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New Separations Technology for Aromatic Chemicals

H. A. Zinnen[a]; S. H. Hobbs[a]; S. A. Gembicki[a]
[a] UOP INC. DES PLAINES, ILLINOIS

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New Separations Technology for Aromatic Chemicals

H. A. ZINNEN, S. H. HOBBS, and S. A. GEMBICKI

UOP INC.
DES PLAINES, ILLINOIS 60016

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Abstract

Separations among substituted aromatic isomers, which are very difficult or impossible by conventional means, can be accomplished by liquid-phase adsorption. Efficient commercial implementation of liquid-phase adsorption for bulk separations has been accomplished via a simulated moving-bed technique. This technique, which can generally be applied to bisubstituted isomers (e.g., cresols, chloronitrobenzenes, nitrotoluenes), is described through the use of laboratory, pilot-plant, and commercial examples.

INTRODUCTION

Substituted aromatic chemicals provide important building blocks for a variety of chemical industries. Many pharmaceuticals, dyestuffs, pesticides, specialty chemicals, and plastics utilize substituted aromatic chemical intermediates as raw materials. Some of these chemicals, such as dichlorobenzenes, represent mature markets and have been produced for many years. Others, such as *p*-ethyltoluene, have only recently become of interest.

Specific isomers often have desirable properties themselves, or may be appropriate intermediates for further chemical processing. In the C_8 aromatics system, *p*-xylene is used predominantly in the manufacture of polyester fibers and films; *o*-xylene is commonly used in the production of phthalic anhydride, an intermediate in alkyd resin and plasticizer manufacture; *m*-xylene can be converted to isophthalic acid, an intermediate for many resins and fibers; and ethylbenzene is a precursor for polystyrene.

In disubstituted aromatic mixtures, the three isomers are present in a distribution which depends to a great extent on the processing history.

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Xylenes derived from a naphtha reforming operation show a distribution similar to that shown in Table 1. In contrast, dichlorobenzenes prepared by monochlorobenzene chlorination show a more skewed isomer distribution, with very little *m*-dichlorobenzene present. Cresols derived from coal tar acids have a fairly even isomer distribution. However, *o*-cresol is frequently removed by fractional distillation, and the isomer distribution shown in Table 1 is obtained.

These mixtures become more complicated at higher degrees of substitution because of the greater number of possibilities. In general, though, a few isomers usually constitute the bulk of the mixture. Dinitrotoluene mixtures, for example, comprise predominantly the 2,4 and 2,6 isomers, with minor amounts of the remaining four "meta" isomers. Both the 2,4- and 2,6-dinitrotoluenes are desirable as toluene diisocyanate precursors in polyurethane manufacture.

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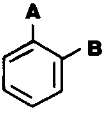
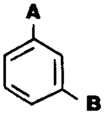
ISOMER SEPARATION

Substituted aromatic isomer separations may sometimes be achieved by utilizing differences in physical properties such as boiling point and melting point. Isomers typically vary only slightly in boiling point, so relative volatility between them is small; however, since fractional distillation and vacuum fractionation are relatively straightforward processes, they are very widely used. In contrast, melting points often differ more markedly because of differences in crystalline structure of the pure components. Thus crystallization is also a commonly applied separation technique, although recovery is often hampered by eutectic formation.

The next level of process complexity includes the solvent-aided processes, such as liquid extraction and extractive distillation. Both of these techniques utilize differences in isomer affinity for the added solvent to achieve the separation. Addition of a solvent provides an important new degree of freedom, but a successful separation process is still contingent on finding a suitable solvent with the appropriate chemical and physical properties. With few important exceptions, this has proved to be difficult.

Adsorptive separation processes represent a potentially higher degree of complexity. Separation between aromatic isomers is achieved by differences in isomer–solvent–adsorbent interactions. Both gas and liquid chromatography are essential techniques in a modern analytical laboratory, and it is generally possible to find, for any mixture, an adsorbent and solvent combination that can satisfactorily resolve the components. For example, from a butane/butene stream it is possible, with different adsorbent/

TABLE 1
Disubstituted Aromatic Isomers

			
Typical composition (wt%)	*ortho*	*meta*	*para*
Xylenes ($A = B = CH_3$)	28	52	20
Dichlorobenzenes ($A = B = Cl$)	39	3	58
Cresols ($A = CH_3$, $B = OH$)	34	65	1

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desorbent combinations, to obtain 1-butene, mixed butenes, and normal butane/butenes as separate products (*1*).

A major advantage of chromatography is that a large number of theoretical stages is possible in equipment of modest size. Fractionator performance, on the other hand, is limited by the number of actual trays or by the interfacial area for mass transfer in packed columns. Chromatographic adsorbents generally exhibit extremely high surface/volume ratios, allowing very effective mass transfer. As a result, the relative selectivities for adsorption of the different components from a mixture need not be very high for a satisfactory separation to be achieved.

COMMERCIAL APPLICATION OF CHROMATOGRAPHY

Large-scale chromatographic separation of chemical mixtures has been achieved in the last 20 years using the Sorbex process. This technique has been reviewed by Broughton (*2*). Sorbex is able, by virtue of its countercurrent nature, to minimize the adsorbent requirement and efficiently utilize desorbent. The Parex process has been successfully applied to the separation of *p*-xylene from mixtures of C_8 aromatics. The first of 34 licensed Parex units came on-stream in 1972. Since then, two additional substituted aromatic Sorbex separation processes have been commercialized: Cresol Sorbex in 1978 and Cymex in 1979. These separate the meta- and para-isomers of cresols and cymenes, respectively.

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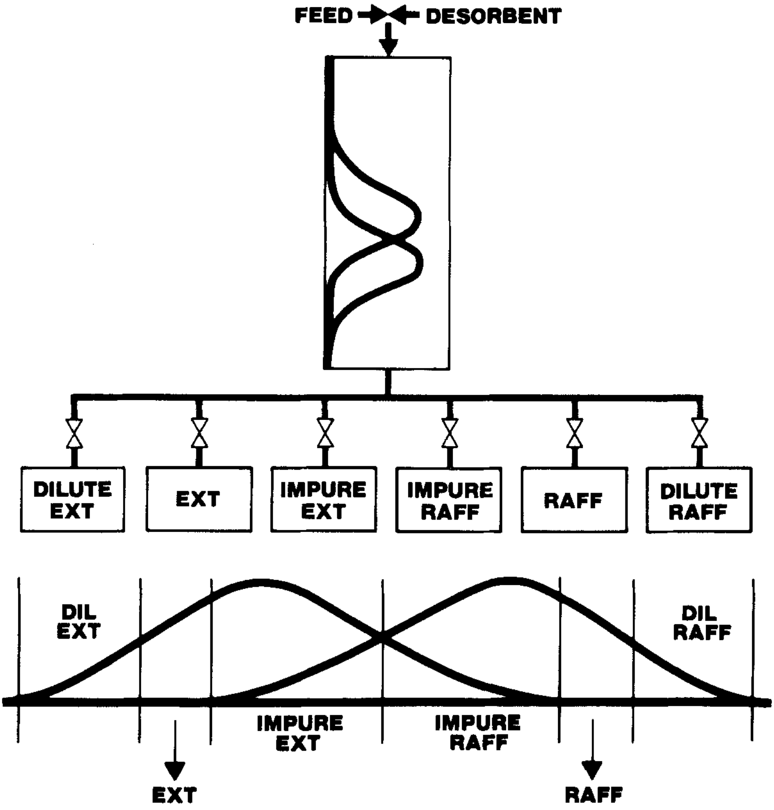

FIG. 1. Simple chromatography. Finite length.

Individual Sorbex units have been used to process between 18,000 and 1,500,000 metric tons per annum of feed. Most aromatic intermediates represent smaller volumes than this, and require a simpler process approach. In these applications, where adsorbent and desorbent efficiency are not as crucial, simpler flow schemes based on the Sorbex principle can be utilized.

The basis for achieving separation is similar to simple chromatography. In Fig. 1 a typical chromatogram for a two-component system is shown. The effluent profiles can be divided into four segments: the extract cut (i.e., the adsorbed component), which contains only the extracted component and desorbent; the raffinate cut, which contains only the rejected component and desorbent; and two impure component cuts. In a simple chromatographic system like this, extract and raffinate products could be removed, and the impure fractions recycled back to the feed. However, in the continuous Sorbex process, extract and raffinate products are continuously removed, with no recycle required.

For feeds containing three components, such as bisubstituted aromatics, the picture is further complicated. A good example is the nitrochlorobenzene (NCB) system. Typical nitration reactor effluent compositions (*3*) are *o*-NCB 34%, *m*-NCB 1%, and *p*-NCB 65%. In this case *o*-NCB and *p*-NCB are the desirable components, and *m*-NCB is frequently not recovered. The goal is to maximize the recovery of a high purity *o*-NCB and *p*-NCB. For a chromatographic separation of these three components, it will be desirable to develop a profile that shows little overlap between *m*-NCB and the other two isomers. This will allow the *m*-NCB fraction to be discarded with relatively little loss of *o*- and *p*-NCB. These possibilities will be developed further in the following section.

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ADSORPTION MECHANISMS

It has been noted that typical separation processes are based on and limited by differences in physical properties of the components, sometimes in the presence of a solvent. In adsorptive separation, however, a virtually infinite variability in the separation system can be obtained because of the number of properties available for modification in both the adsorbent and desorbent. Adsorptive separations are conducted by carefully balancing two opposing forces: the tendency of a particular component to be adsorbed and the desorption power of the solvent used as desorbent.

There is a large number of adjustable factors which affect adsorption, but these can be simplified by looking at the actual mechanisms controlling aromatic adsorptive behavior. These mechanisms can be divided into two

TABLE 2
Base Strengths of Aromatic Hydrocarbons Relative to HF[a]

Component	Relative basicity at 0.1 molal
Toluene	0.63
p-Xylene	1.0
o-Xylene	1.1
m-Xylene	26
Mesitylene	13,000

[a] Adapted from Ref. 5.

TABLE 3
Selectivity of Zeolites in C_8-Aromatic System[a]

	Adsorbent #1	Adsorbent #2	Adsorbent #3	Adsorbent #4
p-Xylene	1	2	3	4
Ethylbenzene	2	1	4	3
m-Xylene	3	3	1	2
o-Xylene	4	4	2	1

[a] 1 = most selectively adsorbed; 4 = least selectively adsorbed.

major categories: those in which the adsorbates are selected on the basis of molecular size (i.e., shape selectivity) and those in which the adsorbates all have access to adsorption sites and are selectively adsorbed based on differences in the adsorbate–adsorbent interaction.

Size selectivity is the simplest adsorptive mechanism. Para-disubstituted aromatics have the smallest molecular cross section of the three isomers, and adsorbents which contain channel structures close in size to this cross section are capable of adsorbing this isomer. For example, zeolites such as Silicalite fulfill this size requirement and will selectively adsorb the para-isomer from a mixture of disubstituted aromatics (*4*). However, such a system is incapable of selecting between *p*-xylene and ethylbenzene since they have the same cross sections.

Adsorptive effects for the general case in which all adsorbate components have access to adsorption sites depend on the magnitude of adsorbate–adsorbent interactions such as dispersion, repulsion, and electrostatic forces. It is necessary to manipulate the adsorbent in a manner which results in a larger interaction, that is, selectivity, for one aromatic component of the mixture to achieve an adsorptive separation. Materials commonly used in aromatic separation lend themselves admirably to such modification.

Zeolites represent an important group of adsorbents which can be ion-exchanged with a variety of metal cations in order to alter their adsorptive characteristics. In addition, different crystalline structures are obtained for different Si/Al ratios which result in an array of cage and channel arrangements as well as electrochemical properties. Using these parameters, it is possible to tailor adsorbents for a specific application.

Within the broad class of competitive adsorption behavior, a few individual mechanisms may be identified. The first of these mechanisms relates to acid base behavior, and will be illustrated using the C_8-aromatic (xylenes) system. It is well known (5) that the xylene isomers vary in basicity in the presence of strong acids (see Table 2) with *m*-xylene being the most basic. Based on this principle, a process for extracting *m*-xylene from a mixture using $HF–BF_3$ has been commercialized by Japan Gas-Chemical

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Co. If the Bronsted acidity of an adsorbent can be adjusted properly, selective adsorption can derive from an acid-base mechanism. Ion exchange and Si/Al ratio are important factors in controlling the acidity distribution of zeolites and, hence, the adsorptive behavior of xylenes. We have found adsorbent/desorbent combinations which can selectively adsorb each of the C_8 aromatics (see Table 3). Thus, production of *m*-xylene, *o*-xylene, ethylbenzene, and *p*-xylene can all be efficiently accomplished by liquid adsorption.

Another special case of this mechanism occurs when the Lewis acid-base characteristics of the adsorbent and adsorbate are used to effect separation. This can be illustrated by considering the toluidine molecule. By virture of the lone electron pair of the amino group, toluidine has a greater Lewis basicity compared to other di- or trisubstituted aromatic hydrocarbons, and this effect can be used in combination with a Lewis acid adsorbent to separate such a mixture. Figure 2 shows the separation which can be obtained between *o*-toluidine and mesitylene, using an adsorbent which has been ion exchanged to provide Lewis acid sites. These sites interact with *o*-toluidine selectively to produce separation; differing degrees of separation can be obtained with different cations and ion exchange function groups.

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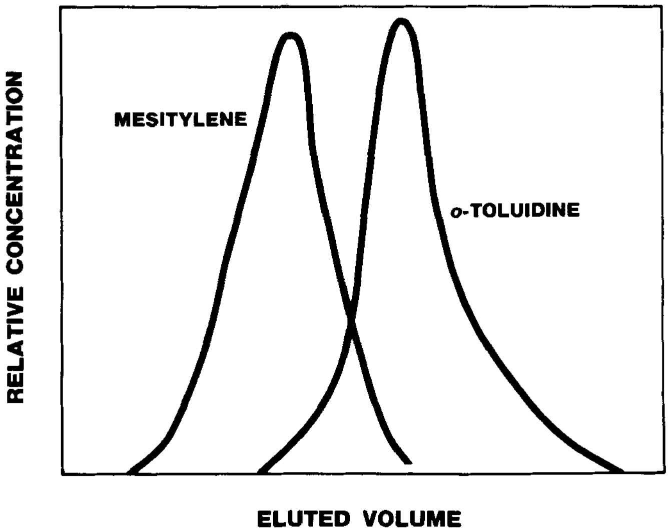

FIG. 2. Separation of *o*-toluidine from mesitylene using an ion-exchanged resin.

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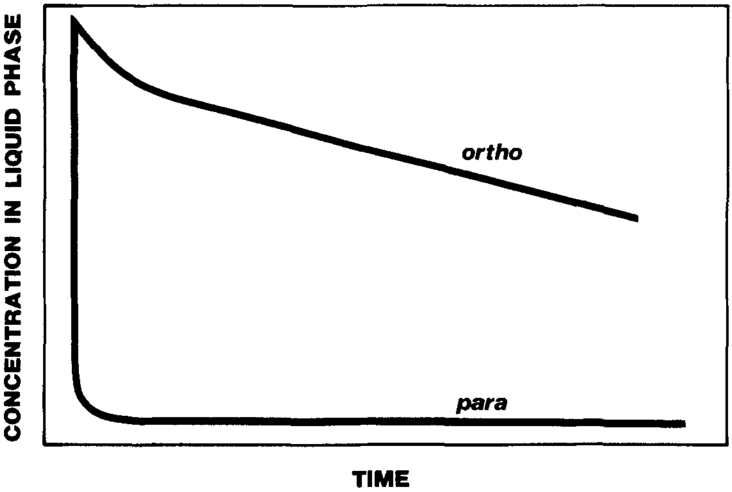

FIG. 3. Rate selective toluidine adsorption.

The final adsorptive mechanism to be discussed is rate selectivity. In this case all components of the mixture have access to the adsorption sites, but differ in the rate at which they are adsorbed. In some instances there may be true equilibrium selectivity as well as rate selectivity. A specific example of this effect occurs in the separation of toluidine isomers on rate selective adsorbents. Figure 3 illustrates the time course of the adsorption of *o*- and *p*-toluidine on such an adsorbent; here, rapid adsorption of *p*-toluidine occurs compared to that of *o*-toluidine. This difference in rate of adsorption may be used as the basis for a chromatographic separation, although in some cases it may prove necessary to adjust adsorbent properties to eliminate such problems as component tailing, particularly of the slowly adsorbed component.

The role of the desorbent is an important one in obtaining a well-behaved system. Clearly the desorbent–adsorbent interaction must be very similar in magnitude to the adsorbate–adsorbent interaction. There are no fixed rules for choice of desorbent, but for most separations it makes sense to try to match the polarity of the adsorbate and the desorbent (*6*). Thus, for paraffin separations, a paraffin desorbent is probably the best choice; for highly polar adsorbates, an alcohol or acid desorbent is probably required. Liquid-phase interactions can also be important, however, and the only way to find the best desorbent is by screening all of the likely compounds.

EXPERIMENTAL RESULTS

In attempting to apply liquid–solid adsorption technology to a particular separation, the best adsorbent/desorbent system must be selected from a large number of candidates. The possibility of large-scale separation can be predicted by a small-scale test. These laboratory tests are run with identical adsorbent, desorbent, and feed as proposed for large-scale use. While the resolution of components may be incomplete by analytical standards, it is sufficient for calculating selectivities. The transient concentration profiles generated in the small laboratory tests correlate well with the steady-state concentration profiles established in a continuous Sorbex plant.

Figures 4, 5, and 6 show laboratory test results for three different aromatic chemical systems (nitrotoluenes, toluidines, and NCB's). These show that successful resolution of the three isomers has been achieved. In the first two cases the feed mixtures contained approximately equal amounts of each isomer. In the case of the chloronitrobenzenes, however, a feed with an equilibrium isomer distribution was used. In this case, complete separation between the *o*-NCB and *p*-NCB isomers was obtained and, in fact, with this degree of separation between all three isomers, it would be possible to obtain all three products at high purity.

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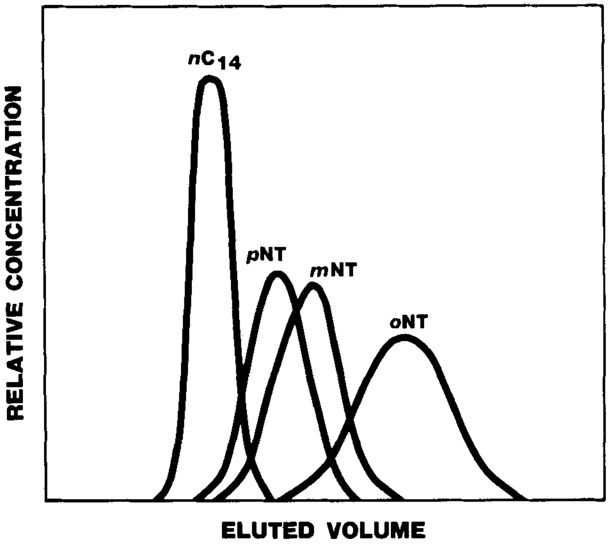

FIG. 4. Laboratory nitrotoluene separation.

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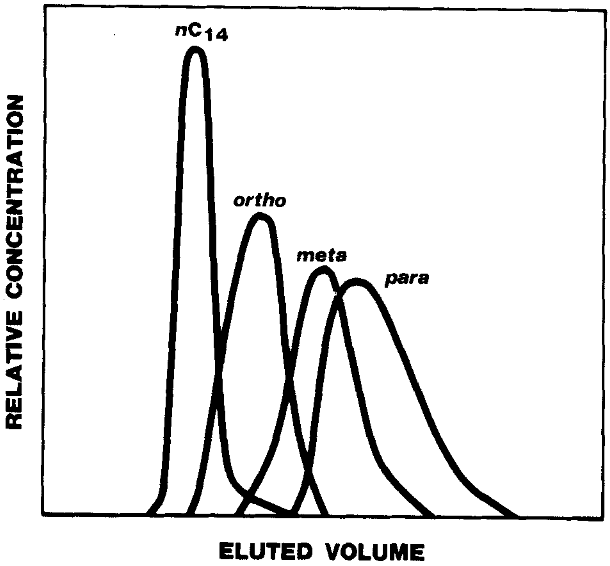

FIG. 5. Laboratory toluidine separation.

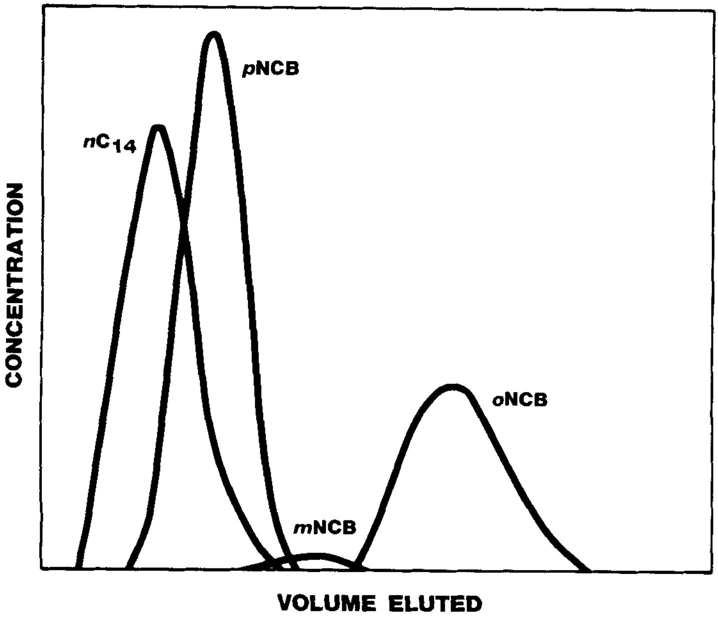

FIG. 6. Laboratory nitrochlorobenzene separation.

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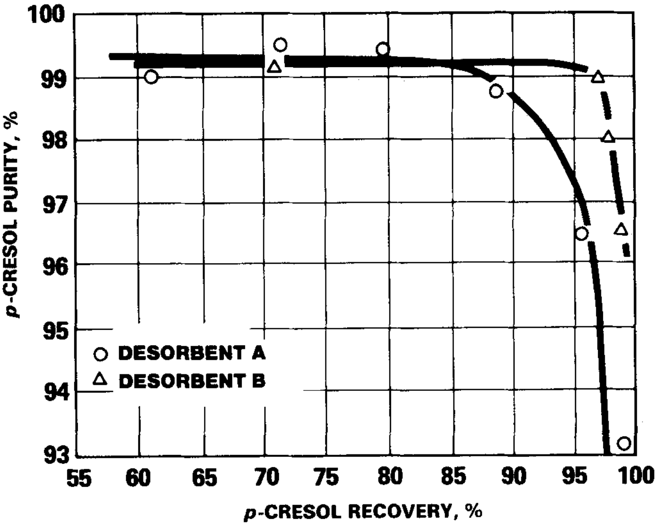

FIG. 7. Performance curves for *p*-cresol extraction.

The next step after laboratory-scale testing is a continuous pilot-plant demonstration. In Fig. 7 Sorbex pilot-plant performance is shown for separation of *p*-cresol from a cresol isomer mixture. Similar performance is obtained, by changes in the plant operating variables, to produce *m*-cresol product. If the cresol feed to the plant is essentially free of the ortho-isomer, then both *m*- and *p*-cresols may be produced simultaneously at high purity. Otherwise, a blocked out operation is required.

As a final example, the pilot-plant separation performance of ethyl toluene (ET) isomers is shown in Table 4. Three separate operations are shown here. In the first operation, the goal is to obtain an extract of high purity *p*-ET. In

TABLE 4
Sorbex Pilot-Plant Performance for Three Ethyltoluene Separations

		p-ET mode[a]		*m*-ET mode[b]		*o*-ET mode[c]	
Component	Feed	Extract	Raffinate	Extract	Raffinate	Extract	Raffinate
o-Ethyltoluene, %	2.6	0.0	3.8	2.5	0.1	65.1	0.0
m-Ethyltoluene, %	60.8	0.5	94.5	2.3	99.1	20.9	62.5
p-Ethyltoluene, %	36.6	99.5	1.7	95.2	0.8	14.0	37.5

[a] *p*-ET mode produces 99.5% *p*-ET extract.
[b] *m*-ET mode produces 99.1% *m*-ET raffinate.
[c] *o*-ET mode produces 100% *p*-ET/*m*-ET raffinate.

TABLE 5
Substituted Aromatic Separations Demonstrated by Adsorption

Mixture	Products			
Xylenes (and EB)	*p*-X	*m*-X	*o*-X	EB
Ethyltoluenes	*p*-ET	*m*-ET	*o*-ET	
Cymenes	*p*-Cymene	*m*-Cymene		
Diisopropylbenzenes	*p*-DIPB	*m*-DIPB		
Cresols and xylenols	*p*-Cresol	*m*-Cresol		Xyl.
Chlorotoluenes	*p*-CT			
Nitrotoluenes	*p*-NT		*o*-NT	
Dichlorobenzenes	*p*-DCB		*o*-DCB	
Nitrochlorobenzenes	*p*-NCB	(*m*-NCB)	*o*-NCB	
Toluidines	*p*-T	*m*-T	*o*-T	
Picolines	γ-P	β-P	α-P	

the second case a high purity *m*-ET raffinate is produced from the same feed. Because of the presence of *o*-ET in the feed in both operations, only one pure product may be obtained at once. In the third operation, the complete removal of *o*-ET from the feed is illustrated. If the raffinate from this operation were then used as feed for the first operation, pure *p*-ET and *m*-ET could both be produced simultaneously.

Other aromatic separations which have been successfully demonstrated in pilot plants, or at the laboratory-scale method, are given in Table 5.

Our commercial experience with substituted aromatic isomer separation comprises licensing a total of 36 separate plants, with a combined production of over 2.7 million metric tons per year.

COMMERCIAL INCENTIVES

Most existing conventional aromatic isomer separations processes based on either fractionation or crystallization are capital intensive, and more importantly, large consumers of utilities, primarily for fractionation. Liquid–solid adsorption processes require desorbent fractionators, but with a judicious choice of desorbent this separation may be achieved readily, with little reflux required. Consequently, the energy input per pound of product can be as much as an order of magnitude less than for more conventional separation techniques. As a result of the milder fractionation conditions, product degradation from prolonged exposure to high temperatures is also eliminated.

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An additional advantage of the adsorptive approach is that, in some cases, several separations may be achieved using the same adsorbent bed. The only difference in some cases is in the choice of desorbent. The ability to make more than one product in the same plant allows a great deal of flexibility in responding to market demands for the desired products.

CONCLUSIONS

The principles of liquid–solid adsorption have been described for the separation of substituted aromatic chemical isomers. This technique is applicable to a wide variety of chemical separations, and the Sorbex process has achieved extensive commercial success. For small-scale separations, simpler process flow schemes are possible.

Adsorbent/desorbent combinations have been identified for many aromatic chemical isomer separations, and a good adsorption system is the basis for an efficient separation. However, it is important to remember that proper engineering scale-up and design are crucial for a workable process. Preliminary evaluation of process economics shows a substantial advantage of adsorptive separations of substituted aromatic isomers over existing process technology. The adsorptive technique is widely applicable, and similarities among the different substituted aromatics mean that one plant could be used to effect several separations in a blocked out mode of operation.

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REFERENCES

1. D. B. Broughton and S. A. Gembicki, *Production Scale Adsorptive Separations of Liquid Mixtures*, Presented at AIChE Diamond Jubilee Meeting, Washington, D.C., October 1983.
2. D. B. Broughton, "Adsorptive Separation—Liquids," in *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 1, 3rd ed., Wiley, New York, 1978.
3. K. L. Dunlap, "Nitrobenzene and Nitrotoluenes," in *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 15, 3rd ed., Wiley, New York, 1978.
4. P. Wu, A. Debebe, and Y. H. Ma, *Adsorption and Diffusion of C_6 and C_8 Hydrocarbons in Silicalite*, Presented at AIChE Orlando Meeting, February 1982.
5. M. Kilpatrick and I. E. Luborsky, "The Base Strengths of Aromatic Hydrocarbons Relative to Hydrofluoric Acid in Anhydrous Hydrofluoric Acid as the Solvent," *J. Am. Chem. Soc.*, 75, 577 (1953).
6. L. R. Snyder, *Principles of Adsorption Chromatography*, Dekker, New York, 1968.