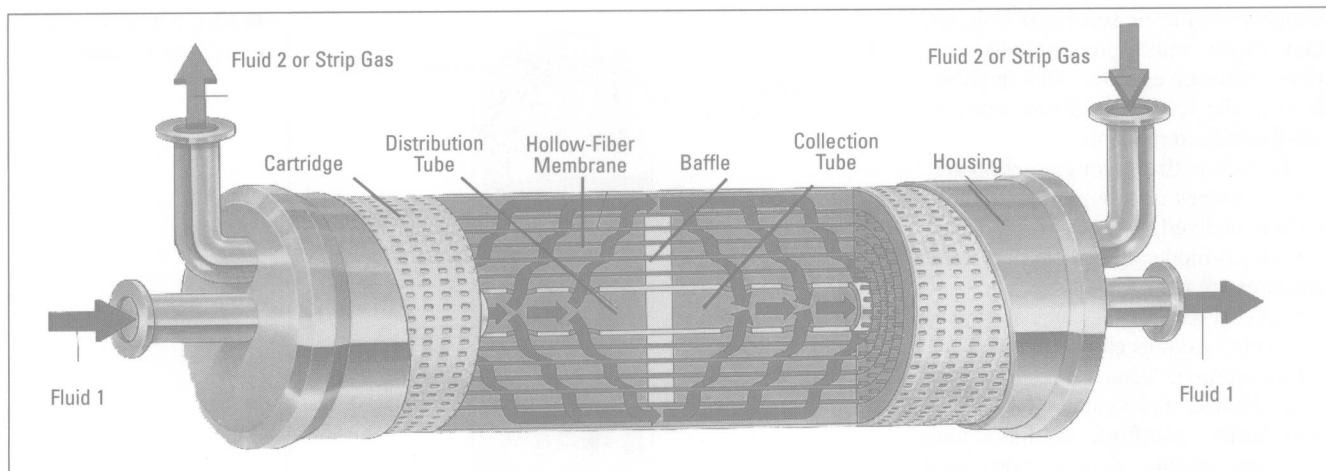
Figure 4. A membrane phase contactor. (Courtesy of Hoechst Celanese.)

Supercritical fluid extraction

Supercritical fluid extraction (SFE) uses a supercritical fluid, such as carbon dioxide, in place of a liquid solvent. In contrast to liquid/liquid extraction, which operates at near-atmospheric pressures, SFE runs at pressures of 1,000–5,000 psig.

SFE is used commercially for the extraction of caffeine from coffee and tea, and for the extraction of hops. The Residual Oil Supercritical Extraction (ROSE) process employs supercritical pentane to recover liquid fuels from heavy oils (27). Supercritical carbon dioxide also is finding important applications for replacing toxic cleaning fluids and organic solvents in spray painting. Table 2 (28) lists some commercial SFE plants.

The biggest single advantage of SFE is the nontoxic nature of supercritical solvents such as carbon dioxide. This feature likely will guide SFE into important new applications where there are concerns about the environment, worker exposure, or purity of products for human consumption. SFE possibly could replace molecular distillation in some applications; SFE can be designed as a staged process whereas, in molecular distillation, staging is difficult and expensive. The stumbling block for SFE centers on the costs associated with high-pressure equipment. Though a number of pilot tests of SFE have been conducted for bulk product separations in the CPI, few have emerged as commercial winners.

The role of extraction

Extraction trails distillation in the amount of research and development, as well as in number of applications. Extraction, however, can offer advantages over distillation because it can be operated at moderate temperatures, thus avoiding damage to thermally sensitive products. It also suits applications where low relative volatilities and azeotropes are involved and where energy savings are possible. SFE adds the benefits of nontoxic solvents.

ADSORPTION

In adsorption, one or more solutes are transferred from a liquid or gas mixture to the surface of a solid adsorbent, where they are held by inter-molecular forces. Desorption is the reverse process whereby the solute, called *adsorbate*, is removed from the surface of the adsorbent.

Fixed-bed adsorption is an unsteady-state process. Once a bed is spent, it must be taken off-line and desorbed (regenerated). To maintain a pseudo-continuous operation, a fresh bed must be brought on-line while the spent bed is being regenerated.

The regeneration step normally represents a major component of total operating cost. In pressure swing adsorption (PSA), the bed is regenerated by reducing the pressure; in temperature swing adsorption (TSA), by increasing temperature. TSA may require hours to days for bed regeneration, while PSA typically needs only a few minutes. TSA processes are limited to applications involving concentrations of a few

Table 2. Some commercial plants using supercritical fluid extraction.		
Product	**Plant Location**	**Capacity, million lb/yr**
Coffee	Bremen, Germany	60
Coffee	Houston	50
Coffee	Veragro, Italy	35
Tea	Munchmeunster, Germany	12
Hops	Munchmeunster, Germany	30
Hops	Sydney, Australia	"Large" but not revealed
Tobacco	Hopewell, VA	Not revealed
Essential oils	Reigate, U.K.	Not revealed
Source: (28).		

thousand ppm of solute, whereas PSA processes can be used to remove solutes present in bulk concentrations of 20–40%.

The factors that favor adsorption are:
• a high degree of solute removal is needed;
• low-to-moderate operating temperatures are desired;
• the spent bed(s) can be regenerated easily; and
• the adsorbent is not susceptible to fouling or attack by feed components.

Because of burgeoning use in clean air and water projects, adsorption has become increasingly important in recent years. There also are applications for adsorption in product recovery and purification. Carbon molecular sieves used with a PSA cycle have revolutionized air separation for medium-scale production of nitrogen. Table 3 (29) gives some examples of applications and adsorbents.

A strength of adsorption is that it can selectively remove solutes present in small concentrations, to obtain a high degree of removal. Additionally, the process can operate at low temperatures, important in applications where thermally sensitive products are involved.

A weakness of adsorption is that it is an unsteady-state process and suffers from the resulting disadvantages associated with a continually changing operation. Also, the performance of an adsorbent can be affected significantly by poisons or solids present in the feed.

Adsorbents

A variety of materials are used as adsorbents. These include:
• activated carbon (generally hydrophobic), which separates approximately by boiling point;
• silica gel (strongly hydrophilic), which generally is employed for dehydration;
• activated alumina (hydrophilic), which is used for dehydration of gas streams;
• zeolite molecular sieves, which separate based on polarity and size, and have a wide variety of uses;

Table 3. The role of adsorbents.

Typical applications (Adsorbates listed first)	Adsorbent
Gas bulk separations	
Oxygen/nitrogen	Carbon molecular sieve
Hydrocarbons/air	Activated carbon
Water/ethanol	Zeolite
Gas purification	
Sulfur compounds/natural gas	Zeolite
Odors/air	Silicalite
Liquid bulk separations	
p-xylene/o-xylene	Zeolite
Fructose/glucose	Zeolite
Liquid purifications	
Water/organics	Silica, alumina, zeolite, corn grits
Organics/water	Activated carbon, silicalite

Source: (29).

• carbon molecular sieves, which separate based on relative diffusion mechanisms.

A relatively new adsorbent material is the hydrophobic molecular sieve called silicalite. It selectively can remove organics from air without being loaded with water vapor, and can be regenerated at lower temperatures than carbon (30). The cost of this adsorbent is about 10 times that of activated carbon, but is expected to decline. Another relatively new commercial adsorbent is styrene divinyl benzene polymer. It overcomes some of the problems, such as unwanted side reactions and fires, associated with the use of activated carbon (31).

New regeneration configurations

Another new development is the marriage of the PSA cycle to activated carbon to obtain a process for removal of organics from air. This process can handle feed rates up to 2,000 std ft³/min and organic concentrations of 30% and higher, and can achieve 99.99% removal of the organics. The adsorption step continues for 5–15 min. During desorption, which takes 3–5 minutes, the process uses a combination of vacuum, heat accumulated during adsorption, and a back purge of clean air to regenerate the adsorbent (32).

For adsorption applications near atmospheric pressure, optimal regeneration pressure is 1–6 psia. The organic contained in the discharge stream from the vacuum pump is condensed and recovered as a liquid. The air mixture leaving the condenser carries an equilibrium concentration of organics and is recycled to the feed. The unit requires only electricity to drive the vacuum pump, and a cooling fluid for operation. Since 1988, at least 20 commercial units have been placed in operation for removal of hydrocarbons, chloroflourocarbons, chlorinated solvents, aromatics, and monomers from air. Figure 5 shows one such commercial unit.

Another highly successful development is the Simulated Moving Bed (SMB) process. Over 100 SMB units are operating commercially. This process uses a rotary valve in combination with a fixed bed to simulate the performance of a moving bed (33). Though developed for large-volume applications, it has found some newer small-scale applications, such as for the recovery of citric acid from fermentation broth in the food industry.

A newer adsorption configuration is the rotary wheel, which is coated with carbon or hydrophobic molecular sieves. It is used to remove organics from air. While one part of the moving wheel is adsorbing, the other part is being regenerated. This process, popular in the automobile industry, is effective when organic concentrations are low (up to 1,000 ppm or so), rates are high, and removal requirements do not exceed 97%.

Adsorption's prospects

Adsorption is expected to increase in importance partly because of its obvious applications in the environmental area. New developments in adsorbents and regeneration configurations will fuel this trend. Predicting process performance from adsorbent characteristics, system properties, and operating conditions, however, should remain an important challenge for researchers. More details on adsorption are provided in "Adsorption: Building Upon a Solid Foundation" on p. 56.

MEMBRANES

Membrane processes separate the components of a gas or liquid mixture on the basis of their relative permeation rates through a membrane material. A key step forward has been the development of the *asymmetric membrane (34)*. This permitted formulation of extremely thin membrane separating layers (of 1,000Å), and allowed fluxes to be increased by a factor of at least 200.

The two primary separation mechanisms in a membrane process are *hydrodynamic sieving*, and *sorption diffusion*. Hydrodynamic-sieving membranes rely on the separation of molecules based on their relative sizes. Such membranes have high permeabilities and low selectivities relative to sorption-diffusion membranes. Sorption-diffusion membranes depend upon both diffusion and solubility.

The permeability (P_A) of component A through a membrane may be expressed as the product of a diffusion coefficient (D_A) and a solubility coeffi-

■ *Figure 5. PSA unit for removal of organics from air. (Courtesy of Dow Environmental.)*

cient (S_A). D_A is kinetic in nature and reflects the ability of the solute to move through the membrane. S_A is thermodynamic in nature and, similar to phase equilibria, relates to the ability of a solute to migrate into the membrane. For two components, A and B, the ability of the membrane to separate A from B can be expressed as a selectivity, α_{AB}, defined as the ratio of the permeability of A to that of B, (P_A/P_B). Selectivity is similar to relative volatility in distillation. A diffusivity selectivity (D_A/D_B) that indicates the ability of the membrane to distinguish between A and B on the basis of size and shape may be defined. So, too, can a solubility selectivity (S_A/S_B) that reflects the relative preference the penetrants have to partition into the membrane material.

Important commercial applications of membrane processes include the separation of air to produce nitrogen, and the recovery of hydrogen from hydrocarbon gas streams. Desalination of salt water for many years has been a key application of RO. Membranes commercially concentrate milk and whey, and clarify fruit juices. Ceramic membranes are being used to concentrate fermentation broths. With two dozen commercial units in operation, removal of organics from air with membranes is a newer commercial development *(35,36)*.

The factors that favor membranes are:
• bulk rather than precise separations are sufficient;
• relatively low rates (such as, for petrochemicals, a few hundred lb/h) are involved;
• the membrane is resistant to fouling by the feed components; and
• energy cost is a key consideration.

One of the strengths of the membrane separation process is energy efficiency. In fact, energy efficiency approaches the thermodynamic minimum as pressure drop across the membrane approaches zero *(37)*. Membrane processes also have simple flow sheets and are easy to scale up. With membranes, only electric energy is required, an important factor at sites where steam or some other form of thermal energy is not available.

The weaknesses of membrane processes include fouling and the lack of durability of membrane materials. Additionally, capital costs for membrane units often are too high to compete with other processes, particularly at higher volumes. Membranes are more effective for bulk rather than for precise separations.