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Low-Energy Separations for the Process Industry

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Low-Energy Separations for the Process Industry

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ABSTRACT

An amount of energy equivalent to 800,000 bpd of crude oil is consumed in distillation processes in the petrochemical and petroleum refining industries in the United States. This paper reviews separation processes, including (1) distillation, (2) adsorption, (3) liquid-liquid and supercritical extraction, and (4) membrane processes. Conclusions are drawn on the merits of each type of separation process.

INTRODUCTION

The total energy consumed by the chemical and petroleum refining industries in converting feedstocks to products is equivalent to approximately 2.9×10^6 bpd crude oil. Table 1 gives the energy consumption, by area, of these two industries combined. Approximately 28% (equivalent to 800,000 bpd of crude oil) is consumed in distillation processes [1, 2]. Because most of the energy supplied to the distillation process is ultimately lost at the condenser, research leading to the development and use of

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TABLE 1

Estimated Energy Use in U.S. Chemical Plants and Petroleum Refineries, 1978

Item	Percentage
Furnaces, heaters	32
Distillation	28
Purchased electric power	18
Steam generation losses	9
Steam drives	6
Miscellaneous process heat	5
Gas engines and turbines	2
Total	100

energy-efficient alternative processes can, for many companies, result in substantial reductions in the consumption of oil, gas, or coal and a corresponding reduction in costs. In this paper we review alternative separation processes of interest to the process industries. The separation processes discussed here include (1) distillation (and improvements), (2) adsorption, (3) liquid-liquid and supercritical extraction, and (4) membrane processes.

DISTILLATION

Distillation is the process by which components of a mixture are separated by their differences in boiling points. In this process there are two phases: liquid and vapor. The components to be separated are present in both phases but in different concentrations. The more volatile components concentrate in the vapor phase, while the less volatile components concentrate in the liquid phase. Although the conventional distillation process is not energy efficient, it is very reliable from a quality-control

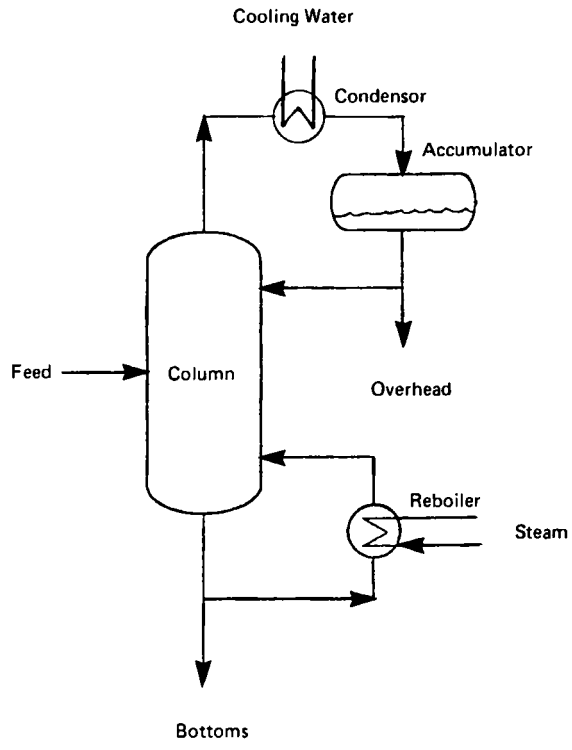


FIGURE 1 Conventional Distillation Column

standpoint and will continue to be the workhorse separation method of the process industries (Fig. 1).

In the simplest terms, distillation systems receive heat at the reboiler and reject heat to the condenser, and thus most of the energy supplied to the process is lost. Generally, the sensible heats of liquid feed and product streams and losses can be neglected, and the overall heat balance for a distillation tower reduces to

$$Q_S = Q_C, \tag{1}$$

where

Q_S = the rate of heat absorption at the reboiler

Q_C = the rate of heat rejection at the condenser.

The combination of Eq. (1) with the heat balance around the condenser yields:

$$Q_S = D\,\Delta H_V(R + 1), \tag{2}$$

where

D = the overhead product rate

ΔH_V = the rate of heat of vaporization of overhead product

R = reflux ratio.

In order to ensure that high-purity product is produced, reflux ratios used in operating systems are typically far in excess of what is actually required to achieve specification purity. The relationship for a simple column for one feed and two products is shown in Fig. 2. This figure illustrates that as the reflux ratio

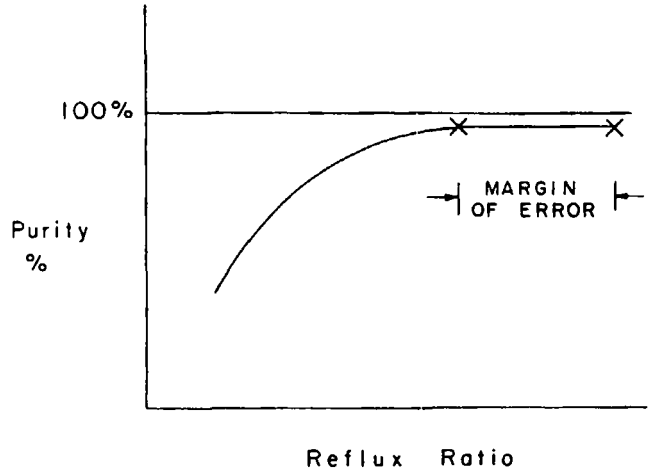


FIGURE 2 Effect of Reflux Ratio on Overhead Product Purity

increases, the product purity tends to levels off, and there is a threshold reflux ratio beyond which no benefit is to be gained. However, with increased reflux ratios there is a penalty in reboiler steam usage as shown by Eq. (2). The reduction of reflux ratios in distillation towers is a key area for potential energy savings in an operating plant.

In order to better characterize the distillation process we shall define several terms. The minimum thermodynamic work for complete separation of an ideal mixture into the individual pure components is given by King [3]:

$$W_M = -RT \sum_j X_{jF} \ln X_{jF}, \tag{3}$$

where

W_M = minimum work of separation

R = gas constant

T = absolute temperature

X_{jF} = mole fraction of component j in feed mixture.

Using the McCabe-Thiele method, Keller [4] developed and presented the minimum heat requirement for complete separation of an ideal binary liquid mixture into the pure components. For the case of a distillation tower equipped with a single reboiler and condenser, assuming equal molal overflow, constant relative volatility, and the feed at the bubble point, Keller found that the minimum heat required for complete separation may be expressed by the following equation:

$$Q_M = \Delta H_V \frac{1}{\alpha - 1} + X_F , \tag{4}$$

where

Q_M = minimum heat required for complete separation

ΔH_V = molar heat of vaporization of the heavy component

α = relative volatility (ratio of the equilibrium K values)

X_F = mole fraction of the more volatile component in the feed

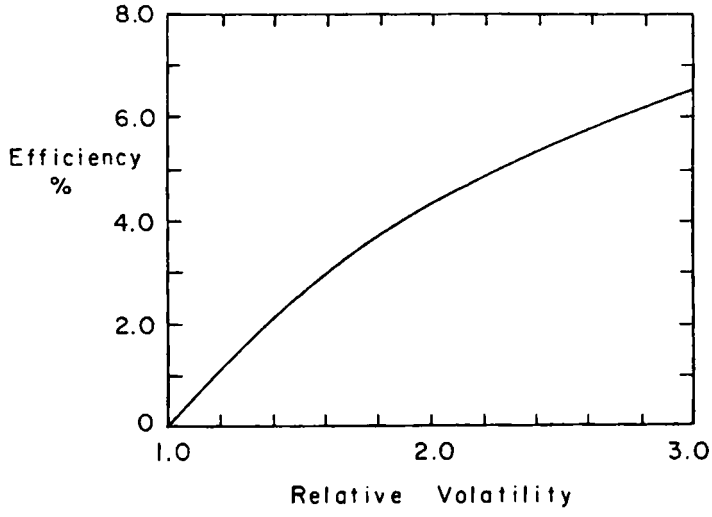
Maximum efficiency of the distillation process may be defined as:

$$\text{Maximum Efficiency} = \frac{\text{Minimum Work of Separation}}{\text{Minimum Heat of Separation}} \times 100$$

$$E_{MAX} = W_M/Q_M. \tag{5}$$

where W_M and Q_M are given by Eqs. (3) and (4), respectively.

Maximum efficiency, for complete separation, E_{MAX}, is shown as a function of relative volatility, α, in Fig. 3. This figure is based on a 50/50 mole percent binary mixture, and the assumption that Trouton's rule for the estimation of latent heat of vaporization applies. This figure shows that at values of relative volatility as high as 3.0, the maximum efficiency, E_{MAX}, for the conventional distillation process is in the range of only 6.6%. This characteristic of the conventional distillation process indicates the opportunity for improvement (such as heat integration and heat pumping) in conventional distillation systems, as well as the need for research and development of more efficient alternative processes.



Efficiency = (Minimum work of separation x 100) / Minimum heat for separation)

FIGURE 3 Effect of Relative Volatility on Maximum Efficiency for Complete Separation of a 50/50 Mole % Binary Mixture by Simple Distillation

Heat Pumping/Mechanical Vapor Recompression

Although heat pumping is not a new concept, its application to distillation processes is in its infancy. Heat pumping may employ an external working fluid, as shown in Fig. 4. Compression is used to raise the temperature of the working fluid above that required to boil the material in the reboiler. The fluid leaving the reboiler is evaporated in an overhead condenser. The net result is that the heat absorbed by the working fluid in the overhead condenser is used to boil the bottom liquid, with the aid of the compressor [5].

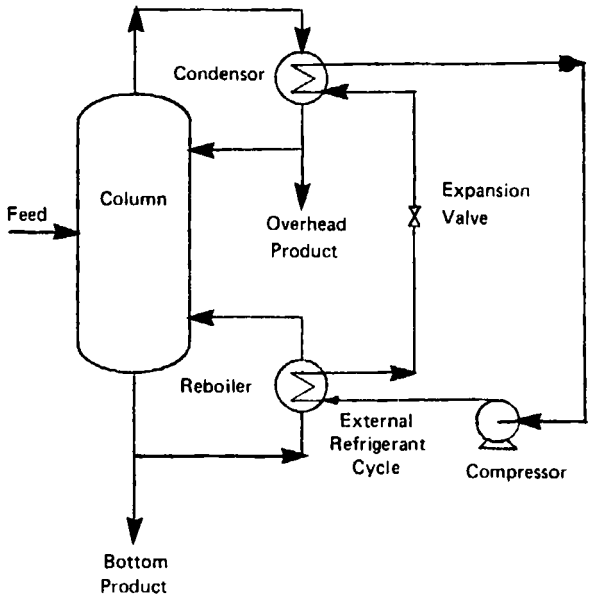


FIGURE 4 Heat Pumping

An alternative to the basic heat-pump concept is to use the column overhead material as the working fluid. This alternative, called mechanical vapor recompression, eliminates the need for an overhead condenser, as shown in Fig. 5.

One measure of efficiency of heat-pump performance is the coefficient of performance (COP). The COP is defined as the ratio of the thermal energy delivered to the energy consumed by the prime mover for the compressor:

$$\text{COP} = \frac{\text{heat delivered}}{\text{work input}}. \tag{6}$$

The delivered-energy cost for an electrically driven heat-pump installation is

$$\text{EC} = \frac{2.93\ \text{ER}}{\text{COP}}, \tag{7}$$

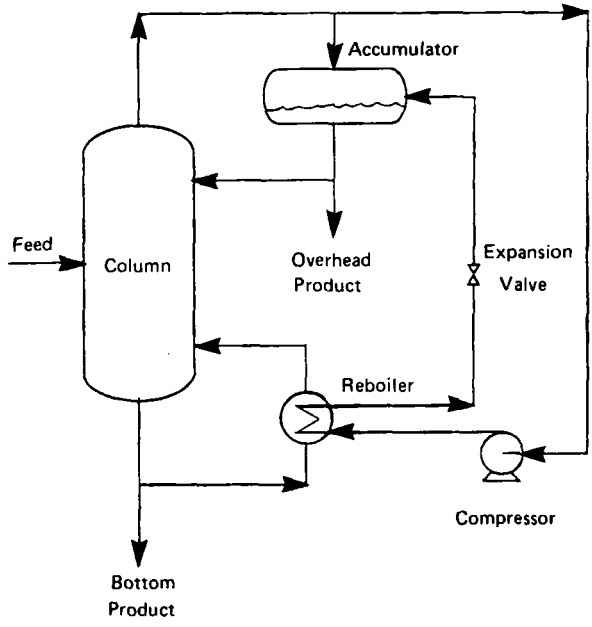


FIGURE 5 Vapor Recompression

where

EC = energy cost ($/thousand pounds of steam)

ER = electric rate (¢/kWh).

With a nominal COP of 3 and an electric rate of 3¢/kWh, the energy cost for the heat delivered by the heat pump is $2.93/thousand pounds. This amount compares quite favorably with the cost of steam generated from boiler fuels, typically $5-7/thousand pounds.

Energy savings achieved by heat pumping or by vapor recompression can be dramatic. For example, it is quite possible to achieve savings of 30,000 to 40,000 lb/hr of steam in single separations involving large volumes of petrochemicals. Good candidates for heat pumping are those columns that consume

expensive utilities such as (1) refrigeration in the condenser, or (2) high-pressure steam in the reboiler.

The heat-pumping concept has these limitations:

- Since work required for compression is largely determined by the difference between the condenser and reboiler temperatures, heat pumping is suited to columns with a small temperature difference (perhaps 50°F or less).
- Columns that use low-pressure steam in the reboiler will often show a marginal pay-out, and there is no incentive at all if the plant is out of steam balance and currently venting the same pressure steam.

ADSORPTION

One or more components of a liquid or gaseous mixture can be removed by passing the mixture across an appropriate solid adsorbent. The components that are removed are held on the surface or in the structure of the adsorbent by intermolecular forces or by shape selectivity, or both. In a significant number of separations in industrial processes the adsorption process can be attractive. For example, in refineries typical by-product fuel gas streams contain 3-10% C2, C3, and C4 hydrocarbons which, if recovered, would be more valuable as chemical feedstock [6]. Because of high capital and energy costs, recovery of these hydrocarbons by cryogenic distillation or by absorption is typically not attractive. However, with the adsorption process, it is not necessary to expend energy on the entire stream--only on the desired components that are selectively adsorbed.

Current commercial applications of the adsorption process include the removal of hydrogen from hydrocarbon gas mixtures, nitrogen and oxygen from air, and organics from air, and the separation of normal paraffins from isoparaffins.

The adsorption process is normally a fixed-bed process which is cyclic in nature and which calls for nearly complete removal of adsorbed material during regeneration. To match the performance of the previous cycle, regeneration must not cause any degradation of the adsorbent. The usual procedure is to drop the pressure to regenerate the bed (pressure swing). Alternatively, the bed may be subjected to a stream of hot gas (thermal swing) that heats the bed to a point where the equilibrium relationship allows no adsorbed material to remain on the surface of the adsorbent. The regeneration step can often be the controlling factor in the economics of the adsorption process; regeneration can require a period of time from a few hours to several days [7]. A flow diagram for the pressure swing adsorption process is shown in Fig. 6.

One of the most important developments in recent years has been that a number of new materials have greatly increased the potential applications of the adsorption process. For example, zeolite adsorbents can now be purchased in a number of different, but quite uniform, pore sizes, allowing sophisticated separations based upon both polarity and shape selectivity. In addition, hydrophobic zeolites have now been synthesized that provide one of the potentially attractive methods for separating polar organics from

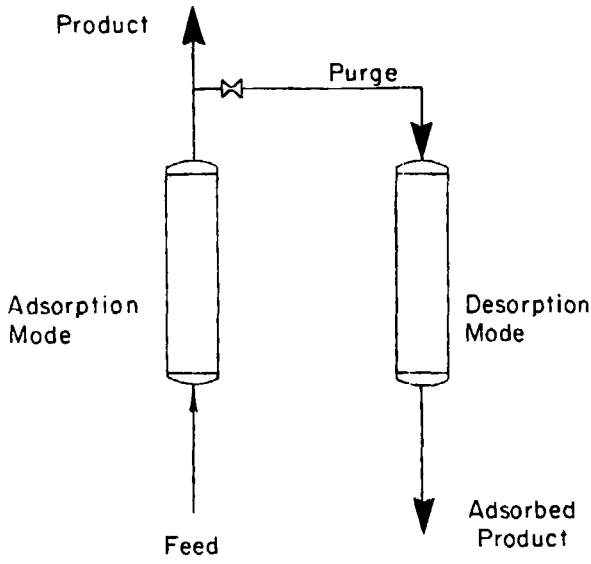


FIGURE 6 Adsorption (Pressure Swing)

water [8]. Since zeolites offer improved mechanical strength, we expect the use of these new types of attrition-resistant adsorbents to make moving-bed and fluidized-bed processes the subject for future investigations. The advantages include both continuous operation and reduced process complexity.

An intriguing possibility for regeneration lies in the concept that the extent of adsorption of substances at the solid-liquid interface depends on the electrical potential difference across the interface [9]. This method offers the prospect of regenerating adsorption beds merely by changing the voltage applied to the bed. This type of regeneration has not been exploited, mainly because fundamental data for such processes have not been obtained and because of the difficulty in the construction of large-scale

columns where a uniform applied potential can be achieved. However, the use of electric voltage to regenerate adsorption beds is an exciting concept that deserves further research.

EXTRACTION

Liquid-Liquid Extraction

Liquid-liquid extraction is the separation of one or more components of a liquid by contact with a second immiscible liquid, called the solvent. If the components in the original liquid solution distribute themselves differently between the two liquid phases, separation will result. This is the principle on which separation by liquid-liquid extraction is based.

Whether the liquid-liquid process is carried out in a laboratory or on an industrial scale, it always involves a contact of liquid phases with an approach toward equilibrium and subsequent separation of the contacted liquid phases. On the laboratory scale, the process can involve shaking the phases in a separatory funnel, allowing them to settle, and then separating the phases.

On an industrial scale, extraction is nearly always carried out continuously with multistages using a variety of contacting methods and devices. The basic concept of this process is illustrated in Fig. 7. Extraction devices may be unagitated or agitated. Agitation may be accomplished with the use of internal devices such as rotary stirrers or reciprocating plates, or by the application of feed pulsations from external pumps. Fig. 8 shows three types of mechanically agitated liquid-liquid extraction devices.

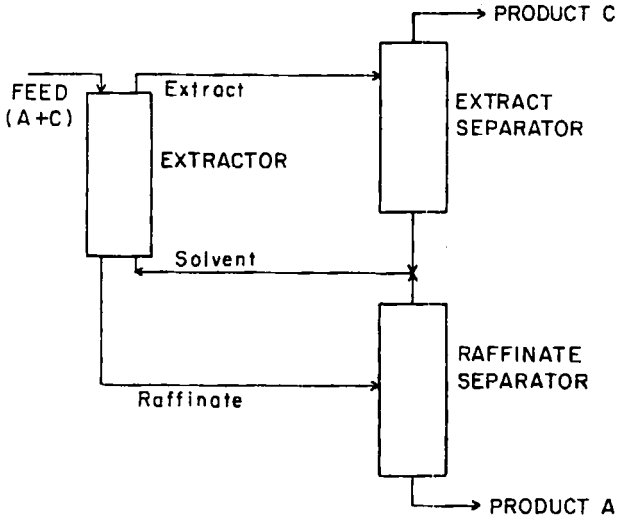


FIGURE 7 Liquid-Liquid Extraction Process

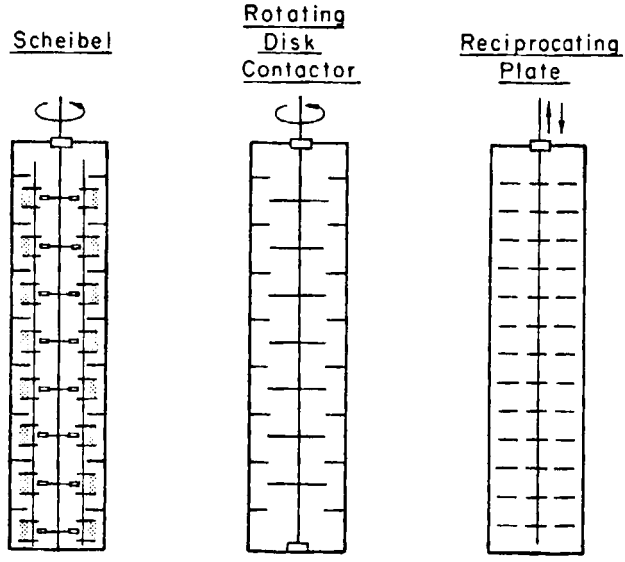


FIGURE 8 Mechanically Agitated Extractor Columns

Liquid-liquid extraction can have improved energy efficiency advantages over the conventional distillation process, and also has the capability of recovering heat-sensitive macromolecules at moderate operating temperatures.

Although developments have advanced liquid-liquid extraction to the point where industrial scaleup is practical, many uncertainties exist for determining the optimum type and size of a liquid-liquid extraction device for a specified application. Therefore emphasis should be placed on carrying out fundamental research in mass transfer that would lead to improved mechanistic models to predict operating performance of large-scale liquid-liquid extractors.

Supercritical Extraction

Supercritical fluid extraction has recently been receiving widespread attention [10]. This process involves the use of a solvent above its critical temperature so that it takes on characteristics intermediate between a gas and a liquid. This fluid has the density advantage of liquid solvents and the penetrative ability of a gas so that it is effective in dissolving and recovering desired fractions from various substrates. A second advantage of a supercritical solvent is that it can be readily separated from the process merely by reducing the system pressure. At reduced pressure the extracted material precipitates from the gas phase and allows for nearly complete recovery and recycling of the solvent in a continuous processing scheme. The cost of

compressing the solvent in supercritical extraction can be significant and must be considered in any serious evaluation of this process.

Some industrial companies have been active in supercritical extraction, as evidenced by the fact that Kerr-McGee is now licensing the Residual Oil Supercritical Extraction (ROSE) process to extract liquid fuels from heavy crudes and residuum [11]. There are several examples of the application of supercritical extraction in the food industry. Here the use of CO_2 has advantages over other solvents because it introduces no possible health hazard. It is also nonflammable, noncorrosive, inexpensive, and readily available in high purity. Since it has a critical temperature only slightly above ambient temperature, it is easily handled and removed from products. Supercritical CO_2 is preferred to liquid CO_2 because the substances to be extracted are much more soluble in the supercritical solvent. The extraction rate is about 2.5 times higher because of the higher diffusivity in the supercritical state, and the range of possible operating temperatures is wider.

One of the first processes that has gone into commercial operation is the removal of caffeine from coffee [12]. In this process, green coffee beans, having been previously soaked in water, are placed in a pressure vessel and extracted with supercritical CO_2. The caffeine diffuses out of the beans into the supercritical fluid and is carried to a recovery tower, where caffeine is removed with a water carrier; CO_2 is continuously recovered, compressed, and recycled (Fig. 9.)

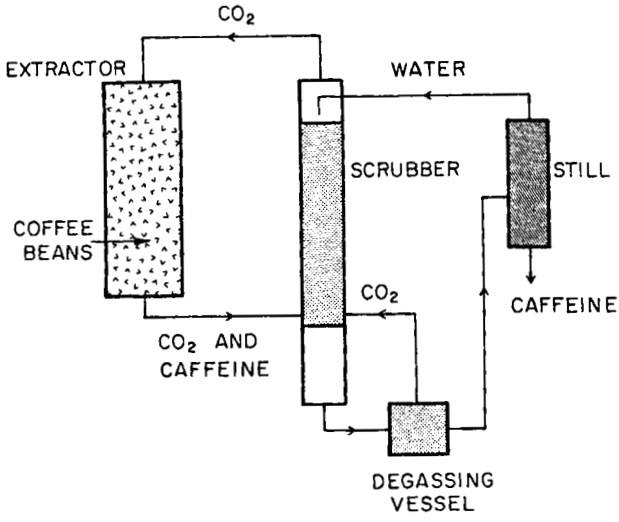


FIGURE 9 Process for Removal of Caffeine from Coffee Using Supercritical CO_2

The use of supercritical solvents in the extraction process is in an active state of research and development with both fossil fuels and natural products. Future studies should focus on a careful choice of the various components of the supercritical mixture so that each component interacts in a specific way with the constituents of the substrate, and combined action of all the components produces an optimal effect. For example, certain polar-nonpolar combinations of supercritical solvents have been observed to display strong synergism in the recovery of fuel components from coal [13].

Bench-scale research on supercritical extraction of coal is currently underway in the Department of Chemical Engineering at The University of Texas at Austin, using a batch-autoclave system.

Supported by a grant from the U.S. Department of Energy, the research focuses on the determination of the specific physical and chemical characterisitics of supercritical solvents--such as polarity, molecular size, and critical density--that can affect the yield and quality of supercritical coal extracts. This program will be expanded to include other substrates such as heavy crude and petroleum coke.

MEMBRANE-BASED SEPARATION PROCESSES

The membrane separation process is based on the difference in permeabilities of different compounds through a membrane material. Membrane processes have attracted attention in recent years because of their inherently low energy requirements for separation [14, 15, 16]. In effect, all that is required is a pressure-driving force to perform a separation. There are a number of existing and prospective industrial applications for membrane processes.

Until recently, hydrogen has been recovered from hydrocarbon streams by cryogenic distillation, a process with high capital and energy costs. Because of its relatively high rate of transport through membranes, hydrogen is particularly suited for recovery by permeation techniques. This characteristic has recently been utilized by the Monsanto Company in its PRISM® Membrane Separator System for recovery of hydrogen from process purge streams.

The PRISM separator resembles a shell-and-tube heat exchanger. Fig. 10 shows how the separator works. The gas stream to be purified is fed into the shell side of the separator but on the outside of the hollow fibers. As the pressurized feed gas flows

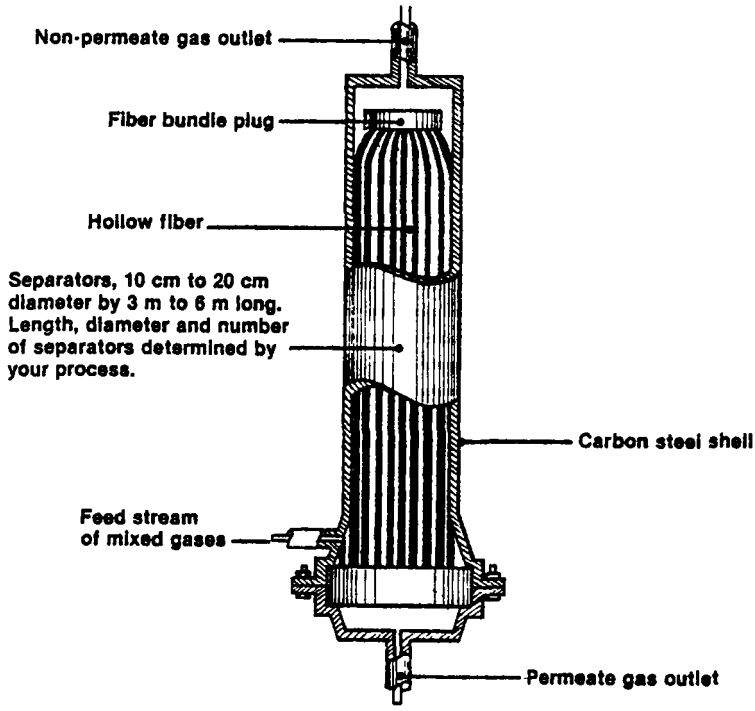


FIGURE 10 PRISM® Separator

through the separators on the shell side, hydrogen selectively permeates through the fiber walls. The hydrogen is collected at reduced pressure at the bottom of the separator. The hydrogen-depleted gas exits through the top of the separator at essentially the same pressure as the feed gas. The driving force for the separation is the difference in hydrogen partial pressure between the shell and bore side of the fiber.

PRISM systems produce recovered hydrogen of 86% to 96% purity and, in some cases, as high as 99% purity. Hydrogen recoveries in

excess of 80% can be obtained for most applications. Recoveries in the range of 95% can be expected in ammonia purge recovery applications.

It is apparent that substantial savings in energy could be realized by development of separation and purification processes that do not depend on the latent heat of vaporization. It is, however, unrealistic to assume that permeation could completely replace distillation. The problems include membrane attack by permeates, low rates of permeation, and low separation factors, especially for isomers and other structurally similar materials having narrow molecular-weight differences. In addition, operating pressure requirements, to overcome osmotic pressures in liquid systems, can be a significant problem that must be evaluated. The immediate priority associated with the research and development of membrane separation processes is problems associated with the membrane material itself in terms of throughput, selectivity, and durability.

There are exciting possibilities for membrane separation processes for the separation of oxygen from air for use in medical or life-support systems, and on a larger scale, for the recovery of oxygen-enriched air for use in combustion processes. Such an application could save a great deal of energy. Similarly, a low-cost source of oxygen-enriched air would be useful in aerobic treatment of organic waste. Another major area for improved gas separations, owing to the increased value of hydrogen, is the recovery of hydrogen from CO in coal gasification streams, from ammonia purge streams, or from various refinery streams.

CONCLUSIONS

When steam costs were in the range of 40-50¢ per thousand pounds, common practice was to use the distillation process for all separations. Other methods were considered only when (1) the operating conditions were too severe, (2) the capital investment was too high, or (3) the distillation process could not be used at all because of overlap in boiling points. However, with steam costs in the range of $5-7 per thousand pounds, process economics dictate that alternative separation processes that will be more energy efficient than distillation be researched and developed. In addition to being more efficient, alternative processes will need to compete with distillation from the standpoint of capital investment. This will be a major challenge. A distillation tower (except for the trays) is empty and will scale up on the basis of the six-tenths power rule. This means that if the throughput is doubled, the capital investment increases by only about 50%. On the other hand, in a membrane separation process, doubling the throughput will also almost double the capital cost.

It is clear that the future of separations will see innovation and change. Some directions and needs include:

1. In distillation systems, there will be increased heat integration; this will involve towers that operate at higher pressures. Improvements do need to be made in the prediction of tray efficiency, perhaps the major research frontier remaining in distillation. We are in agreement with the conclusion of Rush [17] that a real key to

improving the efficiency of separations is to design distillation systems to run "leaner and harder."

2. In liquid-liquid extraction there will be a real need for fundamental mass-transfer studies to develop better mechanistic models that will be useful in the design and scale-up of large-scale extractors.
3. In supercritical extraction the need will be to investigate combinations of solvents. The most efficient future processes will likely involve the use of a combination of solvents tailored to particular applications.
4. Recent developments in the synthesis of zeolites make the field of adsorption exciting, in terms of new applications for the conventional fixed-bed process as well as for the possible development of moving-bed and fluidized-bed processes. Fundamental research needs to be undertaken that will result in improved methods of regeneration.
5. Because all that is required is a pressure-driving force to effect the separation, membrane processes will continue to warrant high research priority. The most significant future improvements coming from membrane research will be in the membrane material itself. New materials will be developed that will be more selective, provide higher throughputs, and possess the durability necessary to withstand poisons, contaminants, and severe operating conditions.

TABLE 2

Separation Processes Summary

Process	Advantages	Disadvantages	Applications
Distillation	Reliable	Energy use	Many in separation of petrochemicals and refinery fractions
	Quality control	May require extreme operating temperatures	
	Scale-up easy		
	Relatively low capital		
Adsorption	Can be energy efficient	Capital cost	H_2 from hydrocarbons
	High product purity	Cyclic process regeneration methods	n-paraffins from i-paraffins
	Can remove trace quantities		
	Low temperature		H_2S from sour gas
Liquid-Liquid Extraction	Can be energy efficient	Capital cost	Acetic acid from water
	Moderate operating temperatures	Solvent recovery	Ketones from water
		Scale-up questionable	
Supercritical Extraction	Energy efficient	Capital cost	Caffeine from coffee
	Ease of solvent recovery	High temperature and pressure may be necessary	Fuel fractions from heavy crude
Membrane Separation	High energy efficiency	Limited throughput	Hydrogen from hydrocarbons
	Low operating temperature	Low-purity product	Recovery of potable water from brackish water
		Poor durability	

The advantages and disadvantages of some alternative separation processes are listed in Table 2.

In the conversion of raw materials to products, separation processes can significantly affect the profit for a given product, and in some cases, determine if a product can be produced at all. In the manufacture of large volume products, reducing energy consumption of separation processes is an effective way to reduce manufacturing costs. On the other hand, in the manufacture of fine chemicals, the emphasis may not be on saving energy but rather on an improved separation process to recover a higher quality product or a completely new product. In either case the goal is to increase bottom-line profit, and separation processes play a key role in achieving this goal. We believe that companies whose business depends significantly on separation processes should aggressively pursue research that leads to the development of improved processes for performing separations.

ACKNOWLEDGMENT

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