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**REVIEW**

# Adsorptive Bulk Separations by Zeolite Molecular Sieves

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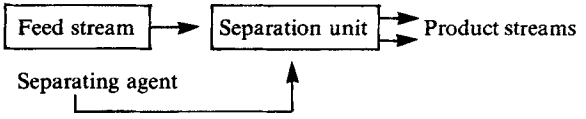
## 1. INTRODUCTION

It is said that nearly 40% of the cost of a chemical process lies in separation processes. Consequently, development in separation technology has been almost parallel to the growth of the chemical industry. A separation process can be schematically represented as




With the growing variety of feedstocks and product mixtures, a large number of separation techniques are being adopted which make use of one or more properties of the components at the molecular level. Some of the most important molecular properties controlling the efficiency of the separation processes are molecular size and shape, electric moments and polarizability, diffusivity and other kinetic properties, and chemical reactivity. Physical adsorption, which is the subject of the present review, involves all the above-mentioned properties excluding chemical reaction.

Bulk separations based on adsorption have gained prominence only recently after the advent of molecular sieve zeolites with unique

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adsorptive properties. Adsorptive purification, which is an extreme case of separation wherein the concentration of the minor components is very low, has been in commercial practice for a long time. All the major developments in adsorption-based separations have been based on zeolite molecular sieves. Among these, the first to gain commercial acceptance was the separation of gas or vapor mixtures by adsorption. Processes, such as $N_2$–$O_2$ separation from air (*1*), separation of light gases (*2*), and vapor-phase separation of normal/isoparaffins (*3*), have been commercialized. However, separation of liquid mixtures is a more recent development, primarily because of the difficulties in experimental techniques, commercial-scale desorption, and regeneration of the adsorbent. In fact, the large-scale use of liquid adsorption processes began only after the development of the Sorbex process by Universal Oil Products (*4*). Some of the important commercial separation processes are given in Table 1.

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## Zeolite Molecular Sieve Adsorbents

The choice of an adsorbent for a separation process is dictated by the following considerations:

High selectivity of the adsorbent
High product yield or capacity
Chemical and thermal stability of the adsorbent
Economics

Prior to the introduction of zeolite molecular sieves in the mid-1950s (*5*), silica and alumina were used primarily for dehydration and activated carbon for selective hydrocarbon separation. But the arrival of zeolite molecular sieves has changed the whole scenario of adsorptive processes. Not only have these made inroads into almost all drying processes but they have made selective adsorption a major separation technology (*6–10*). This has been possible because zeolites, which are hydrated crystalline aluminosilicates with the general formula

$$M_{x/n}[(AlO_2)_x(SiO_2)_y]W \cdot H_2O$$

have certain unique features (*6*). Those which make zeolites attractive for separation processes are:

1. Three-dimensional crystalline microporous structures impart unusual thermal and hydrothermal stability.

TABLE 1
Some of the Major Developments in Adsorptive Separation Processes

| |
|---|
| Kerosene range normal paraffin recovery via Union Carbide's Isosiv process → vapor phase |
| Universal Oil Products' Molex process for normal paraffins recovery from kerosene → liquid phase |
| UOP's Parex process for separation of *p*-xylene from $C_8$ aromatic stream → individual isomers |
| UOP's Sarex process for separation of sucrose from dextrose, polysaccharides → aqueous medium |

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2. Zeolites have a uniform pore structure. Unlike carbon or other adsorbents, pore size distribution is very sharp.
3. There is a degree of freedom which allows manipulation of the zeolite pore dimensions by using differently charged cations (M).
4. The zeolite surface can be qualitatively changed from highly polar or hydrophilic to nonpolar organophilic or hydrophobic surface by changing the Si/Al ratio.
5. Zeolite molecular sieves have high adsorption capacities even at low adsorbate concentrations. Much of this adsorption capacity is maintained at moderately elevated temperature. This is very significant because commercial adsorbents work adiabatically and the release of the heat of adsorption results in a temperature rise.

During the last 30 years of research and development over 150 species of synthetic zeolites have been synthesized. Major volume commercial molecular sieve zeolites used in adsorption/catalysis are A, X, Y, and ZSM. Some of their characteristics are given in Table 2.

## Adsorption Separation Process

Selective adsorption and recovery of the desired products by desorption are the two principal steps in the adsorptive separation process. In addition, there is an activation step prior to the first adsorption step or whenever the adsorbent is found to be loaded with moisture or any other undesirable adsorbate. Besides, the adsorbent may periodically be subjected to a regeneration step to strip off any carbonaceous deposit or irreversibly adsorbed poisons.

TABLE 2
Some Zeolites and Their Characteristics

| Zeolite | Chemical composition | Pore volume ($cm^3/cm^3$) | Pore diameter (Å) |
|---|---|---|---|
| | *A Type* | | |
| NaA | $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O$ | 0.47 | 4.2 |
| KA | | | 3.0 |
| CaA | | | 5.0 |
| | *X Type* | | |
| NaX | $Na_2O \cdot Al_2O_3 \cdot 2.5SiO_2 \cdot 6H_2O$ | 0.50 | 7.4 |
| CaX | | | |
| | *Y Type* | | |
| NaY | $Na_2O \cdot Al_2O_3 \cdot 5.0SiO_2 \cdot 8.9H_2O$ | 0.48 | 7.4 |
| Mordenite (two-dimensional pore system) | $Na_2O \cdot Al_2O_3 \cdot 9.10SiO_2 \cdot 6H_2O$ | 0.20 | 6.7 × 7.0 |
| Erionite | $(Na,K)_2O \cdot Al_2O_3 \cdot 6SiO_2 \cdot 6H_2O$ | 0.35 | 3.6 × 5.2 |
| ZSM | $(TPA,Na)_2O \cdot Al_2O_3 \cdot 5\text{–}100SiO_2 \cdot 4H_2O$ | 0.10 | 6 |

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### *Selective Adsorption*

When a mixture is exposed to an adsorbent, adsorption of the components takes place but to different extents. An equilibrium is established between the adsorbed phase and bulk phase compositions. Such an equilibrium can be expressed in terms of phase diagrams (Fig. 1) by plotting the concentration of a component in the adsorbed phase against that in the bulk phase. A straight line diagonally across the graph represents an equilibrium where the adsorbent surface does not show a preference for any of the components. When the graph is convex to the Y axis, a higher preference for the adsorbent concentration is indicated. The selectivity or separation factor of a mixture is defined as

$$S_{A/B} = \frac{\text{concentration of A in the adsorbed phase} \times \text{concentration of B in the bulk phase}}{\text{concentration of A in the bulk phase} \times \text{concentration of B in the adsorbed phase}}$$

Determining selectivities is very important for choosing a suitable adsorbent. Both static and dynamic methods (*11–13*) can be employed for

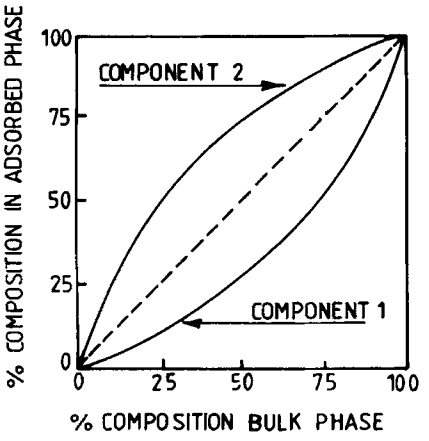


FIG. 1. Phase diagram for the adsorption of binary mixtures on solids.

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this purpose. Some of the factors, in addition to temperature, pressure, and concentration, which influence selectivities are

Steric factors
Equilibrium effect
Kinetic effect

These factors alone or in combination with each other are used for achieving separation. We shall show some examples where separations are achieved by exploiting these effects.

***Steric Effect.*** Steric differences among molecules can only be exploited for separation if the adsorbents have molecular size pores. Zeolites and carbon molecular sieves fulfill this condition (3–10 Å). In some cases a unique selectivity can be achieved; for example, separation of normal paraffins from branched or cyclic paraffins by using molecular sieve 5A is done on this basis. In this case, only linear molecules can enter the pores, all others being completely excluded because of their large cross sections.

***Equilibrium Effect.*** Equilibrium effects are employed for separation when adsorption isotherms of the components differ appreciably. The position of equilibrium adsorption isotherms of a single component depends on such factors as the affinity of an adsorbate molecule for the

adsorbent surface, and the nature of the adsorbent surface and adsorbate molecule. Highly polar adsorbents like X and Y zeolite will preferentially adsorb polar molecules whereas silicalite with a nonpolar surface will prefer nonpolar molecules. Separation of xylene isomers using modified faujasite-type zeolites is based on the difference in the acid-base interactions of the isomers. Similarly, separation of *o*-toluidine and mesitylene is based on Lewis acid-base interactions which are present only in the case of toluidine.

***Kinetic Effect.*** Separation by adsorption can also be achieved if one component diffuses faster than the other. If the micropore diameter of the adsorbent and the molecular diameter of the adsorbate are approximately the same, a steric-kinetic effect can occur. A component whose molecular diameter is nearly the same as that of the micropores will diffuse much slower than a component with a smaller molecular diameter. A specific example of this effect occurs in the separation of toluidine isomers on a rate selective adsorbent (*14*).

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## Product Recovery

The desired product is recovered by desorbing the adsorbed product from the adsorbent. The following basic techniques (*9*), separately or in combination, are employed for desorption.

Thermal swing desorption
Pressure swing desorption
Purge gas stripping
Displacement desorption

Displacement desorption is widely used in bulk separation processes. In this case an initial adsorbate is desorbed by the action of a second sorbable fluid which displaces the initial one fully or partly. The choice of a particular desorbing fluid is dictated by the following considerations.

The desorbent material must displace the adsorbed component from the adsorbent at a reasonable rate without itself being so strongly adsorbed as to unduly prevent the adsorbing component from displacing the desorbent material in the subsequent adsorption cycle.

The desorbent material must be compatible with the particular adsorbent and the particular feed mixture. Most specifically, they must

not reduce or destroy the critical selectivity of the adsorbent for the main component.

The desorbent must be easily separable from the feed mixture.

In terms of selectivity, it is preferred that the adsorbent be more selective for the component desired with respect to others in the mixture than it is for the desorbent material with respect to non-desirable components of the mixture.

The main disadvantage of this technique is the need for downstream desorbent recovery facilitates to separate the desorbent from its mixture with the adsorbates.

## 2. SEPARATION OF NORMAL PARAFFINS

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The need for separation of normal paraffins arose due to their use in the manufacture of biodegradable detergents and synthetic proteins. Prior to the discovery of an efficient adsorption process, *n*-paraffins were separated from other hydrocarbons by employing the urea adduct principle (*15–17*). One of the first commercial applications of molecular sieves for bulk separation included the recovery of *n*-paraffins from a mixed refinery stream. Presently there are several commercial processes (Table 3) employing zeolite molecular sieve 5A for the separation of *n*-paraffins. The underlying principle in these processes is the selective adsorption by the molecular sieve of normal paraffins whose critical molecular diameter is 4.8 Å along the molecular axis. This is less than the pore diameter (5 Å) of molecular sieve 5A. Other hydrocarbons, such as branched paraffins, naphthenes, and aromatics, have larger molecular diameters and hence are excluded by the adsorbent. These processes differ from one another with respect to the desorption step, the desorbent, the operating temperatures and pressure, the cycle time, the purging agent, etc. The most important of these processes are described below.

### Isosiv Process (Union Carbide Corporation)

The Isosiv process is operated (*18*) in the vapor phase and at temperatures optimized for the type of feedstock. For example, when kerosene is the feedstock, the operating temperature is 315–343°C and for gas oil the temperature range is 315–398°C. The inlet pressure has been cited (*19*) as 60 psia and the pressure in the sieve bed is 20–60 psia (30 psia

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TABLE 3
Processes Commercially Available for the Separation of Normal Paraffins from Hydrocarbon Streams

| Carbon number range | Process | Adsorbent | Desorbent | Phase | Temperature (°C) | Pressure |
|---|---|---|---|---|---|---|
| $C_{10}$-$C_{14}$ | Universal Oil Products' Molex process | 5A | *n*-Pentane | Liquid | 180 | 18 kg/cm$^2$ |
| Gasoline range *n*-paraffins | Union Carbide Corporation's Isosiv process | 5A | Pressure swing desorption | Vapor | — | — |
| $C_{10}$-$C_{14}$ | Union Carbide Corporation's Isosiv process | 5A | *n*-Hexane | Vapor | 315–343 | 20 psig |
| Gas oil range *n*-paraffins | Union Carbide Corporation's Isosiv process | 5A | *n*-Hexane | Vapor | 354 | 25 psig |
| $C_{10}$-$C_{18}$ | Exxon's ensorb process | 5A | Ammonia | Vapor | 329 | Atmospheric |
| Light naphtha range *n*-paraffins | Elf-N-Iself | 5A | Hydrogen | Vapor | 250 | 13.2 atm |
| 30–450°C bp range hydrocarbons | British Petroleum process | 5A | *n*-Heptane | Vapor | 380 | — |
| $C_8$-$C_{24}$ *n*-paraffins | Texaco's process | 5A | | Vapor | | |
| — | VEB Leuna's Parex process | 5A | Ammonia | Vapor | — | — |

being optimum). Adsorbed *n*-paraffins are desorbed from the molecular sieve bed by a countercurrent stream of *n*-hexane at the same temperature and pressure as the sorption step. A schematic diagram of *n*-paraffin separation is give in Fig. 2. One version of the Isosiv process operates in the pressure swing mode in which desorption is carried out at a lower pressure than adsorption. The pressure swing operation is feasible with low molecular weight *n*-paraffins but not for kerosene and gas oil boiling range *n*-paraffins because their equilibrium adsorption capacities are less sensitive (*18*) to pressure variations. Thus, in the case of higher molecular weight paraffins, desorption is achieved by purging with a desorbing medium through the bed and the mass action of an excess of less strongly adsorbed desorbent. The vapor-phase separation process has an advantage over the liquid phase in that it leaves less nonadsorbed hydrocarbons in the voids around the molecular sieve crystals and gives a high purity of the product. However, because of the higher temperature, a small amount of cracking of the hydrocarbon is likely to occur. So the advantage of having a higher rate of desorption should be weighed against the disadvantage of coking of the adsorbent at a higher temperature.

For the recovery of *n*-paraffins of the $C_{16}$–$C_{25}$ range from gas oil, the

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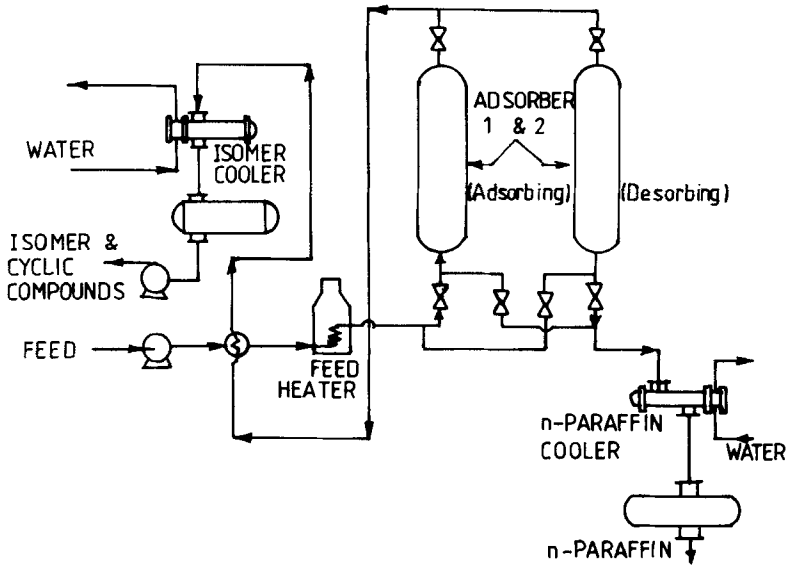


FIG. 2. Schematic flow diagram for *n*-paraffins separation process.

Isosiv process still remains the more or less lone commercial process though it faces a serious challenge from UOP's liquid-phase process for *n*-paraffin in the kerosene range.

An isobaric process for the separation of *n*-paraffins from hydrocarbon feestock having $C_{10}$–$C_{25}$ carbon atoms per molecule is described in the literature (*20–22*). There are some special problems when hydrocarbons higher than $C_{16}$ are processed: capillary condensation and formation of a liquid meniscus in the micropores of the adsorbent pellet. This is avoided by raising the bed temperature beyond the dew point of the hydrocarbon. If such precautions are not taken, the condensate in the adsorbent macropores will not be completely removed during the copurge or displacement step, with the result the normal paraffins' purity will be lower. Capillary condensation can be avoided by ensuring that the ratio of feed saturation pressure (dew point pressure) to operating pressure is more than 2. For this purpose a gas oil feedstock having a dew point of 354°C at a typical operating pressure of 25 psi should be contacted with a molecular sieve adsorbent at a temperature of about 388°C. However, excessive coke formation and rapid deactivation of the adsorbent results at such a temperature. In the Isosiv process this problem has been overcome by the introduction of a sufficient amount of redistilled *n*-hexane purge gas to lower the resultant mixture's dew point and avoid capillary condensation at the desired operating pressure.

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## Molex Process (Universal Oil Products)

The Molex process is the only liquid-phase process for the separation of normal paraffins from kerosene (Table 3). It employs a 5A-type molecular sieve and typically operates at 20 kg pressure and 180°C. Normal pentane is used as the desorbent and isooctane as the purge medium to remove unadsorbed hydrocarbons from the sieve. The molecular sieve adsorbent has a life of 4–5 years. Deactivation by sulfur or other polar compounds may occur. It is generally considered that the lifetime of the sieve is limited by its mechanical soundness. A change of sieve is occasioned by a high pressure drop or some other plant condition rather than by a permanent loss of capacity of the adsorbent. The Molex process is a typical Sorbex process patented by UOP and widely described in literature (*4, 23, 24*). It has two major features:

It is a continuous process for the separation of the components of a mixture with at least one component which is selectively sorbed by the molecular sieve.

It simulates the countercurrent movement of the fluid with respect to that of the adsorbent bed. This is achieved by keeping the adsorbent bed stationery and periodically moving the position at which the various streams (feed and desorbent) enter or leave the adsorbent bed.

In its simple form, the process operates with the help of four main components as shown in the Fig. 3.

(a) An adsorbent bed which has been divided into a series of interconnected compartments, each having a conduit connected to a fluid distributing valve.
(b) A rotary valve for directing the fluid circulation. This functions on a principle similar to that of a multiport stopcock. A number of distribution lines from the adsorbent bed are connected to it.
(c) A fluid circulation pump which is put in between two pairs of

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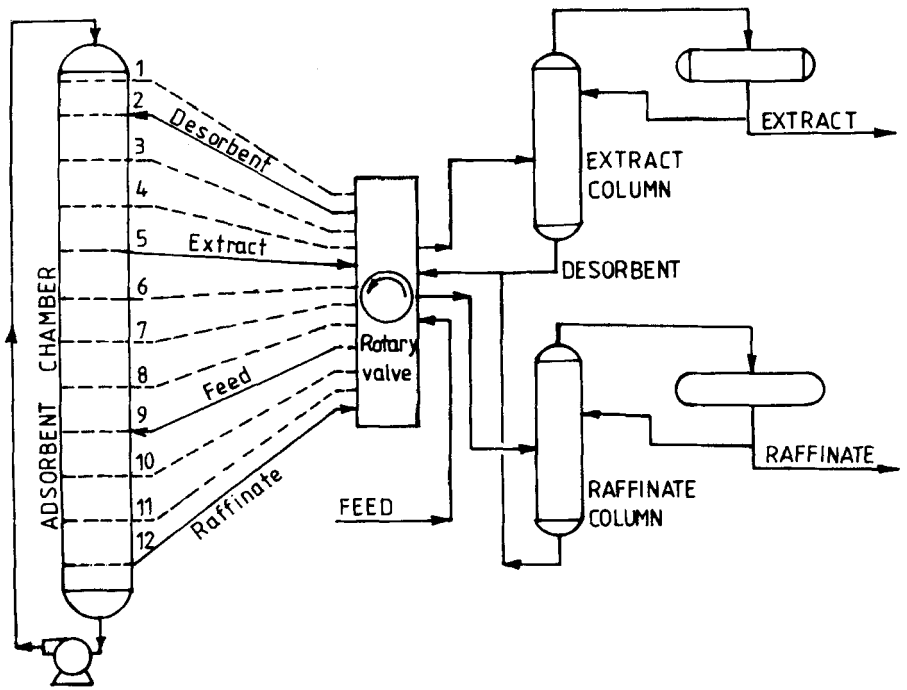


FIG. 3. Sorbex-simulated moving bed for adsorptive separation process.

adjacent adsorbent compartments to provide a positive unidirectional flow of fluid.

(d) Fractionation facilitates used for the separation of extract or raffinate from the desorbent.

The process operation can be visualized as a series of four interconnected zones: sorption, primary rectification, secondary rectification, and desorption. These zones are defined solely by the points of inlet (feed and desorbent) or withdrawal (extract and raffinate) for the various fluid streams as shown in the diagram. As the feedstock enters one of the adsorbent compartments, the more selective component is sorbed into the micropores of the adsorbent. As a result, the feed coming out of the last compartment of the sorption zone consists of the nonsorbed raffinate in admixture with the continuously circulating fluid. The number of compartments in a sorption zone is fixed depending upon the selectivity of the sorbable component so that this component is effectively removed from the feestock. The adsorbent containing the adsorbed normal paraffins is allowed to move into the primary rectification zone which is fed by the desorbent in order to displace the nonsorbed components in the nonselective void volumes. The adsorbent then moves into the desorption zone wherein the desorption of the normal paraffins take place, and they are recovered from the product stream by fractionation. The secondary rectification zone acts as a buffer, preventing any product contamination by the feedstock. In actual practice, the movement of the adsorbent is simulated by a stepwise advance of the points of introduction of the feedstock and desorbent and the points of withdrawal of the raffinate and extract components along the adsorbent bed.

There are 16 commercial units based on the Molex process operating in the world (*24*). Normal paraffins recovery is around 98% with 99% purity.

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## Ensorb Process (Exxon Inc.)

In the Ensorb process (*25–27*) the feed is diluted with ammonia (0.5 to 0.8 mol ammonia per mol of the feed) and heated to about 329°C. Stream is passed through the adsorbent bed (5A) at approximately atmospheric pressure. *n*-Paraffins are adsorbed and ammonia is desorbed from the sieve. Ammonia in the feed prevents complete removal of ammonia from the sieve. Ammonia in the sieve has been found to reduce coking and improve product purity by suppressing the adsorption of polynuclear aromatics on the external surface of the zeolite. The adsorbed paraffins

are desorbed by ammonia at the same temperature. The advantage of ammonia as a desorbent lies in the very large volatility difference between ammonia and the linear paraffins. This ensures the easy separation of desorbent from the desorbate by flash distillation. $C_{10}$–$C_{18}$ linear paraffins are adsorbed more strongly than ammonia, with the result that a very high rate (four times the hydrocarbon feed rate) is required to achieve desorption.

### Elf-N-Iself Process (Elf-SRTI)

This process for selective separation of normal paraffins from light naphtha was reported recently (*9*, *28*). This is an alternative to the conventional type of cycle batch Isosiv process and is based on gas–solid chromatography with a 5A molecular sieve as an adsorbent. Periodically, some vaporized hydrocarbons carried by the hydrogen stream come into contact with the sieve bed. Normal paraffins are retained in the bed, the others (naphthenes/aromatics/isoparaffins) flow out of the bed followed by those adsorbed molecules which are desorbed by the hydrogen purge. Although the process operates in the chromatographic mode, the kinetic separation between linear and branched hydrocarbons on a 5A molecular sieve is so sharp that only a very few theoretical plates are required in the column so the process may properly be regarded as a variant of the traditional batch-type process in which desorption is achieved by purge gas stripping rather than thermal or pressure swing. A flow sheet for the process is given in Fig. 4. Five columns are operated in parallel with the feed, after vaporizing and preheating, injected into each column in sequence over a period corresponding to 1/5th of the cycle time to achieve continuity of flow. At each injection process one isoparaffin-rich and one *n*-paraffin-rich mixture leaves the bed. The products are then cooled and separated from hydrogen gas. The columns operate at 250°C and 13.2 atm.

Some other processes for the separation of *n*-paraffins are the British co-process (*29*), the Texaco selective finishing process (*30*), and VEB Leuna work's Parex process (*31*). These processes are variants of the Isosiv process and are not discussed in detail here.

As seen in the literature, processes for the separation of normal paraffins are mostly variants of the Isosiv or Molex processes. Research work has been largely confined to the reinforcement of these processes. Lewis and Nelson (*21*) established a correlation between the crystal size of the 5A molecular sieve and its rate of deactivation during *n*-paraffin

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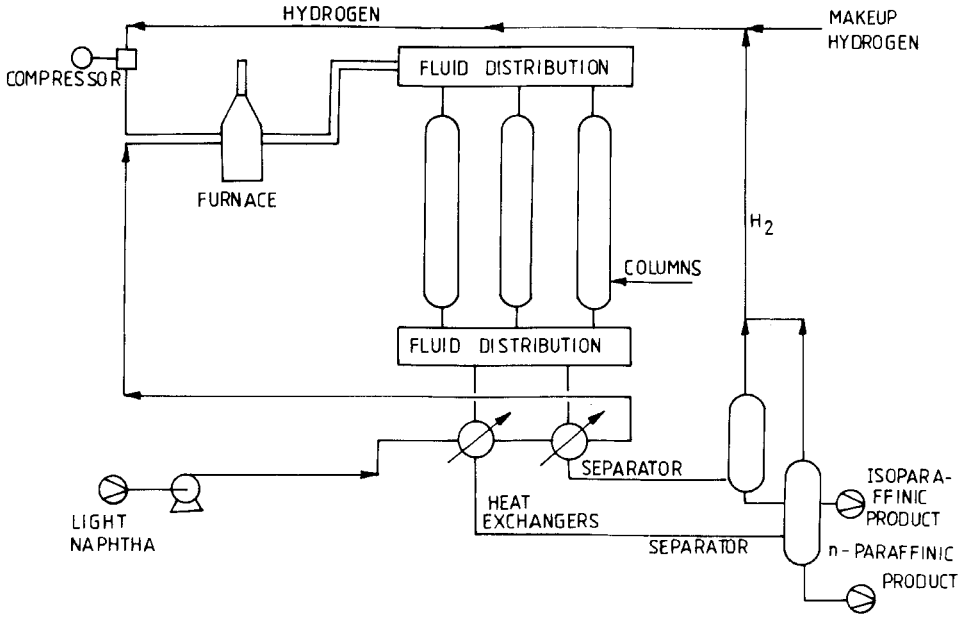


FIG. 4. Flow sheet for N-Iself process.

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separation from a sulfur-containing hydrocarbon stream. They showed that zeolite crystals with an average crystal size greater than 700 Å have a more useful life than those with a crystal size smaller than 700 Å.

Although 5A-type zeolite appears to be an ideal molecular sieve for normal paraffin separation, Kulprathipanja and Neuzil (*32*, *33*) reported that silicalite shows better performance than 5A molecular sieve in the separation of tetradecane from its mixture with isooctane.

## 3. OLEFINS SEPARATION BY ADSORPTION

Olefins are the starting materials for many end products of commercial importance. They are generally obtained by separation from the products of steam cracking, pyrolysis, or dehydrogenation of saturated hydrocarbons (*34*). In practice, adsorptive separation of olefins by employing zeolite molecular sieve has been used for

(1) Class separation of olefins from paraffins as in the case of normal $C_{10}$-$C_{14}$ olefins from the corresponding normal paraffins (Olex process of UOP).
(2) Separation from linear olefins from branched compounds as in the case of the Olefinsiv process of Union Carbide for the separation of normal butylenes from isobutylene (*35*, *36*).
(3) Selective adsorption of individual isomers such as isobutene in the Sorbutene process of UOP (*24*, *37*).

## Adsorbents for Olefin Separation

In general, Type A and faujasite-type zeolites are used for olefin separation. In the case of Type A the calcium exchanged form is invariably used; different alkali and alkaline earth forms are used when Types X or Y zeolite is employed for optimizing adsorbed selectivity. An important step in the adsorbent preparation is the neutralization of the residual acidity of the zeolite surface which, otherwise, would catalyze some chemical transformations of the olefins in the feedstock. Reactions such as isomerization or oligomerization of olefins, if allowed to occur, tend to decrease the useful capacity of the adsorbent rapidly. Some of the neutralization techniques employed are treatment with aqueous alkali solutions and with organic amines (*38–42*).

Some of the processes for olefins separation are discussed below.

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## Sorbutene Process for Butene-1 Recovery (Universal Oil Products)

UOP developed an adsorptive method for the separation of *i*-butene from its mixtures with other butene isomers and from $C_4$ paraffin. It is called the Sorbutene process. This process belongs to the Sorbex group of processes patented by UOP and employs a modified faujasite zeolite molecular sieve (*24*, *37*). The adsorbent is more selective to *i*-butene compared to other components of the $C_4$ hydrocarbons. Adsorbed butene is recovered by displacing it with a desorbent which may be another olefin, such as *i*-hexene, or a mixture of cyclohexane with cyclohexene. Pilot-plant studies carried out by UOP on various adsorbent/desorbent systems on mixed $C_4$ feedstocks resembling those derived from the FCC and thermal cracking units showed recoveries exceeding 90% and product purity of 99% by weight.

The feedstock must be pretreated to remove acetylenes, dienes, and sulfur, which are generally found in the $C_4$ streams obtained from the

cracking units. UOP recommends an extractive version of the Merox process for sulfur removal and selective hydrogenation to remove the acetylenes and dienes (*43*). UOP recently patented a silicalite-based adsorbent and process for the separation of isobutylene from its mixtures with *i*-butene and isobutane. Normal olefins (e.g., *i*-pentene) are used as the desorbent (*37*).

## Olefinsiv Process (Union Carbide Company)

This process for the separation of normal butylenes from isobutylenes in high purity (>99%), employing molecular sieve 5A, was developed by Union Carbide (*35, 36*). Isobutylenes with higher critical diameters (5.6 Å) compared to normal butene isomers (5.1 Å) are excluded from being adsorbed within the molecular sieve cages. The adsorbed butenes are desorbed by gas, purged, and subsequently separated. A small quantity of $C_8$ olefins is usually formed, and it is removed as a by-product. In the Union Carbide process, coke deposition occurring in the sieves is removed by integral continuous burn-off systems. A schematic diagram of this gas-phase separation process is given in Fig. 5.

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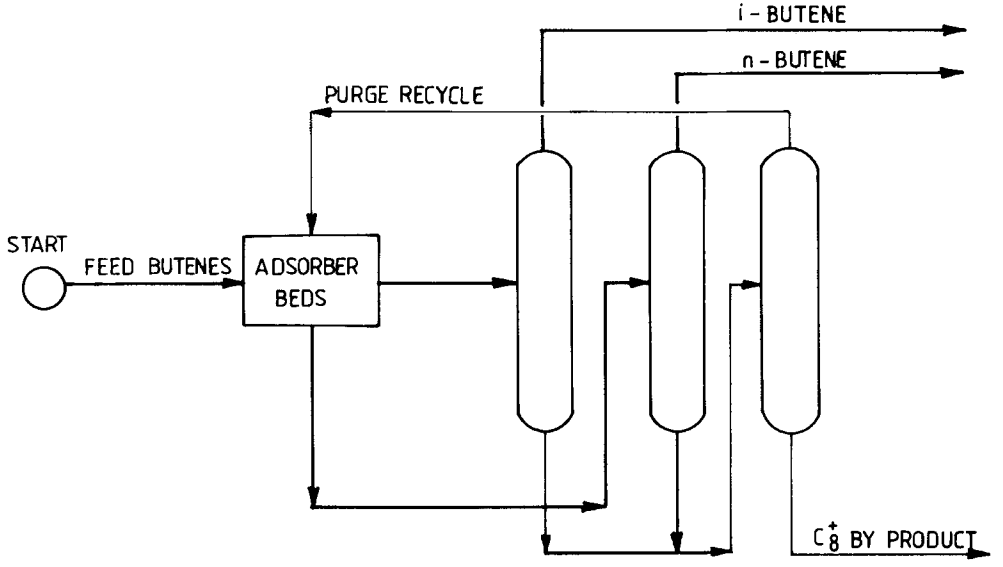


FIG. 5. A schematic flow diagram of Union Carbide's Olefinsiv process.

## The Olex Process (Universal Oil Products)

The separation of higher olefins (carbon numbers above $C_{10}$) is achieved by another Sorbex-type liquid-phase process developed by UOP and called the Olex process. This process was developed to separate higher normal olefins from the corresponding *n*-paraffins. Zeolites of the modified faujasite type show a higher adsorption affinity for olefins than for paraffins. According to Broughton (*24*), the relative solubilities of paraffins and olefins in extracting solvents tend to decrease with an increase in the carbon chain length. Consequently, with a mixture of hydrocarbons with various carbon chain lengths, the relative solubilities of paraffins and olefins overlap, which renders separation by solvent extraction incomplete. On the other hand, the selectivities for olefins and saturated hydrocarbons on zeolites are quite distinct. As a result, the separation of these two classes of hydrocarbons can be achieved successfully from their mixtures. Table 4 gives data from a commercial operation for the separation of linear $C_{11}$–$C_{14}$ olefins from the corresponding paraffins (*44*). The desorbent used is a hydrocarbon with a boiling range lower than that of the feed. Similar results have been reported for $C_8$–$C_{10}$ and $C_{15}$–$C_{18}$ feedstocks (*44*).

From the available disclosures (*38*, *39*, *45*, *46*) it is found that X or Y zeolites modified suitably to optimize their olefin selectivity are used as the adsorbent. Modification of the surface is also carried out to neutralize the catalytic activity of the surface. Rosback and Neuzil reported (*38*, *39*) that an X-type zeolite after treatment with sodium hydroxide solution not only decreased the catalytic activity but also increased the adsorption capacity for olefins.

The selectivity of 5A molecular sieve for olefins has also been studied in some detail. In this case it was found (*47*) that the selectivity of olefins decreased with an increase in carbon chain length in 5A molecular sieve.

## Some More Examples of Olefin Separation

In recent patents (*48*, *49*), the separation of 1,3-butadiene from a feed mixture containing 1,3-butadiene and at least one other $C_4$ hydrocarbon has been claimed. The process is said to operate in the liquid phase with activated carbon or molecular sieve carbon as the adsorbent which selectively adsorbs 1,3-butadiene. Adsorbed 1,3-butadiene is desorbed with a liquid hydrocarbon, probably $C_3$ or $C_5$–$C_{10}$ *n*-olefins.

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TABLE 4
Commercial Operation Data for Linear $C_{11}$–$C_{14}$ Olefin Extraction

| Component | Feed (wt%) | Extract (wt%) | Raffinate (wt%) |
|---|---|---|---|
| *n*-Olefins | 9.0 | 96.2 | 0.6 |
| *n*-Paraffins | 90.1 | 1.1 | 98.5 |
| Other components such as adsorbed aromatics and branched paraffins | 0.7 | 2.7 | 0.9 |

Separation of a diene such as octadiene from 1-octene was earlier reported by Bertsil (*50*) using 13X molecular sieve.

Cyclohexene is a starting material for the manufacture of such organic compounds as cyclohexanol and adipic acid. Cyclohexene is generally prepared by selective partial hydrogeneration of benzene or selective dehydrogenation or oxidative dehydrogenation of cyclohexane. The reaction products in each case are likely to consist of benzene, cyclohexene, and cyclohexane. Benzene can be separated extractively, and the separation of cyclohexene from cyclohexane is by adsorption. A process for the separation of cyclohexene from its mixture with cyclohexane was reported by Kondo (*51*). Zeolite X or Y (13X or NaY) is used as the adsorbent. The process is preferably carried out at 200°C and 13 kg/cm$^2$ pressure in the liquid phase with 1,3,5-trimethylbenzene as the desorbing medium. The selectivities for different adsorbents are shown in Table 5. Preferential adsorption of cyclohexene is due to the presence of a double bond which results in stronger interactions with the electrostatic field of the zeolite surface.

Kulprathipanja and Neuzil (*26*) showed the complete separation of 1-hexene from its mixture with 4-methylpentene with $Al_2O_3$-bound silicalite adsorbent using isooctane and 1-pentene as desorbents.

Geometrical isomers like *cis*- and *trans*-butene and *trans*-3-heptene can also be separated by selective sorption on zeolites (*53*, *54*).

## 4. SEPARATION OF SUBSTITUTED BENZENES

### Separation of Xylenes

The separation of xylene isomers and ethylbenzene is the most important process among liquid-phase adsorptive separations. This

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TABLE 5
Selectivities of Cyclohexene for Different Adsorbents at 80°C and 2 kg/cm$^2$ Pressure

| Adsorbent | $\alpha \frac{\text{Cyclohexene}}{\text{Cyclohexane}}$ | $\alpha \frac{\text{Cyclohexene}}{\text{1,3,5-Trimethylbenzene}}$ |
|---|---|---|
| 13X | 7.1 | 0.98 |
| NaY | 26.7 | 0.60 |
| KY | 3.6 | 0.59 |

process has replaced older and less efficient processes based on low temperature crystallization, because it yields higher recovery and purity than is attainable by the adsorptive process. The adsorbent generally used for xylene separation is based on molecular sieves X and Y after proper modification of cation type, content, and Si/Al ratio. The selectivity to any of the xylene isomers is presumed to be controlled by the acid-base-type interaction between the zeolite and the xylene isomer. The highest selectivity toward *p*-xylene is achieved when the surface is the least basic (Fig. 6). Consequently, all factors which influence the zeolite acidity (viz., Si/Al ratio, moisture content, degree and nature of cation exchange) influence (*55*) the *p*-xylene selectivity (Figs. 7 and 8). The various commercial adsorptive processes used for *p*-xylene separation include the Parex process (UOP Inc.), the Aromax process (Toray, Japan), and the Asahi process; these processes are discussed below.

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### *Parex Process*

This process of *p*-xylene separation from $C_8$ aromatic isomers was developed in the late 1960s and first commercialized in 1971 by UOP. As of 1985, 34 licensed commercially operating units were reported (*24*). Some of the salient features of this process include

Continuous separation based on selective adsorption of *p*-xylene on a zeolite molecular sieve.
Operation in a liquid base at 177°C and 8.8 kg/cm$^2$ pressure.
*p*-Xylene product recovery about 94%, with 99.5% product purity.

***Process.*** The Parex process belongs to the family of Sorbex processes of countercurrent simulated moving bed adsorption processes. The mixed xylene feed is directed through a multiport directional valve to the

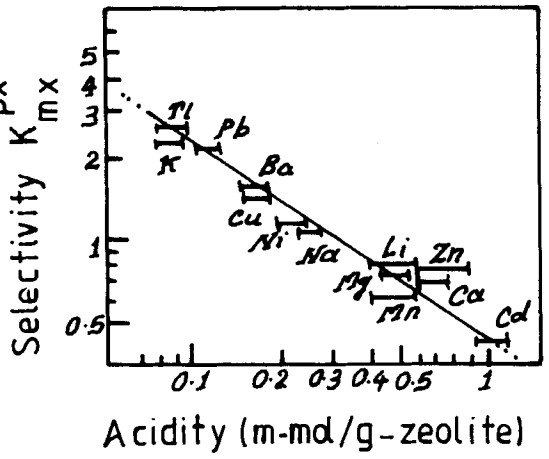


FIG. 6. Dependence of *p*-xylene selectivity on the acidity of a zeolite.

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adsorbent bed. The adsorbent preferentially retains *p*-xylene and adsorbs only a minor portion of the other feed components. *p*-Xylene is separated from the adsorbent by displacing it with a hydrocarbon desorbent. The raffinate (unadsorbed feed + desorbent) and extract (*p*-xylene + desorbent) that leave the adsorbent bed are routed through their respective fractionators. The desorbent is returned to the adsorbent chamber. This process has been discussed in detail in the literature (*4*, *23*, *24*, *56*, *57*).

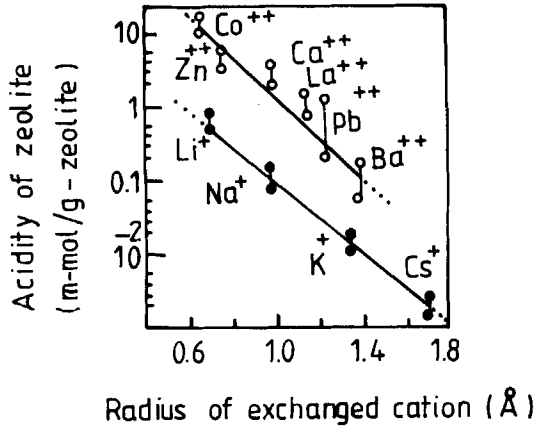


FIG. 7. Dependence of *p*-xylene selectivity on the radius of an exchanged cation.

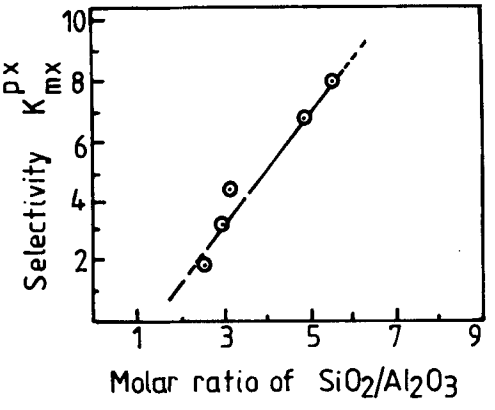


FIG. 8. Dependence of *p*-xylene selectivity on the molar ratio of $SiO_2/AlO_3$ in a zeolite.

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According to the information available from various patents (*4*, *58*), the adsorbent is of the X- or Y-type zeolite modified by ion exchange with $Ba^{2+}$, $Sr^{2+}$, or $K^+$ to improve the selectivity for *p*-xylene. The selectivity factor between *p*-xylene and the other $C_8$ aromatic isomers is about 3. Thus, in this case all the components are adsorbed but *p*-xylene, being preferentially adsorbed, is retained selectively.

The desorbent is a liquid hydrocarbon with a different boiling point than the feed component and is capable of displacing the feed component from the pores of the adsorbent. Optimally, the desorbent should have an affinity smaller than *p*-xylene but larger than other $C_8$ isomers. Depending upon the use, either a light (toluene) or a heavy (diethylbenzene) desorbent is specified. Toluene has advantages with respect to adsorption affinity and cost. Toluene has been used as a feed which is substantially free of $C_8$ naphthenes, generally obtained as a fraction of a reformate. However, *p*-diethylbenzene has the following advantages as a desorbent:

Desorbent is separated from the feed components by fractionation. This involves vaporizing and condensing a vast amount of desorbent. If a desorbent is a relatively heavier material which remains as a liquid at the bottom of the fractionator, it will only be necessary to vaporize/condense the feed components which comprise the smaller fraction.

With toluene as the desorbent, it is not possible to add a $C_8$ aromatic isomerization unit to the separation process because isomerization units commonly produce a small amount of $C_8$ naphthenes which

accumulate in the toluene desorbent. The adsorbent is sensitive to strongly adsorbing molecules which therefore should be removed from the feed and the desorbent. The common contaminants which affect adsorbent life and selectivity are olefins, sulfur-, nitrogen-, and oxygen-containing organic compounds, heating oil, etc. The desorbent is usually treated with acidic clay to remove unsaturates. The feed is also appropriately treated to reduce S, N, Cl, and O to acceptable levels. The level of water in the process fluid is monitored since it is a factor in controlling adsorbent selectivity.

### *Aromax Process*

An adsorption-based process for separating *p*-xylene from $C_8$ aromatic feed has also been developed by Toray Industries Inc. under the trade name Aromax. The first Aromax unit with a capacity of 110,000 metric tons/year went on stream in 1971. This process also employs a zeolite-type adsorbent modified by ion exchange to give a desired selectivity (*59*, *60*) and is quite similar to UOP's Sorbex process. A process flow diagram is given in Fig. 9. In this case the adsorbent beds consist of a series of horizontal independent chambers containing the adsorbent. Mixed xylenes are introduced as shown, and a raffinate containing a small amount of residual *p*-xylene is withdrawn at a point several chambers downstream of the feed chambers. In the recovery zone, *p*-xylene is selectively adsorbed.

Reflux, primarily *p*-xylene, is introduced to the adsorbent several chambers upstream of the feed point to increase the purity of the adsorbed *p*-xylene in the enrichment zone. The adsorbed *p*-xylene is desorbed above the reflux by an aromatic purge material which is introduced to the top of the desorption zone and withdrawn as extract. Desorbent is recycled to the adsorbent after distillation in the extract and raffinate columns.

The adsorbent bed contacts the feed xylenes in a countercurrent fashion. Countercurrent flow is simulated by switching the inlet and outlet positions of the xylene streams periodically by means of automatically sequenced on-off valves. Adsorption is carried out at a temperature below 200°C and at a pressure between atmospheric and 215 psi. Product with 99.5% purity and above 90% recovery is obtained.

Though the Aromax process appears to be a variation of the Parex process, it has some advantages:

The amount of desorbent present in the enrichment zone is much less.

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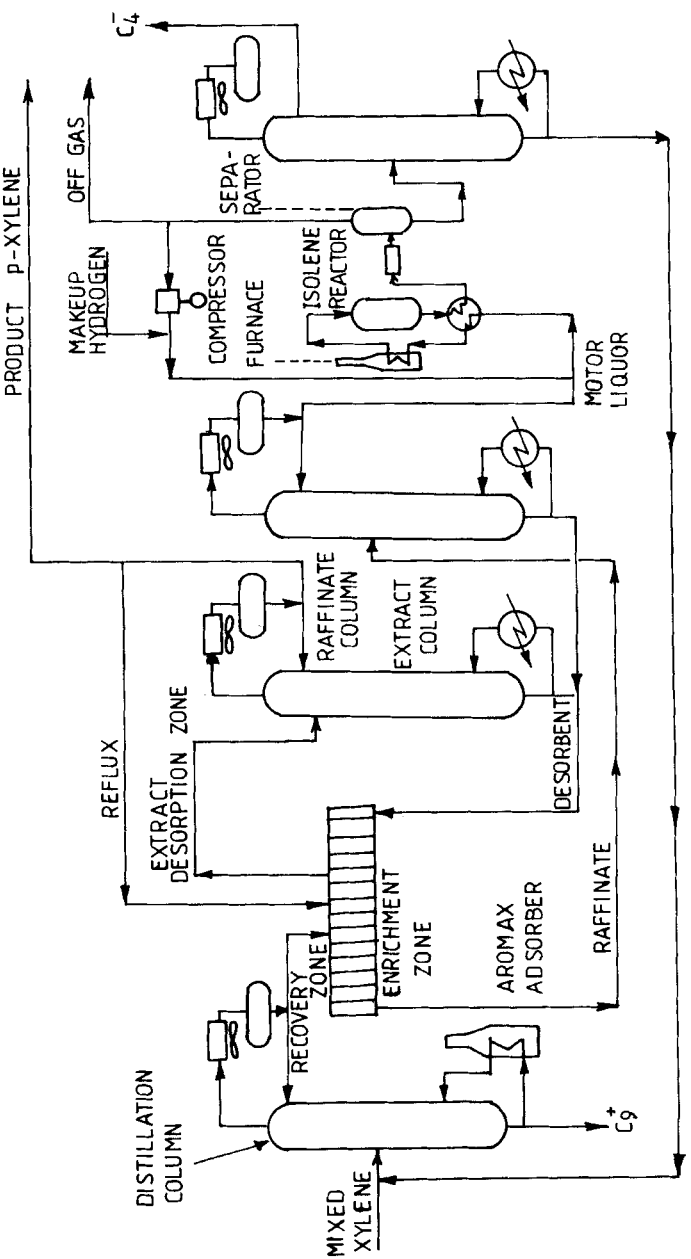


FIG. 9. Process flow sheet for Aromax process.

The horizontal column permits the changing of the adsorbent in any chamber without interfering with the operation of the remainder of the plant.

However, a disadvantage is the need for more ground area for the horizontal column.

### *Asahi Process*

This process, developed by the Asahi Chemical Ind. Co., is based on the selective adsorption principle and is reported (*55*) to separate *p*-xylene and ethylbenzene as products. A block flow sheet for the process is shown in Fig. 10. It is claimed that this works on the principle of displacement chromatography unlike other processes which are based on elution chromatography. This difference in basic principle is because of the high selectivity of the zeolite adsorbent which is also of the X or Y type. In this case the desorbent may not substantially migrate ahead of the adsorbate band during migration. Not much information about the adsorbent, desorbent, or process conditions is available. This process appears so far to have been operated only on a pilot scale, but the performance of a full-scale unit (200 ton/day) has been predicted from a detailed numerical analysis. This is claimed to be the most economical process to produce *p*-xylene and ethylbenzene simultaneously, requiring about half the adsorbent inventory and desorbent circulation rate of the Sorbex process. Such an advantage is claimed because the adsorbent has been developed to have a much higher selectivity by proper adjustment of the Si/Al ratio and the acidity of the zeolite adsorbent (*55*).

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### *Idemitsu Process*

This process is a combination of adsorption and crystallization processes (*61*). Fresh feed and recycle from the crystallization section are mixed in the feed tank. Mixed feed is preheated by exchange against raffinate and then in a fired heater. Feed enters the adsorbent bed at 200°C and 200 psig. *p*-Xylene is adsorbed by a X-type molecular sieve which is later desorbed by toluene.

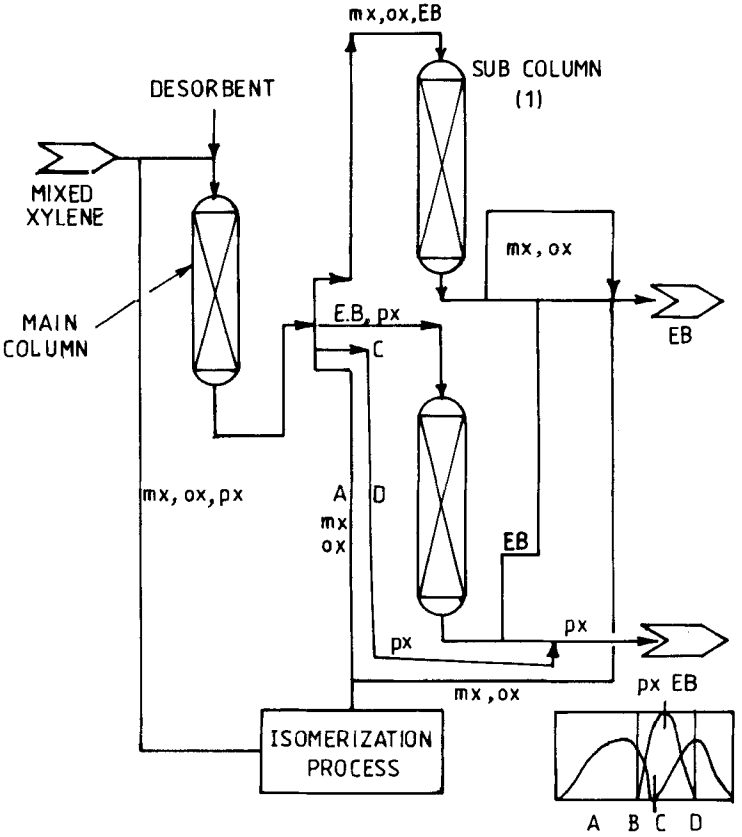
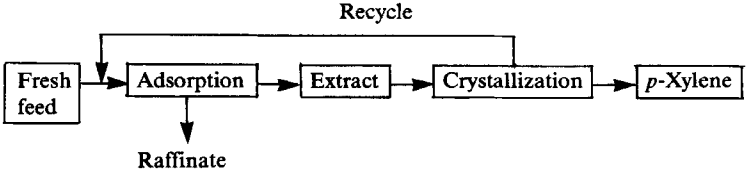



FIG. 10. Block flow sheet of Asahi process.




The crude *p*-xylene (86%) is collected in a surge tank and sent to crystallization. After crystallization, 99.5% pure *p*-xylene is obtained. Crude *p*-xylene is cooled in steps from 140°C and finally chilled to −3°C.

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The above process is interesting because the adsorption step can be much simpler than in th Parex or Aromax processes. Also, the refrigeration level needed is −3°C, compared with −67 to −73°C encountered in the first stage of the conventional crystallization process.

In addition to the above-mentioned processes which have been commercialized, newer developments or modifications are taking place on *p*-xylene separation by adsorptive separation techniques. Santacesaria et al. (*62*) reported having separated $C_8$ aromatic isomers to obtain specifically high purity *m*-xylene from the mixture in the vapor phase (145–235°C, 1–2 atm) with potassium-exchanged Y zeolite and toluene desorbent. The zeolite used is reported to have the following order of affinity for the different isomers: *p*-xylene > ethylbenzene > *m*- or *o*-xylene.

According to these authors, certain advantages found in displacement chromatography can be obtained by operating in the vapor phase. The various components of the mixtures leave the adsorbent column with their characteristic retention time depending on their respective distribution coefficients. The component having the lowest distribution coefficient acts as a piston. As a consequence, *m*-xylene, with the lowest distribution coefficient, is pushed out of the column first at a concentration near 100%. Detailed fundamental studies [selectivities, mass transfer coefficients (*63*), breakthrough curves (*64*), and pulse curves (*65*)] on the xylenes/zeolite system have been reported by the same group.

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Though most of the work reported on *p*-xylene separation makes use of Y-type zeolite, other adsorbents [e.g., X (*66*, *67*), silicalite (*68*), mordenite (*69*, *70*), ZSM (*69*, *70*), and activated carbon (*71*)] have also been reported (Table 6). *p*-Xylene may be separated as a front-end product in high purity with a NaX- or LiX-type zeolite in the presence of pyridine. Pyridine has been used to modify the adsorbent so that all isomers except *p*-xylene are adsorbed. In fact, the selectivity orders with and without pyridine are:

$$\text{para} < \text{ortho} < \text{EB} < \text{meta} \qquad \text{(pyridine)}$$

$$\text{meta} < \text{EB} < \text{para} < \text{ortho} \qquad \text{(no pyridine)}$$

Silicalite (*68*) has greater selectivity for *p*-xylene than ethylbenzene and other hydrocarbons ranging from $C_6$ to $C_9$. This selectivity has been improved upon by bringing silicalite into contact with a solution of concentration *m* (g ions/L) of a salt of a polyvalent cation of charge density (*e*/*r*), where (*e*/*r*)*m* is at least 45, after which it is filtered, washed, and dried to decompose to the salt, leaving the metal cation in the crystalline state.

TABLE 6
Various Adsorbents Investigated for Xylene Separations

| Zeolite type | Exchanged cations | Selectivity order[a] | Ref. |
|---|---|---|---|
| Y | $Ba^{2+}$ or $K^+$ or both | para > EB ~ D > ortho ~ meta | *56* |
| X | $Na^+$ or $Li^+$ with pyridine | meta > EB > ortho > para | *66* |
| Y | $Na^+$ | meta > toluene ~ ortho ~ para > EB | *67* |
| X | $K^+$, $Ba^{2+}$ | PDEB > para > EB > ortho ~ meta | *74* |
| X | $Ba^{2+}$, $Sr^{2+}$ | para > PDEB > EB > ortho > meta | *74* |
| X | $Ca^{2+}$ | meta > ortho > toluene > para > EB | *13* |
| X | $Sr^{2+}$, $K^+$ | meta > para ~ ortho > toluene > EB | *13* |
| Mordenite | $Ba^{2+}$ | para > meta > ortho | *69* |
| ZSM-5 | H-ZSM-5 | para > meta > ortho | *69* |
| | Na-ZSM-5 | para > meta | |

[a]PDEB = *p*-diethylbenzene. D = desorbent.

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*m*-Xylene usually constitutes about one half of the total product stream in the current processes for the manufacture of $C_8$ aromatics (Table 7). Adsorptive methods have been reported for exclusively separating *m*-xylene as well. Broughton (*72*) has reported another process for separating *m*-xylene, *p*-xylene, or *o*-xylene and EB in that order with the Sorbex adsorptive process. A Y-type zeolite with sodium at exchangeable cationic sites has been found to show the selectivities as *m*-xylene (1.80), *p*-xylene (1.00), *o*-xylene (1.00), and EB (0.44).

Maintaining adsorbent water contact within a range of about 2–7 wt% is necessary for optimum adsorbent and process performance. Toluene is used as a desorbent.

Another UOP patent (*73*) describes the use of a zeolite with a Si/Al ratio of 4.5–5.0 at 150–200°C and 100 psig to get *m*-xylene at 98% purity and 95% recovery.

The Ebex process for the recovery of ethylbenzene from mixed $C_8$ aromatics has also been developed (*13*, *24*, *74*). With NaY or SrKX zeolite

TABLE 7
A Typical $C_8$ Aromatic Isomeric Composition

| Isomer | % |
|---|---|
| *o*-Xylene | 21 |
| *m*-Xylene | 41 |
| *p*-Xylene | 20 |
| Ethylbenzene | 18 |

adsorbent and toluene desorbent, a pilot scale operation has been demonstrated, but no full-scale commercial unit has yet been built. Whereas in the Parex process the *p*-xylene is most strongly adsorbed and removed as the extract, in the Ebex process ethylbenzene is the least strongly held and is recovered as raffinate. Representative steady-state concentration profiles measured in a pilot-scale Ebex unit are shown in Fig. 11.

## Separation of Other Substituted Aromatics

Processes employed for the separation of *p*-xylene involve over 1.5 million mt/yr of xylene feed. However, recent developments (*75*) in adsorptive separation technology are concerned with aromatic intermediates of smaller volume. In such cases the process becomes simpler and the adsorption/desorption efficiencies are not very crucial. Developments in the separation of substituted aromatic chemicals which serve as building blocks for such varied industries as pharmaceuticals, dyestuffs, and pesticides follow.

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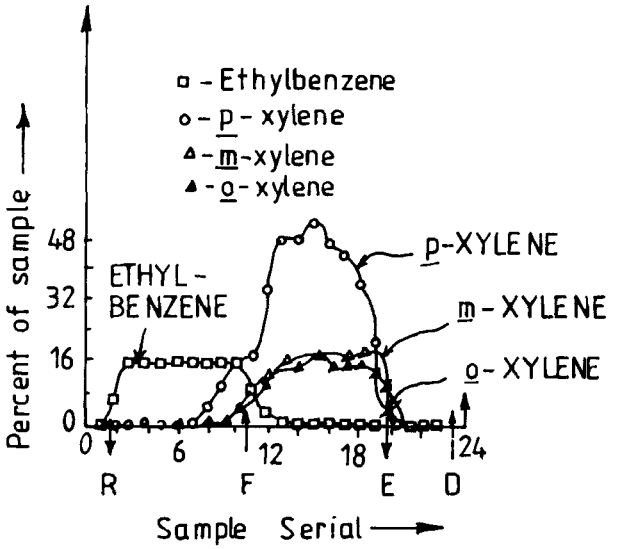


FIG. 11. Steady-state column concentration profiles in continuous bench-scale separation of ethylbenzene from mixed $C_8$ aromatics.

### Chlorotoluenes

During the synthesis of monochlorotoluene, a mixture of different isomers is formed with *m*-chlorotoluene present in negligible amounts (about 0.3%). Separation of the ortho and para isomers is difficult by conventional methods because of the closeness of their boiling points (3°C difference) and the similarities in their chemical and physical properties. Separation of the ortho and para isomers has been reported by adsorption (*75–78*). In one discovery (*76*), separation was achieved by adsorption on CaX and KY (98% exchange) in the vapor phase at 180–250°C and 0.8 to 1.5 atm by using two desorbents: toluene and monochlorobenzene. Both components are claimed to be recovered with more than 99% purity. In another study (*78*), a KY-type zeolite with two desorbents, alkylbenzene and dihalotoluene, was used at 250°C and 30 $kg/cm^2$ pressure. It is claimed that both vapor- and liquid-phase operations are possible.

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### Cresols and Xylenols

During the gasification of coal, a cresol–xylenol mixture with 10 vol% of the feed as *o*-, *m*-, and *p*-cresol is obtained. 2,6-Xylenol is useful for the preparation of coal-tar disinfectants and in the manufacture of artificial resins. Separation of xylenols from cresols is very difficult because of the closeness of their relative volatilities. However, the separation of cresol from xylenol by using zeolites (Ba- or K-exchanged X), has been reported (*79*). The separation of *m*- and *p*-cresols from xylenol by the Sorbex process is also claimed (*75*). Basic selectivities measurements for *p*-cresol over other isomers on H-ZSM-5 zeolite adsorbent are described by Namba et al. (*69*); selectivities for the para isomer are given the Table 8. A commercial plant is in operation for the separation of *p*- and *m*-cresols.

### Nitrotoluene

Nitrotoluenes are important starting materials for the manufacture of dyes and explosives. A method involving selective adsorption employing zeolite for the separation of isomeric nitrotoluenes, particularly ortho and para, from isomeric mixtures has been reported (*75, 80*). In one study (*80*), chromium-exchanged X or CaY is reported to adsorb *p*-nitrotoluene

TABLE 8
Competitive Adsorption of Cresol Isomers on ZSM-Type Adsorbent

| Adsorbent | Amount of cresol isomer adsorbed | | | | |
|---|---|---|---|---|---|
| | *o* | *m* | *p* | Total | $S_p^a$ |
| H-ZSM-5 | 31.8 | 37.2 | 39.0 | 108.0 | 0.361 |
| P-ZSM-5 (P = 0.35 mmol/g) | 10.5 | 15.4 | 29.3 | 55.2 | 0.530 |
| B-ZSM-5 (B = 0.35 mmol/g) | 14.6 | 22.2 | 35.3 | 72.0 | 0.489 |
| Mg-ZSM-5 (Mg = 0.20 mmol/g) | 10.9 | 17.1 | 51.0 | 79.6 | 0.648 |

[a] $S_p$ = (amount of *p*-isomer adsorbed at equilibrium)/(total amount of disubstituted benzene adsorbed at equilibrium).

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selectively. However, X-type zeolite exchanged with K, Zn, Ni, Ba, Ca, Co, and Sr, and Y-type zeolite exchanged with Ca, Na, K, Fe, and/or Co are reported to adsorb ortho isomers selectively (Table 9).

### *Diisopropyl Benzenes*

Some studies (*13*, *69*) have shown the possibility of separating diisopropyl benzen isomers by employing adsorption. H-ZSM-5 and mordenite exchanged with barium have been tried (*69*), and they were found to show $S_p$ (see Table 9) as 0.84 and 1.0, respectively.

### *Toluidine Isomers*

Toluidine isomers find substantial use in dyes and dye intermediates. For example, *o*-toluidine is a precursor of such azo dyes as acid red 24, solvent yellow 3, solvent red 26, and direct red 62, while *p*-toluidine is a precursor of basic red 9, acid green 95, and acid blue 78. Toluidines are disubstituted benzens with amino and methyl substituent groups and have quite close properties. Separation of these isomers has been reported (*14*) by contacting the mixture with an adsorbent X- or Y-type zeolite cation exchanged with a cation in the group Fe, Mn, Co, Ni, or Zn, and thereby selectively adsorbing *p*-toluidine isomer. Adsorbed *p*-toluidine is recovered by desorbing with a material comprising aniline or alkylamines, but excluding alkylamines having eight or more carbon

TABLE 9
Different Adsorbent Systems for the Separation of Nitrotoluene Isomers[a]

| Separation effected | Zeolite type | Possible exchange cation |
|---|---|---|
| 1. *p*-Isomer from a mixture of para and at least one other isomer | X | Cr |
| | Y | Ca |
| 2. *o*-Isomer from a mixture of ortho and at least one other mixture | X | K, Zn, Ni, Ba, Ca, Co, Sr, Cu, and Mg |
| | Y | Ca, K, Na, Fe, Co, and K-Ba |
| 3. *o*- and *p*-Isomer from a mixture of *o*, *m*, and *p* | X | Na, Ni, Ba, Cu, Mg, Ca, Co, and Sr |
| | Y | Ca, Na, Fe, Co, K, and K-Ba |

[a]Temperature: 20–230°C. Pressure: 1–35 kg/cm$^2$. Desorbent: toluene, 1-hexanol admixture.

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atoms per molecule when the adsorbent is an X-type zeolite. The selectivities reported for various adsorbent/desorbent systems are presented in Table 10.

The separation of the isomers of toluidine on transition metal exchanged X and Y zeolites is based on the chemical interaction between the amino group of toluidine and the cations of the zeolite, where the lone pair of electrons present on the nitrogen atom of the amino group is donated to the metal ion, resulting in a Lewis acid-base complex. However, the steric component of this interaction differs for the three isomers, with the ortho component having the maximum steric hinderance followed by meta and para isomers. This effect is manifested in their selectivities, with the ortho isomer being the least strongly retained on zeolite adsorbent.

Some other substituted aromatics isomers whose separation with zeolite adsorbents is claimed (*23*, *75*, *81–84*) include ethyltoluenes (para, meta, and ortho), cymenes (para and ortho), dichlorobenzenes (para and ortho), picolines, and tri- and tetramethylbenzenes.

## 5. ADSORPTIVE SEPARATIONS IN AQUEOUS SYSTEMS

In the eighties, the horizon of zeolite molecular sieve applications has been expanding into aqueous systems as well. However, large-scale application to aqueous systems is mostly confined to the separation of carbohydrates. The demand for pure sugar isomers (e.g., fructose and

TABLE 10
Toluidine Selectivity Values for Different Adsorbent/Desorbent Systems as Determined by the Pulse Technique

| Adsorbent | Metal content (wt%) | | $B_{(p/o)}$ | $B_{(p/m)}$ | $B_{(m/o)}$ | Desorbent |
|---|---|---|---|---|---|---|
| | Ni | Na | | | | |
| NiX | 7.03 | 6.92 | 2.41 | 1.29 | 2.10 | 15% aniline/toluene |
| NiY | 4.79 | 4.28 | 2.48 | 1.27 | 1.95 | 15% aniline/toluene |
| NiY | 7.47 | 2.47 | 2.54 | 1.17 | 2.17 | 15% aniline/toluene |
| NiY | 4.79 | 4.28 | 1.96 | 1.36 | 1.44 | 15% *n*-butylamine/toluene |
| CoY | 6.50 | 3.66 | 2.84 | 1.28 | 2.21 | 15% aniline/toluene |
| NiX | 7.03 | 6.92 | 1.80 | 1.30[a] | 2.32 | 15% *n*-octylamine/toluene |
| NiX | 7.03 | 6.92 | 1.29 | 1.38[a] | 1.78 | 50% *n*-propanol/toluene |
| NaY | | | 1.37 | | 1.14 | 15% aniline/toluene |

[a]These are $B_{(m/p)}$.

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lactose) for medicinal purposes or in the food industry has spurred this development. Sugar isomers such as aldoses and ketoses are difficult to separate. Since most conventional separation techniques involve chemical means, obtaining a pure sugar isomer is an involved process. Consequently, adsorptive separations of these isomers are making rapid progress. In the following we discuss separations of carbohydrates and some other compounds from an aqueous medium employing zeolites.

## Separation of Fructose from Glucose

Fructose is considered to be the most soluble and the sweetest of the sugars. It finds extensive use in medicine and as a source of energy for patients. A method of obtaining fructose involves hydrolysis of sucrose to dextrose and fructose, separation of fructose as an insoluble lime-fructose complex, liberation of fructose by acidification of the complex with acids forming insoluble salts, removal of ions by ion exchange, concentration of the syrup, and finally crystallization. However, because of the difficulty in concentrating and separating fructose, a solution of fructose with other sugars is generally used to get the benefits of fructose; e.g., an invert sugar solution which contains fructose, glucose, and "higher fructose" corn syrup which typically contains 40–45% fructose. The separation of fructose from glucose using a zeolite molecular sieve has been reported in the literature (*85–88*). It is commercially used for the manufacture of high fructose corn syrup.

Neuzil and Priegnitz (*85*, *86*) reported a process for the separation of fructose from a glucose-fructose mixture by selective adsorption on a cation exchanged X- or Y-type zeolites. UOP has licensed a unit under the trade name of Sarex for separating fructose from its mixture with glucose and polysaccharides (*24*). In their patent, Neuzil and Priegnitz reported that fructose selectively adsorbed and later desorbed with water. They determined the selectivities (Table 11) of fructose over glucose and water for various zeolites using the pulse method at 20–100°C, 250 psig, and in the liquid phase. As seen in the table, CaY having α(fructose/glucose) = 10 and α(fructose/water) = 1.4 appears to be the best candidate, followed by BaX or SrX. The adsorbents with calcium or magnesium as cations are not suitable because of their higher acidity.

The adsorption selectivity of the zeolites to monosaccharide is not governed by the dimensions of the zeolite cavities but by the extent of interaction of different isomers with the cations present. It is known (*89–94*) that sugars and polyhydroxy alcohols have different interactions with cations depending on their stereochemistry. For example, it has been shown (*89*) that mannitol, which has a planar configuration in water, has weaker interactions with cations than nonplaner sorbitol. Such a

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TABLE 11
Selectivities of Fructose over Glucose and Water for Various Cation-Exchanged Zeolites

| Adsorbent | $\alpha \frac{\text{Fructose}}{\text{Glucose}}$ | $\alpha \frac{\text{Fructose}}{\text{Water}}$ |
|---|---|---|
| $NH_4Y$ | 6.5 | 0.71 |
| HY | Both eluted simultaneously | |
| NaY | 4.3 | 0.66 |
| KY | 3.0 | 0.85 |
| CSY | Both eluted simultaneously | |
| MgY | Both eluted simultaneously | |
| CaY | 10.0 | 1.4 |
| SrY | 5.6 | 1.9 |
| BaY | 3.7 | 3.1 |
| NaX | 1.42 | — |
| KX | 0.55 | — |
| SrX | 6.15 | — |
| BaX | 2.82 | — |
| Ba-K-X | 2.19 | — |
| Ba-Sr-X | 5.0 | — |
| CSX, MgX, CaX, CaH | Both glucose and fructose relatively unadsorbed | |

dependence of interactions on stereochemistry needs to be further exploited to achieve separation of polyhydroxy compounds which are difficult to separate by conventional means.

The separation of glucose from polysaccharide by using selective adsorption on potassium-exchanged X-type zeolites in the liquid phase has been reported (*95*). This is an important study, because glucose prepared from the hydrolysis of starch will need to be separated from other water-soluble polysaccharides which are invariably present. The recovery of sucrose from molasses (which may have as high a sucrose content as 50% in the case of beet root molasses) has been reported by employing Y-type zeolites (*96*).

Lactulose, a disaccharide of fructose and galactose, has properties of considerable interest to the medical and food industries. Lactulose is prepared from lactose, a disaccharide of galactose resins or enzymes. Because the reaction is usually incomplete, the reaction product is invariably a mixture of lactose and lactulose. Recovery of pure lactulose has been reported by Sherman and Chao (*97*) by selective adsorption. Adsorbents found suitable are steam-treated barium or potassium Y. The process has been shown to be feasible at 30–100°C and at pressures sufficient to maintain the liquid state. In Table 12 we present the reported separation factors for various sugar and polyol isomers on zeolite adsorbents.

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## Separation of Chemicals Other Than Carbohydrates

By using a naturally occurring zeolite clinoptilolite which selectively adsorbs water, Hartline (*104*) determined the concentration of ethanol from fermentation beers. Teo and Ruthven (*105*) made some fundamental studies on adsorption and kinetics of water from aqueous ethanol on molecular sieve 3A. In both cases it is the size effect which is made use of; the water molecule, being smaller, is adsorbed inside the zeolite cavity, and alcohol is excluded. Recent reports (*106*) of alcohol separation from water describe the selective adsorption of an alcohol on a hydrophobic zeolite like silicalite. It has been shown (*107*) that silicalite-type zeolites, because of their hydrophobic nature, are more selective toward organic compounds. They are capable of removing small organic molecules such as methanol, *n*-butanol, methylcellosolve, and phenol from water. The adsorbent claimed for ethyl alcohol separation is a high silica zeolite having an Si/Al ratio of about 40–60. The adsorbed alcohol can be recovered by desorption with another adsorbate or by heating the

TABLE 12
Separation Factors for Some Sugar Components on Zeolite Adsorbents

| Mixture | Adsorbent | Separation factor | Ref. |
|---|---|---|---|
| 1. L-Arabinose/xylose | BaX | 3.1 | *98, 99* |
| L-Arabinose/glucose | BaX | 5.6 | |
| L-Arabinose/mannose | BaX | 3.1 | |
| L-Arabinose/sucrose | BaX | 84.0 | |
| L-Arabinose/cellobiose | BaX | 42.0 | |
| 2. Lactulose/lactose | BaX | 1.0 | *97* |
| | BaY | 1.82 | |
| | BaSY[a] | 1.66 | |
| | KY | 1.0 | |
| | KSY[a] | 1.52 | |
| 3. Lactose/galactose/glucose | BaY | | *99, 101* |
| Galactose/glucose | | 1.9 | |
| Glucose/lactose | | 2.9 | |
| 4. Mannose/glucose | BaX | 2.7 | *101* |
| | BaY | 2.6 | |
| | CaY | 2.4 | |
| | NaY | 1.6 | |
| 5. Mannitol/galactitol | BaX | 1.6 | *99, 102* |
| Mannitol/sorbitol | BaX | 0.6 | |
| 6. Inositol/sorbitol | NaY | 20.0 | *103* |
| Inositol/mannitol | NaX | 40 | |

[a]Steam treated.

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adsorbent. It is claimed that the heat required to desorb the alcohol is much less than the heat needed to evaporate a mixture of water and ethanol by distillation.

After measuring the heats of adsorption of various compounds, Groszek (*108*) reported the feasibility of separating carboxylic acid from its aqueous mixture with one or more oxygenated compounds. This idea is based on the premise that the heat of adsorption is not only dependent on the amount of heat adsorbed from a given solution and the nature of adsorbent, but also on the rate of adsorption. Thus, although the amounts of adsorption are similar for ethyl alcohol and acetic acid, as shown in Table 13, when they are adsorbed from their aqueous solutions the heat of adsorption of acetic acid is much higher, thus reflecting its selectivity toward zeolite. Groszek also claims that it is possible to separate higher carboxylic acids from lower ones, which may be required when carboxylic acids are obtained by oxidation of paraffinic hydrocarbons.

TABLE 13
Adsorption of Carboxylic Acids from Aqueous Solutions Using an Adsorbent MFI($NH_3$) Zeolite Having a Silica to Alumina Ratio of 53.2:1

| Adsorbate | Heat of adsorption (J/g adsorbent) | Amount of adsorption [(mg/g)/g adsorbent] |
|---|---|---|
| Formic acid | 8.2 | 13.1 |
| Acetic acid | 17.0 | 45.0 |
| Propionic acid | 21.2 | 64.0 |
| Ethanol | 13.0 | 53.0 |
| Ammonia | 5.4 | 11.4 |

## 6. FUTURE DIRECTIONS

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During the last two decades or so, the adsorptive separation process has been firmly established as an energy-efficient unit operation in the hydrocarbon industry. Based on current developments, potential growth areas appear to be the development of new types of molecular sieves, the search for new applications, and improvements in the processes. It is difficult to visualize radically different processes with more than 60 units, based on the already commercialized Sorbex process. However, improvements in hardware are likely to lead to more energy-efficient processes.

### Development of New Types of Molecular Sieves

#### *Zeolites*

Of all the porous materials, crystalline aluminosilicates, i.e., zeolites, have had the greatest technological impact. The preeminent position of zeolites among porous adsorbents will continue in the future because zeolites offer a wide range of porosity, surface hydrophilicity and hydrophobicity, excellent thermal stability, and shape-selective sorption. Nevertheless, the future will see the emergence of novel molecular sieves based on structural modifications of existing types or on altogether new structures. High silica zeolites such as ZSM and silicalite will attract greater attention because of their separation potential, as is evident from the recent literature where these zeolites have been used for the separation of aromatics (*13*, *69*, *70*) and alcohols from aqueous solutions

(*106*). The predominently hydrophobic silicalite and ZSM-type zeolites may find increased use in separating nonpolar compounds from aqueous solutions such as in wastewater treatment.

### *Porous Aluminum Phosphates*

A new class of microporous aluminum phosphates (*109*, *110*) which forms a structural framework akin to zeolites with alternating $AlPO_4$ and $SiO_4$ tetrahedra has been developed by Union Carbide Corporation. These are known as AlPO's, SAPO's (silicon aluminum phosphates), and MAPO's (metal aluminum phosphates). They have the general composition

$$xR \cdot Al_2O_3 \cdot 1.0 \pm 0.2P_2O_5 \cdot yH_2O$$

where R is an amine or quarternary ammonium ion. Of the twenty 3-dimensional structures synthesized, 14 are reported to be microporous. Three structures, $AlPO_4$-20, $AlPO_4$-17, and $AlPO_4$-24, are structural analogs of zeolites sodalite, erionite, and analcime, respectively. Some of the main characteristics of AlPO's are:

A broad range of pore sizes (from 3 to 10 Å) and pore volumes almost as broad as those found in synthetic zeolites (Table 14).

Moderate hydrophilicity is shown by AlPO's despite the fact that they possess a cation-free neutral framework. This hydrophilicity

TABLE 14
Pore Sizes and Pore Volumes for $AlPO_4$ Molecular Sieves

| | | Pore volume ($cm^3/g$) | |
|---|---|---|---|
| $AlPO_4$ type | Pore size (nm) | $O_2$ | $H_2O$ |
| 5 | 0.8 | 0.18 | 0.3 |
| 31 | 0.8 | 0.09 | 0.17 |
| 11 | 0.61 | 0.11 | 0.16 |
| 17 | 0.46 | 0.20 | 0.28 |
| 18 | 0.46 | 0.27 | 0.35 |
| 14 | 0.41 | 0.19 | 0.28 |
| 33 | 0.41 | 0.23 | 0.23 |
| 16 | 0.3 | 0 | 0.3 |
| 20 | 0.3 | 0 | 0.2 |

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apparently arises because of the difference in the electronegativities of aluminum and phosphorus atoms.

AlPO's have a high thermal stability and resist the loss of structure, even at 1000°C. AlPO-5, -11, and -17 show no structural loss when treated with 16% steam at 600°C.

Though the application potential of these materials is being still explored (*109–111*), many alumino phosphates have shown air-drying characteristics similar to Linde types A and X. Although hydrophilic, as demonstrated by the removal of water from solutions of 2-butanone, these are inferior desiccants compared to aluminous zeolites but need less severe outgassing facilities. Their selective sorption properties are shwon in Table 15. From this, it is clear that they will find applications in separating organic compounds. The literature on the preparative methods for aluminum phosphates has been available for quite some time, but development of molecular sieve aluminum phosphate has taken place only in the current decade. This is an interesting example of how the technological impact of zeolite molecular sieves in the seventies has made scientists look for newer molecular sieve materials.

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TABLE 15
Selective Sorption Properties of Some $AlPO_4$ Molecular Sieves

| | $AlPO_4$ number | | | |
|---|---|---|---|---|
| Adsorbate | 5 and 31 | 11 | 17 and 18 | 14 |
| $H_2O$ | sorbed | sorbed | sorbed | sorbed |
| $O_2$ | | | | |
| Xe | | | | |
| *n*-Butane | | | | ← cut off |
| *n*-Hexane | | | ← cut off | |
| Isobutane | | ← cut off | | |
| Cyclohexane | | | | |
| Neopentane | ← cut off | | | |

### *Intercalated Clay Minerals*

The search for solids having well-defined pore structures in the range of 10–30 Å for dealing with bulkier molecules in the "bottom of barrel" has led to clay minerals which can be intercalcated with an appropriate cation to develop the desired pore dimensions. Clays are made up of layers formed by the condensation of sheets of linked $Si(O,OH)_4$ tetrahedra with those of linked $M_{2-3}(OH)_6$ octahedra, where M is either a divalent or trivalent cation. The distance between these layers can be controlled by means of the intercalcated cations which act as "pillars" (Fig. 12) and hold together the negatively charged layers on either side of them. By varying the size of the pillaring cations or the spacing between cations, or both, one may adjust the pore size to suit a particular application. The feasibility of such pillaring was first shown by Barrer and McLeod (*7*, *112*), who introduced organic cations like tetraalkylammonium into montmorillonite. However, these clays did not have high thermal stability. For example, alkylammonium and bicyclic amine cations decompose below 250°C. This problem of low thermal stability has been overcome by using inorganic pillars which produce clays stable

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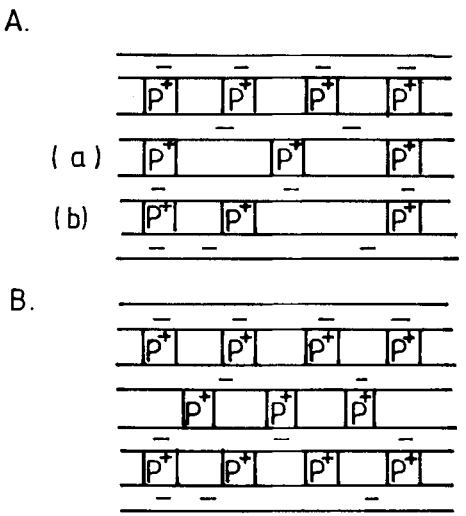


FIG. 12. Pillaring cation ($P^+$) distribution in clay interlayers. (A) Irregular distribution: (a) irregular spacing from interlayer to interlayer, (b) irregular spacing within an interlayer. (B) Regular distribution.

above 500°C. Two of the polynuclear hydroxy cations studied in detail are hydroxy aluminum and hydroxy zirconium (*113–116*).

Occelli et al. (*117*) developed such molecular sieves by pillaring commercial samples of calcium-bentonite with hydroxy aluminum oligomer $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. These have been shown to possess large pore openings (8 × 14 Å), with a pore volume of 0.16–0.20 $cm^3/g$ and a surface area of 250–350 $m^2/g$. The cavities in this clay were easily accessible to $C_6$–$C_{10}$ normal paraffins and 1,3,5-trimethylbenzene, but not to 1,2,3,5-tetramethylbenzene. Since the sorbed molecules are constrained to move along the silicate layers and cannot diffuse from one layer to another, pillared clays behave as two-dimensional molecular sieves. They are thermally stable up to 500°C. Partial structural collapse occurs between 500–700°. The hydroxy zirconium pillar is a $Zr_4$ oligomer of the type $Zr_4(OH)_{16-x}$ (*114*). The remarkable thermal stability of the $Zr_4$ and $Al_{13}$ pillared clays has been attributed to the formation of metal oxide clusters upon dehydroxylation of the hydroxy cations at elevated temperature.

The development of highly selective molecular sieves from clays requires a regular distribution of pillars and pores in the interlayer region (Fig. 12). However, the charge distribution in the layers of the widely used smectite clays is highly irregular (*118*), with the result that nonuniform distribution of pillars and a range of pore sizes are obtained.

Although polynuclear hydroxymetal ions can yield pillared clays with interlayer free spacings in the range of 5 to 20 Å, the number of metal ions that form suitable oligomeric species is limited. New approaches to pillaring of clays promise to extend the number of pillaring species. It has been shown that montmorillonite clay can also be pillared with silicic acid by hydrolyzing silicon acetylacetonate (*119*, *120*), polyoxychromium oligomer by hydrolyzing chromium nitrate, and iron oxide by hydrolyzing trinuclear acetato-hydroxo iron(III) nitrate (*121*, *122*).

### *Other Adsorbents*

Besides the above-mentioned adsorbents, others which are likely to draw attention because of their molecular sieve action include:

Carbon molecular sieves
Werner's compounds
Clathrates

A larger number of papers (*123–125*) on the development of carbon

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molecular sieves and their applications has appeared. Carbon molecular sieves with pore diameters from 3–10 Å have been developed. However, their applications are confined to gas separations. These adsorbents may also be used for isomer separations in the future because it has been shown that *p*-xylene can be effectively separated from $C_8$ aromatics with carbon molecular sieves.

Among the Werner-type compounds which form inclusion complexes, the cyanometallate forms show molecular sieve potentials. Water-free $Zn_3[Co(CN)_6]_2$ obtained by outgassing at 310°C, readily sorbs *n*-hexane and 3-methylpentane but not 2,2-dimethylbutane (*126*). The channels have pore openings estimated at 5.6 × 8.6 Å. $Zn[Fe(CN)_5NO]$ has smaller openings and readily separates $CO_2$ from $CH_4$ (*111*, *126*).

Dianin's compound, like 4-*p*-hydroxy-phenol-2,2,4-trimethyl chroman and its thio analog, crystallize to form hour-glass shaped cavities 11 Å long (*111*) in the absence or presence of guest molecules. These compounds have been shown (*111*) to sorb molecules selectively. They have the capability of not only selecting certain isomers but of making a cut of paraffins up to *n*-$C_7$ from *n*-$C_8$. The selectivity of clathration among branched chain isomers is reportedly due to the "waist" in the cavity. If a methyl or ethyl group is near the middle of the backbone chain of a guest molecule, it is obstructed by the waist, and clathration cannot occur.

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## Search for New Applications

With the availability of molecular sieves having a wide range of pore sizes, the future applications of adsorptive separations appear to be immense.

The ability to separate closely related molecules in aqueous solutions under moderate conditions (Section 5) points to future applications in the biomass area in which conventional separation methods are expensive. In aqueous medium the separation of isomers which have medicinal values, like fructose, glucose, or lactulose, may also be done by adsorptive means, because the separation of these stereoisomers by other methods is generally an involved process. For example, in a recently granted patent (*127*), separation of methanol from its stereoisomeric mixture using selective adsorption on Y-type zeolites has been reported. Applications where specific isomers are required will increase in the future.

Until recently, adsorptive separations have largely been confined to high volume chemicals, be it a class of compounds, e.g., *n*-paraffins, or individual isomers, e.g., *p*-xylene or glucose/fructose. Future applications

are likely to increase the separation of smaller volume commercially important isomers, as mentioned in Section 4. For the hydrocarbon industries, the small volume adsorptive separation process is likely to encompass the recovery of value-added solvents from a large number of by-product streams in refineries and petrochemical complexes. Molecular sieve adsorption process facilities for methanol recovery and by-product oxide removal have been established (*128*) at the methyl tertiary butyl ether plant of the Valero refinery in Texas.

We have not touched upon gas separations because these applications have been excellently reviewed recently (*124*, *125*, *129*, *130*), but we should mention the development of pressure swing adsorption for separating oxygen from air. This has resulted in small portable medical oxygen units being commercialized by medical equipment suppliers. These units can deliver 2 to 4 L/min of 85%+ oxygen.

We have also not dealt with topics such as purification of streams; for example, removal of nitrogenous or sulfur (*131*, *132*) compounds from hydrocarbon feedstock and wastewater purification, but these areas do offer great challenges and scope.

It is not inconceivable that the traditional separation methods, such as fractionation and crystallization, will gradually yield their place to newer adsorption or membrane-based techniques. It is possible, in principle, to tailor adsorbents for separating components of a cracked gas stream. Likewise, the development of adsorbents with controlled porosity and hydrophobicity will enable the enrichment/separation of components of aqueous solutions, which is otherwise a highly energy-intensive step. The separation of glycols from aqueous solutions in an ethylene glycol plant is a good candidate for such a process. How rapidly these developments take place depends on several technoeconomic and environmental factors.

However, keeping in mind the rapid expansion of the petrochemical industry, adsorption-based separation processes have good potential and merit substantial research input and investment.

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