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Production-Scale Adsorptive Separations of Liquid Mixtures by Simulated Moving-Bed Technology

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Abstract

The commercial use of liquid chromatography for separation of bulk components from mixtures has undergone a rapid expansion in recent years. This expansion has been accomplished largely by use of a flow scheme that realizes the process advantages of continuous countercurrent movement of liquid and solid without actual movement of the adsorbent. Since startup of the first such plant in 1963, a total of 60 units has been licensed in six different applications. These have an aggregate capacity in excess of five million tons per annum of selectively adsorbed purified product. The sequence of research and development studies leading to commercialization of this process are outlined, and the present and projected applications are reviewed.

INTRODUCTION

Adsorption from the liquid phase has long been used for removal of trace contaminants from process streams. However, its application to separation of bulk components of mixtures in large-scale operations is a relatively recent development and has been accomplished largely by use of a simulated moving-bed technique known generally as the Sorbex* process. The process has been commercialized extensively, as illustrated by the licensing of 60 such units in six different applications, with an aggregate capacity of 10×10^9 pounds per year of selectively adsorbed purified products.

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*Sorbex, Parex, Olex, Molex, Sarex, Cresex, and Cymex are registered or unregistered trademarks and/or service marks of UOP Inc.

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In this paper, steps leading to the development of the process and its various applications are described.

During the work described here, a major activity of the UOP Process Division was the invention, development, and licensing of new or improved processes, largely in the areas of petroleum refining and petrochemicals. In order to create a wide licensing base, effort was focused on production of large-volume items. It was, therefore, desirable to develop technology that could be applied to very large-scale operations, and this has been a major objective. More recently, emphasis has been shifted to encompass smaller volume operations in speciality areas.

ADSORPTION VS OTHER SEPARATIVE METHODS

In some respects adsorption is a more complex operation than some of the more conventional separative methods in large-scale commercial use: special problems arise from the immobility of the absorbent and from the tendency of adsorbents to foul. In order to consider adsorption as the method of choice, there should, therefore, be some compensating advantages associated with its use.

It has been found that, in a number of commercially important systems, such advantages do in fact exist. In some cases separations can be accomplished by adsorption which are either very difficult or impossible to obtain by other known means.

To provide some perspective on the position of adsorption relative to other methods, consider the following separations:

1. Fractional Distillation
2. Solvent-Aided Separations
    a. Liquid–Liquid Extraction
    b. Azeotropic or Extractive Distillation
3. Crystallization
4. Rate-Selective Processes—Membrane Permeation
5. Adsorption

Fractional Distillation

If relative volatilities between key components are high, fractional distillation is probably the simplest and cheapest method of separation. However, at low relative volatilities—perhaps below about 1.25—the operation becomes very difficult and expensive, and other methods should be considered.

Solvent-Aided Processes

If simple distillation is difficult, the next step of complexity is the use of selective solvents which alter the relative activities of the components to be separated. Such solvents can be used either in liquid–liquid extraction or in azeotropic or extractive distillation processes. These operations are well-developed and in widespread use. Liquid–liquid extraction, for instance, is used extensively for separation of aromatic hydrocarbons from other types; extractive distillation is conventionally used for separation of butadiene from other C_4 hydrocarbons.

In a number of systems, however, there are no known solvents of adequate selectivity. This is frequently the case when the feed components are isomers. Polar solvents appear to recognize the presence or absence of various functional groups in the molecules to be separated but do not distinguish particularly between different geometries of attachment.

Crystallization

If the foregoing methods are not suitable, crystallization can be considered when the freezing points of the components are sufficiently different. It is often possible to obtain a pure product by crystallization, but there is one general limitation; namely, it is never possible to obtain complete separation. When the recovery of the desired component reaches a certain value, the other components start to crystallize simultaneously.

Crystallization is used commercially to separate *p*-xylene from C_8-aromatic mixtures. However, the recovery of *p*-xylene is limited by equilibrium to 55–60% per pass. In contrast, adsorptive methods easily achieve 96% recovery.

Rate-Selective Processes

A separation process might be considered, based, not on differences in phase compositions at equilibrium, but on differences in diffusion rates through a permeable barrier. These are designated as "rate-selective" processes in contrast to "equilibrium selective."

While membrane processes have been used successfully in some gas separations and aqueous systems, suitable permeable barriers have not been developed for other applications. One might conceive of adsorbentlike porous solid particles that show no selectivity at equilibrium but which allow the feed components to diffuse into the pores at different rates; material of this type could also be classed as a rate-selective agent.

Unless the permeation coefficients of the feed components are widely different, a rate-selective process will not give good separation unless it is multistaged by constructing a cascade. Cascades generally consume large quantities of energy. For instance, a paper study of a hypothetical rate-selective process to achieve good separation with a permeability ratio of 2:1 shows an energy requirement 30 times as great as for an equilibrium-selective process with an enrichment ratio of 2:1.

The relatively high energy requirement of rate-selective processes is probably related to the fact that, in order to achieve separation, transfer must take place at conditions far removed from equilibrium—i.e., in a highly irreversible manner.

Adsorption

A major advantage of adsorbents over other separative agents lies in the fact that very favorable equilibrium phase relations can be developed for particular separations; adsorbents can be produced which are much more selective in their affinity for various substances than are any known solvents. This is particularly true of the synthetic crystalline zeolites (*1*) containing exchangeable cations, which became available about 30 years ago under the name of molecular sieves.

An extreme example of unique selectivity is provided by the use of 5A molecular sieves for separation of linear hydrocarbons from branched and cyclic types. In this system, only the linear molecules can enter the pores; others are completely excluded because of their larger cross section. Thus, the selectivity for linear molecules with respect to other types is infinite.

In the more usual case, all the feed components can enter the pores and each will fill the pores completely if present alone. In a mixture, however, some components are adsorbed more strongly than others, and a selectivity is thus established which can be used to accomplish separation.

In systems of this type, modifications of the adsorbent have been found that alter not only the magnitudes of the selectivities but even their sequence. For instance, in a system comprising the four C_8-aromatic isomers, it is possible to extract selectively either *p*-xylene, *m*-xylene, or ethylbenzene. No chemically unreactive solvents are known that are usefully effective for any of these three operations.

A further example of unique selectivities is provided by the separation of olefins from paraffins in feed mixtures containing about five successive molecular sizes—e.g., C_{10}–C_{14}. Liquid–liquid extraction might be con-

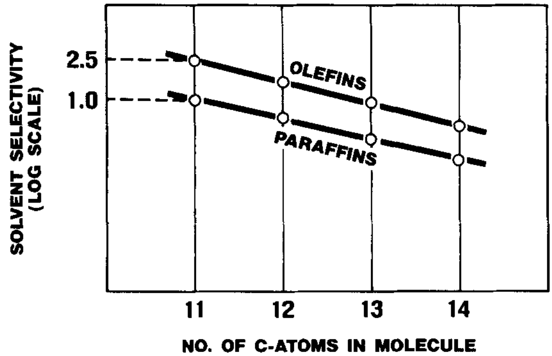

FIG. 1. Liquid–liquid extraction selectivity of polar solvents in paraffin–olefin system.

sidered for this separation. It is found, however, that polar solvents give solubility patterns of the type shown in Fig. 1. Here, each olefin is more soluble than the paraffin of the same chain length. However, the solubility of both species declines as chain length increases. Thus, in a broad-boiling mixture, solubilities of paraffins and olefins overlap and separation becomes impossible.

In contrast, the relative adsorption from the liquid phase on the adsorbent used commercially for this operation is as shown in Fig. 2. Here, not only is the selectivity between an olefin and paraffin of the same chain length much higher, but, additionally, there is very little effect of chain length. Consequently, complete separation of olefins from paraffins becomes possible.

An additional potential advantage of adsorption is the fact that much higher efficiency of transfer of material between liquid and adsorbed phases can be achieved in adsorptive operations than in the conventional equipment

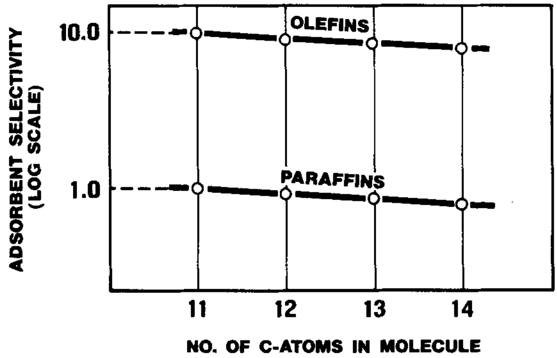

FIG. 2. Adsorption from liquid-phase selectivity of Olex adsorbent.

used for extraction or extractive distillation. This is illustrated by laboratory-scale chromatographs that commonly show separation efficiency equivalent to thousands of theoretical equilibrium stages in columns of modest length. This high efficiency results from the use of small particle sizes to provide high interfacial area and low diffusional resistance, and from the absence of significant axial mixing of either phase.

In contrast, the trays of fractionating columns and liquid–liquid extractors are designed to obtain practically complete axial mixing in each physical element in order to create interfacial area. With this arrangement, regardless of actual transfer rate coefficients, the number of theoretical equilibrium stages is limited substantially to the number of physical mixing stages installed. This limitation could be avoided, in theory, by the use of packed columns. However, if the particle diameter of the packing is small enough to give interfacial areas comparable to those obtainable in adsorptive beds, the capacity for accommodating counterflow of two fluid phases becomes low, and great difficulty is encountered in obtaining uniform unchanneled flow of both fluid phases. These limitations are much less severe in an adsorptive bed, because only one fluid phase is involved.

DEVELOPMENT OF THE SORBEX PROCESS

Conventional Liquid Chromatography

In the early stages of our work, we considered the commercial application of standard methods of liquid chromatography as shown in Fig. 3. Here, liquid streams of feed and desorbent are fed alternately at constant temperature and pressure to a fixed bed of adsorbent. As the feed components travel through the bed, they gradually form separate bands, which are withdrawn alternately as extract and raffinate. The desorbent is a liquid of different boiling point from the feedstock and is subsequently recovered from the product streams by fractionation.

By a combination of experimental studies (*2*) and mathematical modeling (*3*), we were able to define our system in terms of equilibrium and kinetic constants and thereby roughly estimate the requirements for a large commercial unit. Before proceeding to pilot-plant construction, however, we considered whether there might be a more advantageous alternative mode of operation.

Conventional liquid chromatography is a simple, easily implemented operation and is certainly well suited for small-scale preparation. In a large-

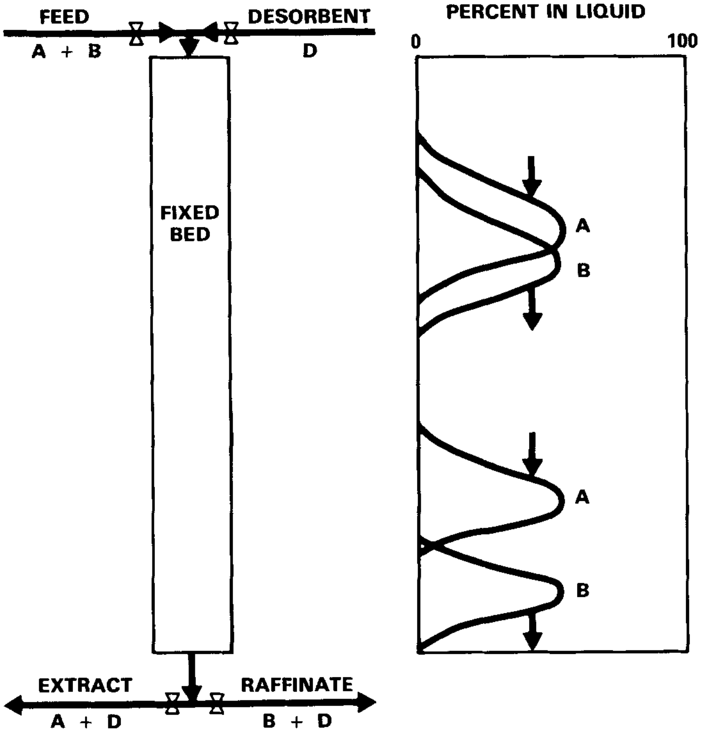

FIG. 3. Batch adsorption conventional chromatographic operation.

scale operation, however, it has some inconvenient features. Feed streams are discontinuous and the product streams vary continuously in composition. It is difficult to integrate such intermittent processes with continuous processes operating upstream and downstream from it, and problems of control are troublesome. For instance, the product streams from the bed cannot be fed directly to continuous fractionators for recovery of desorbent; large well-mixed surge tanks must be interposed to damp fluctuations in rates and compositions.

An additional weakness of the system appeared in the course of modeling studies—namely that various parts of the bed at various times are not accomplishing any separation, but are simply lying idle, awaiting the time when they will be useful. This is most clearly seen near the entrance of the bed in the operation of Fig. 3. As feed enters, the adsorbent near the inlet rapidly comes to complete equilibrium with the feed; as feed continues to enter, this section performs no further function except that of an inert

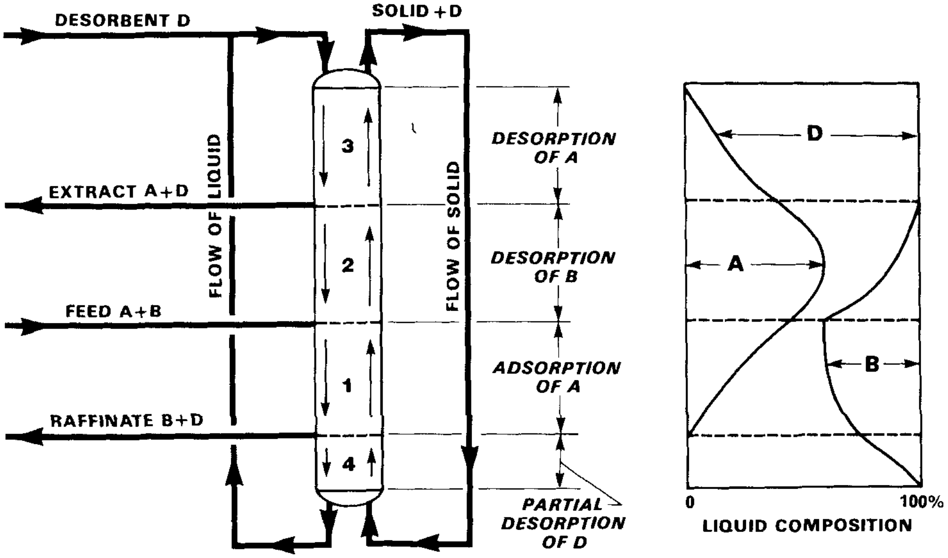

FIG. 4. Adsorptive separation with moving bed.

conduit, carrying the feed down into the part of the bed where separative action is occurring. A similar situation exists when desorbent is introduced.

Other nonfunctioning sections, in which no feed components at all are present, can be identified further down the bed.

Moving-Bed Operation

We next considered the possibility of establishing a continuous steady-state operation by moving the adsorbent, as a dense bed, countercurrent to the liquid streams (*4*). A hypothetical system of this type is shown in Fig. 4. Here, the adsorbent circulates continuously as a dense bed in a closed cycle and moves up the adsorbent chamber from bottom to top. Liquid streams flow down through the bed, countercurrently to the solid. The feed is assumed to be a binary mixture of A and B, with component A being adsorbed selectively. Feed is introduced to the bed as shown.

Desorbent D is introduced to the bed at a higher level as shown. It is a liquid of different boiling point from the feed components and can displace feed components from the pores. Conversely, feed components can displace desorbent from the pores with proper adjustment of relative flow rates of solid and liquid.

Raffinate product, consisting of the less strongly adsorbed component B mixed with desorbent, is withdrawn from a position below the feed entry. Only a portion of the liquid flowing in the bed is withdrawn at this point; the remainder continues to flow into the next section of the bed. Extract product, consisting of the more strongly adsorbed component A mixed with desorbent, is withdrawn from the bed; again, only a portion of the flowing liquid in the bed is withdrawn, the remainder continues to flow into the next bed section.

If it is assumed that the equilibrium and kinetic characteristics (including axial mixing) of this system will be the same as observed experimentally for liquid flow through stationary beds, the continuous operation can be modeled mathematically to compare performance with conventional chromatography. Results of this procedure showed (*3*) that, in the range of adsorbent selectivities being considered, the adsorbent requirement for the continuous operation was smaller by a factor of 3 to 4. Since we were considering large plants, in which the cost of adsorbent alone could be million of dollars, this was an important item.

A typical concentration profile in the bed is shown in Fig. 4. The positions of feed and withdrawal of liquid divide the bed into four zones in which the major actions taking place are as follows:

Zone 1. Adsorption of component A
Zone 2. Desorption of B (Purification of A)
Zone 3. Desorption of A
Zone 4. Partial recovery of desorbent from pores by displacement with B

Difficulties of Moving-Bed Operation

It appeared to us that an actual moving-bed operation would introduce a new set of difficult problems. In the first place, available adsorbents were not strong enough to resist the abrasion accompanying movement. Just as importantly, it would be difficult to maintain uniform plug-wise flow of both phases. How could the adsorbent be moved uniformly through a column of large diameter, particularly since it must be removed from one end and reintroduced at the other? And how could the bed be moved without opening up cracks that would allow the liquid phase to channel?

Some consideration was given to the use of a series of fluidized beds in which solids would overflow from each stage to the next. This arrangement, however, would limit the number of theoretical stages obtainable to the actual number of fluidized beds. The potential advantage of adsorption of providing highly efficient mass transfer would thus be lost.

Simulated Moving-Bed Operation

At this point we looked for a way of preserving the process characteristics of the continuous countercurrent system without actual movement of the adsorbent. This can be accomplished, at least to a reasonable approximation, by the operation described below (*4, 5*).

In the moving-bed system of Fig. 4, solid is moving continuously in a closed circuit past fixed points of introduction and withdrawal of liquid. The same results can be obtained by holding the bed stationary and periodically moving the positions at which the various streams enter and leave. A shift in the positions of liquid feed and withdrawal in the direction of fluid flow through the bed simulates the movement of solid in the opposite direction.

It is, of course, impractical to move the liquid feed and withdrawal positions continuously. However, approximately the same effect can be produced by providing multiple liquid-access lines to the bed, and periodically switching each stream to the adjacent line. Functionally, the adsorbent bed has no top or bottom and is equivalent to an annular bed. Therefore, the four liquid-access positions can be moved around the bed continually, always maintaining the same distance between the various streams.

The commercial application of this concept is shown in Fig. 5 where the adsorbent is a stationary bed. A liquid circulating pump is provided to pump liquid from the bottom outlet to the top inlet of the adsorbent chamber. A fluid-directing device known as a rotary valve is provided which functions on the same principle as a multiport stopcock in directing each of several streams to different lines. At the right-hand face of the valve, the four streams to and from the process are continuously fed and withdrawn. At the left-hand face of the valve, a number of lines are connected that terminate in distributors within the adsorbent bed.

At any particular moment, only four lines from the rotary valve to the adsorbent chamber are active. Figure 5 shows the flows at a time when Lines 2, 5, 9, and 12 are active. When the rotating element of the rotary valve is moved to its next position, each net flow is transferred to the adjacent line. Thus, desorbent enters Line 3 instead of Line 2, extract is drawn from 6 instead of 5, feed enters 10 instead of 9, and raffinate is drawn from 1 instead of 12.

Figure 4 shows that in the moving-bed operation the liquid flow rate in each of the four zones is different because of the addition or withdrawal of the various streams. In the simulated moving bed of Fig. 5, the liquid flow rate is controlled by the circulating pump. At the position in Fig. 5, the pump is between the raffinate and desorbent ports and, therefore, should be pumping at a rate appropriate for Zone 4. However, after the next switch in position of

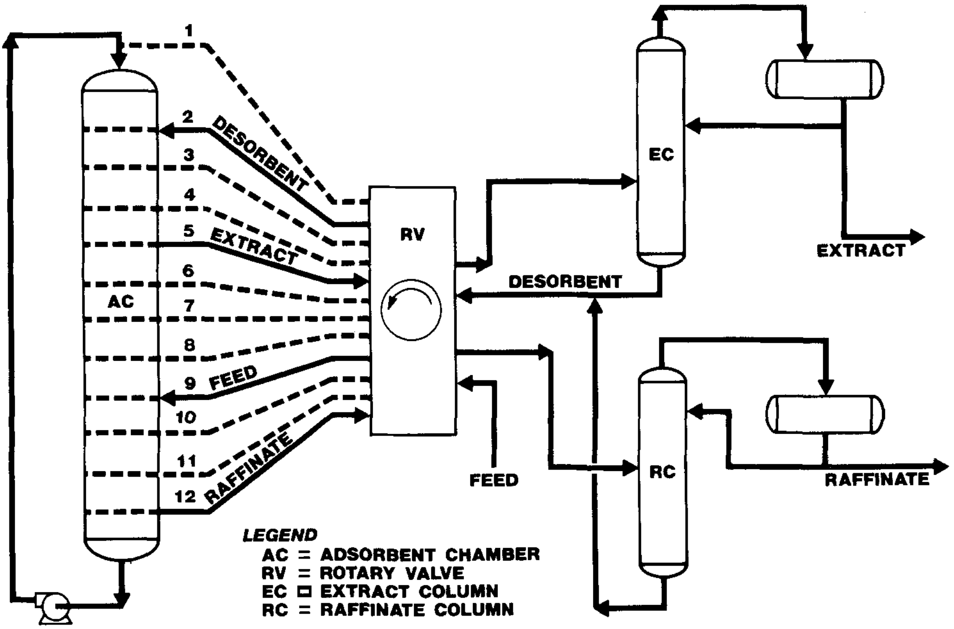

FIG. 5. Sorbex-simulated moving bed for adsorptive separation.

the rotary valve, the pump will be between the feed and raffinate ports and should, therefore, be pumping at a rate appropriate for Zone 1. Stated briefly, the circulating pump must be programmed to pump at four different rates. The control point will be altered each time a stream is transferred from Line 12 to Line 1.

To complete the simulation, the liquid-flow rate relative to the solid must be the same in both the moving-bed and simulated moving-bed operations. Since the solid is physically stationary in the simulated moving-bed operation, the liquid velocity relative to the vessel wall must be higher than in an actual moving-bed operation.

DEVELOPMENTAL PROBLEMS

Successful commercialization required the solution of a number of subsidiary problems, both mechanical and chemical (*6*).

Rotary Valve

The operation of Fig. 5 could have been implemented by the use of multiple on-off valves. However, a large number would have been required, and problems were anticipated in obtaining reliable operation of such a large number of elements and in locating leakages that might occur. As an alternative, we undertook development of a rotary valve, similar in principle to a multiport stopcock, in which the movement of a single rotating element would automatically direct all streams to their desired locations. This development has been completely successful. Prior to commercialization, a prototype valve was built to demonstrate operability.

Flow Distribution

In liquid chromatographic operations in general, it is highly important to obtain uniform flow of liquid in the beds. Departure from "plug flow," which might result from channeling or the presence of obstructions in the bed, can degrade performance seriously.

These problems could not be studied adequately in the pilot plant because of the small diameter of the beds. In a large commercial unit, each bed must be supported by a screen which is, in turn, supported by beams. The beam surfaces provide obstructions which lead to nonuniformity of flow.

A related problem is that of introducing and withdrawing the net liquid stream uniformly over the cross section of large-diameter beds. To accomplish this, a system of baffles and distributors was devised to be installed between the individual bed sections. These elements also mitigate to some extent the adverse effects of nonuniform flow in each bed section by remixing the liquid before it enters the next.

Our success in handling these problems is indicated by the operation of commercial units, with bed diameters up to 22 ft, to give as good performance as obtained in the pilot plant with a bed diameter of 3 in.

Adsorbent–Desorbent Development

The heart of this work has been, of course, the development of combinations to perform efficiently a number of specific separations. Experimental studies (*2*) were facilitated by the development of a simple test for evaluating various adsorbent–desorbent combinations. Accumulation of data was greatly accelerated by development of an on-line analyzer, which automatically withdrew and analyzed successive samples of effluent, thus eliminating the time-consuming steps of sample handling and independent analysis that would otherwise be required.

The properties of the desorbent must be coordinated with those of the adsorbent and feedstock. It must be a material of sufficiently different boiling point (either higher or lower) from the feed to permit easy separation by distillation. Additionally, it should not be adsorbed either very strongly or very weakly relative to the feedstock components, because adsorptive interchange, in both directions, between feed components and desorbent must occur. A further requirement is that its presence does not degrade the selectivities between the feedstock components. A desorbent suitable for operation with one particular adsorbent may be unsuitable for operation with another. An additional requirement is stability of the adsorbent in long-term operation with commercial types of feedstock.

COMMERCIAL OPERATIONS

Commercially operating and licensed Sorbex units are summarized in Table 1. These total 60 units performing six different types of separation. Their aggregate capacity is 10×10^9 pounds per year of selectively adsorbed purified product. Other applications, not yet licensed, are in development.

TABLE 1
Licensed Sorbex Units

Process	Separation	Number of units
Parex	*p*-Xylene/C_8-hydrocarbons	34
Olex	Olefins/paraffins	4
Molex	*n*-Paraffins/branched and cyclic hydrocarbons	16
Sarex	Fructose/dextrose + polysaccharides	4
Cresex	*p*- or *m*-Cresol/cresol isomers	1
Cymex	*p*-Cymene or *m*-cymene/cymene isomers	1
		60

Total liquid capacity = 10×10^9 pounds/year product

CONCLUSION

In common with most technical developments, the development of the Sorbex group of processes depended on many diverse but coordinated individual contributions. The final commercial success required a number of secondary decisions, developments, innovations, and discoveries, each of which was indispensable to the final accomplishment.

Important steps have included the development and use of mathematical models, laboratory test methods and equipment, pilot plant, prototype models of nonconventional components, and the discovery and production of unique adsorbents.

The role of the administrative staff in supporting the work and in encouraging formation of the lines of communication needed for coordination was essential.

REFERENCES

1. D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974.
2. A. J. DeRosset, R. W. Neuzil, and D. J. Korous, *Ind. Eng. Chem., Process Des. Dev., 15,* 261 (April 1976).
3. D. B. Broughton, R. W. Neuzil, J. M. Pharis, and C. S. Brearley, *CEP, 66*(9), 70–75 (1970).
4. D. B. Broughton, *Ibid., 64*(4), 60–65 (1968).
5. D. B. Broughton, "Adsorptive Separations—Liquids," in *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 1, 3rd ed., Wiley, New York, 1978.
6. D. B. Broughton, *Development of the Parex Process for Separation of* p-*Xylene from* C_8-*Hydrocarbon Mixtures*, Presented at the ACS Petroleum Division Symposium on Innovation in the Petrochemical Industry, Washington, D.C., August 28–September 1, 1983.