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# SEPARATION OF ETHYLBENZENE FROM MIXED XYLENES BY CONTINUOUS ADSORPTIVE PROCESSING

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## ABSTRACT

Separation of ethylbenzene at high purity from its mixtures with xylenes has been accomplished commercially by superfractionation. Because of the low relative volatility (1.05) between ethylbenzene and para-xylene, this operation is difficult and energy-intensive, requiring the use of several hundred fractionation trays at a reflux/feed ratio of about 18.

To improve economics and reduce energy usage, a process has been developed to accomplish this separation by selective adsorption from the liquid phase onto a solid adsorbent. In this operation, ethylbenzene is separated from the mixed xylenes within the adsorbent bed, and the two products are recovered from the adsorbent by displacement with a liquid of different boiling point, referred to as desorbent. Desorbent is recovered from the net products by distillation and is recycled.

Results of liquid chromatographic tests used to screen various adsorbents are presented. Adsorbents have been developed that show a higher separation factor than the 1.05 existing in distillation, with ethylbenzene being the least strongly adsorbed component.

The process has been demonstrated by operation of a pilot plant in which a simulated moving-bed technique is used to obtain the process characteristics of continuous countercurrent flow of adsorbent and process fluid, without actual movement of solids. Results of these operations are presented.

The adsorptive process requires less than half of the energy input required by superfractionation. An economic comparison of the two operations is presented.

# SEPARATION OF ETHYLBENZENE FROM MIXED XYLENES BY CONTINUOUS ADSORPTIVE PROCESSING

## INTRODUCTION

The three xylene isomers and ethylbenzene, which constitute the eight carbon aromatic system, $C_8A$, are important intermediates in the petrochemical industry. Ethylbenzene and para-xylene, the two most important isomers, are used in the production of styrene and polyester respectively. The other two isomers, ortho- and meta-xylene, are used in the manufacture of various plastics and specialty chemicals. Separation of any one of these isomers from their mixtures into a high purity feedstock for petrochemicals is a very important industrial endeavor. The feedstock is usually obtained by extraction of the $C_8A$ from a petroleum naphtha. All of the separation processes involve consumption of substantial amounts of energy, and processors have much incentive to explore new energy-efficient separation techniques that will conserve high priced fuel and thus improve profit margins in a time of rising feedstock costs.



The $C_8A$ isomers boil at about the same temperature and there are only small volatility differences between them (Table 1). Therefore, the separation of one $C_8A$ isomer from another by superfractionation is difficult, except for ortho-xylene. Simple calculations show that to separate high purity ethylbenzene from

TABLE 1. - Physical Properties of $C_8$ Aromatics

| | Boiling Point °C | Relative Volatility at 138°C |
|---|---|---|
| Ethylbenzene | 136.2 | 1.056 |
| para-Xylene | 138.4 | 1.000 |
| meta-Xylene | 139.1 | 0.981 |
| ortho-Xylene | 144.4 | 0.855 |

the xylenes requires several hundred distillation trays operated at a reflux ratio of about 18. Operation at this high reflux ratio requires large amounts of fuel and coolant as well as a large column diameter to handle the high liquid flows down the column. Thus, superfractionation for ethylbenzene production from mixed $C_8A$ is energy-intensive as well as expensive from an equipment standpoint.

In the last decade, UOP has developed several new separation processes for the $C_8A$ system that are economically more attractive than conventional techniques. These new processes involve adsorption from the liquid phase on a solid adsorbent. The adsorbent is carefully prepared to accentuate the relative strengths of adsorption of the various components of the feed material. The adsorbent exhibits a selectivity difference between the components that is in general more favorable than liquid phase relative volatilities. This selectivity advantage is theorized to be due to the more favorable nature of electronic force fields in solids than in a continuous liquid phase. Thus, an adsorptive process can be more efficient than fractional distillation.



In the case of para-xylene manufacture, the UOP Parex® process is highly applied and offers attractive economic incentives over other technology. Thirteen Parex plants are now on stream worldwide and an additional eleven are in various stages of engineering or construction. The UOP Ebex® process for the separation of ethylbenzene from mixed xylenes utilizes the same general principles as the Parex process. This processing principle is designated Sorbex®.

## THE SORBEX SYSTEM

The Sorbex family of processes involves the separation of a desired component from a given liquid phase mixture by continuous contacting with a solid adsorbent. The system operates in a

manner that simulates the desirable features of a continuous countercurrent multistage operation without actual movement of the solid adsorbent. This is accomplished by use of a unique rotary distributing valve that switches the process flows along a column of adsorbent.

In the general process arrangement (Figure 1), the adsorbent chamber, filled with adsorbent, is fitted with distributors (12 shown) for introduction and removal of process fluid. Lines from the distributor connect the adsorbent beds to the inlet (feed and desorbent) and outlet (extract and raffinate) process streams through the rotary valve. The rotary valve is programmed to switch the four process streams down the system of distributors. Liquid in the adsorbent chamber is circulated in the direction in which the four process streams are switched. Moving the process streams past the fixed solid adsorbent produces all the process aspects of moving the solid past fixed positions of the process



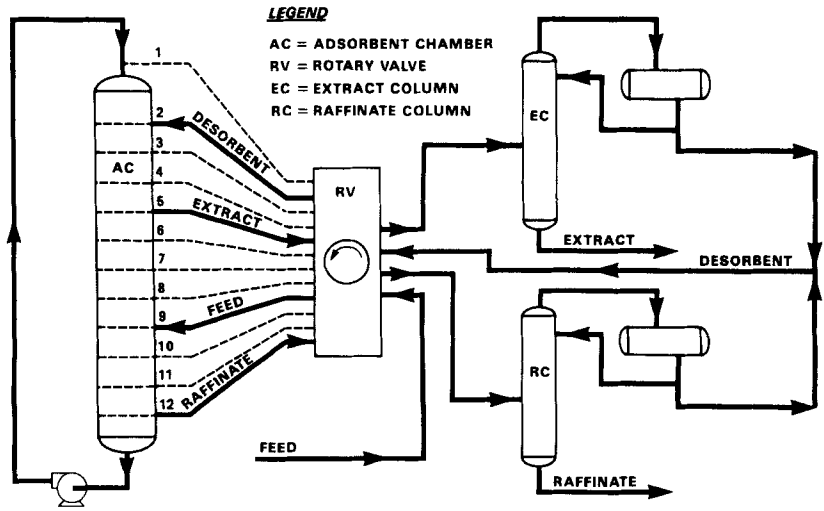


FIGURE 1. Sorbex - Simulated Moving Bed for Adsorptive Separation

streams. The system can then be visualized as if the solid were moving up the chamber countercurrently to the downward-flowing liquid.

The extract and the raffinate are each sent to respective fractionators wherein the extracted and rejected feed components are separated from the desorbent. The desorbent is recirculated to the adsorbent chamber.

The process flow for a hypothetical two component system is depicted in Figure 2. In a "rejective" system like Ebex, B, the least strongly adsorbed component is to be produced in high purity by separation from A, the more strongly adsorbed component. The points of introduction and removal of the four process streams effectively divide the adsorber into four separate zones, each of which has a unique function. For discussion purposes, it is easiest to assume that the solids move in the chamber, although in fact they are fixed.



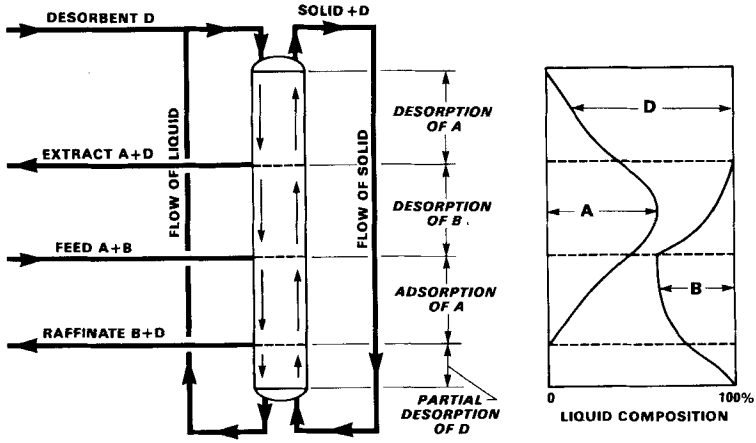


FIGURE 2. Adsorptive Separation with Moving Bed

A schematic profile of the liquid phase composition is also shown in Figure 2. This profile moves through the bed as the valve rotates, but it is fixed with respect to the location of the four process streams. In general, the liquid flow rates in the four zones are not equal. The regulation of the liquid flow rates in the four zones can be used to enhance the separation of B from A.

There are many advantages to the Sorbex system over moving bed adsorptive separations or batch adsorption operation. The Sorbex system is designed to operate with essentially plug flow of liquid past small adsorbent particles. This produces excellent contacting with many available mass transfer stages and an almost total lack of channeling. Calculations have shown that, for a separation of moderate difficulty, compared to the same separation by batch adsorption operation, Sorbex requires 1/4 the adsorbent and 1/2 the desorbent circulation. This is primarily because in the Sorbex system all of the adsorbent is in active use all of the time, whereas in a batch system there is a considerable amount of adsorbent that is inactive, waiting for the next cycle.



## PROCESS DEVELOPMENT

In general, after a given separation has been shown economically attractive, process development proceeds in three steps.

First, suitable adsorbent/desorbent combinations are developed in small, bench-scale batch equipment. These are then tested in a small, continuous pilot plant to find the best adsorbent/desorbent combination and to develop preliminary operating variables. Finally, after the best combination has been found from the first two steps, the system is tested in another pilot plant wherein the detailed process variables are developed using feedstock and adsorbent that are representative of commercial operation.

Adsorbent/Desorbent Selection

The initial step in the development of a Sorbex separation process is to find an adsorbent/desorbent system that will effectively carry out the desired separation. The technique used is to screen candidate adsorbents under operating conditions that are in line with those used in the Sorbex process. Also, the adsorbents tested are those that are used in the commercial unit.

The equipment used for the test for the separation of ethylbenzene from a $C_8A$ mixture is shown schematically in Figure 3. The adsorbent test column is a small diameter stainless steel coiled tube. The test is carried out at the proper temperature which is maintained by enclosing the column in a thermostated compartment. To ensure that the test is carried out in the liquid phase the entire system is operated at a pressure sufficient to prevent vaporization of the desorbent and feed at the desired test temperature.



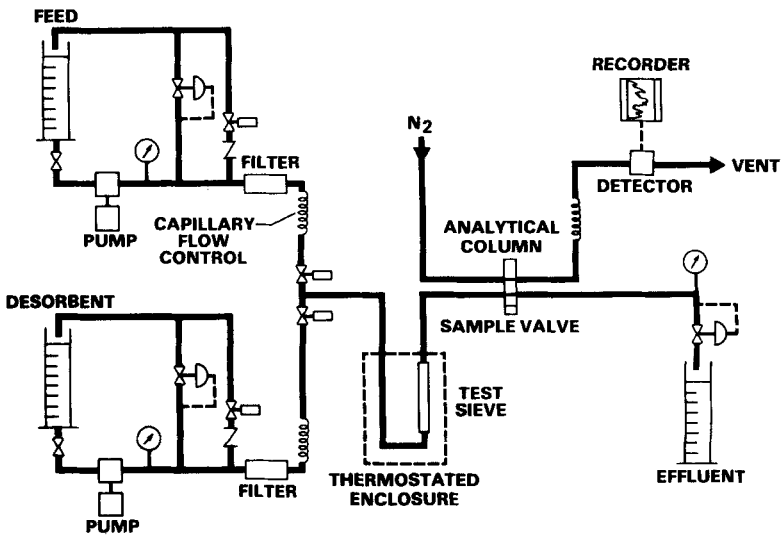


FIGURE 3. Test Unit

Both feed and desorbent can be pumped to the test column under capillary flow control as shown in Figure 3. Initially desorbent is pumped at a rate to line out the equipment. At some convenient time the desorbent is stopped and the feed is then run into the test column. Immediately after the feed injection is completed the desorbent flow is resumed.

As shown in Figure 3, the effluent stream is sampled and analyzed automatically by means of the on-stream GC analyzer. Each sample injection is displayed as a series of peaks corresponding to the components that are present in the effluent at the time of injection. A concentration profile of each of the feed components versus the effluent volume is established by joining the respective peak maxima of each component. The composite plot resembles a chromatogram of the component peaks obtained from an analytical column of poor resolving power.



Figure 4 is a schematic representation of a test. For simplicity, the example illustrated is for a binary mixture of two adsorbed species A and B and a non-absorbed species which serves as a tracer. The net retention volumes of components A and B are measured from the center of the peak envelope of the tracer to the respective centers of the component peak envelopes. The ratio of the net retention volumes is related to the selectivity of the adsorbent for the more strongly adsorbed component (larger net retention volume) with respect to the less strongly adsorbed component (smaller net retention volume).

The peak envelope widths at half peak height give some indication of the mass transfer rates. This indication of mass transfer rates is more of a qualitative than a quantitative concept, and is more useful when comparing the performance of one adsorbent to that of another.

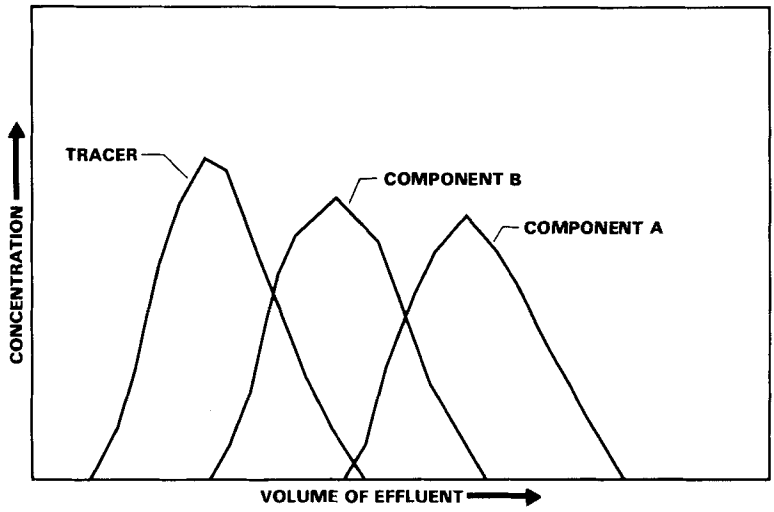


FIGURE 4. Schematic Representation of Two Component Test



## ETHYLBENZENE SEPARATION

Generally in the Sorbex process the desired compound or class of compounds separated from a mixture is recovered in the extract and the rest of the mixture is rejected into the raffinate. Thus, the adsorbent is selective for the desired compound or class of compounds. However, in the case of the separation of ethylbenzene from the xylenes, the desired product, ethylbenzene, is rejected into the raffinate and the mixture of xylenes is extracted. Although an adsorbent/desorbent system has been found that is selective for ethylbenzene with respect to the xylenes, the limiting selectivity for this system is rather low and would require a large inventory of adsorbent to carry out an effective separation. This is in contrast to rather high limiting selectivities that are provided by many adsorbents that reject the ethylbenzene and extract the mixed xylenes.

In a Sorbex system, all non-adsorbed material present in the feed is rejected into the raffinate. This material will contaminate the ethylbenzene product in the Ebex process. Another characteristic of Ebex is that if the ethylbenzene is a minor component of the $C_8A$ mixture the larger portion of the feed must be extracted. Thus, for a given quantity of ethylbenzene separated, a larger inventory of adsorbent is required than if the ethylbenzene were selectively extracted at comparable selectivity values. Under these conditions use of the low selectivity extractive system mentioned earlier may be the preferred system.

The results obtained with an adsorbent that is selective for the xylenes and rejects the ethylbenzene are illustrated in Figure 5. The data from this test indicate that the limiting selectivity, i.e., para-xylene/ethylbenzene, and the mass transfer rates as indicated by the peak envelope widths qualify the adsorbent and desorbent as good candidates for use in the Ebex process. In contrast, the data illustrated in Figure 6 clearly show that



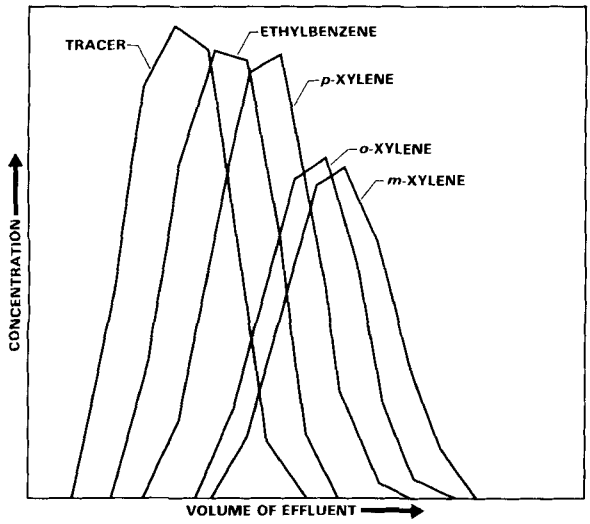


FIGURE 5. Test of Adsorbent Showing Good Selectivities and Rates for Ethylbenzene Separation

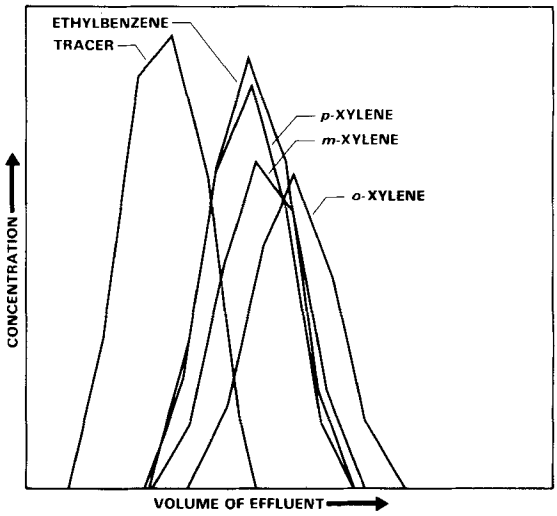


FIGURE 6. Test of Adsorbent Showing Poor Selectivity for Ethylbenzene Separation



this adsorbent/desorbent combination would be totally ineffective for this separation because of the lack of selectivity for the xylenes with respect to ethylbenzene.

The data illustrated in Figure 7 are an example of an adsorbent/desorbent combination that is marginally acceptable for use in the Ebex process. Although this system has a high value for the limiting para-xylene/ethylbenzene selectivity, the mass transfer rates as manifested by the broad peak envelope width and the extensive "tailing" of the meta-xylene would probably cause problems in the Ebex process. An excessively high desorbent flow rate would be required to obtain complete desorption. Incomplete desorption of meta-xylene in the desorption zone would result in contamination of the ethylbenzene in the desorption raffinate since the remaining meta-xylene would be completely desorbed in the adsorption zone. The high desorbent rate requirement would reduce the overall efficiency of the separation process.

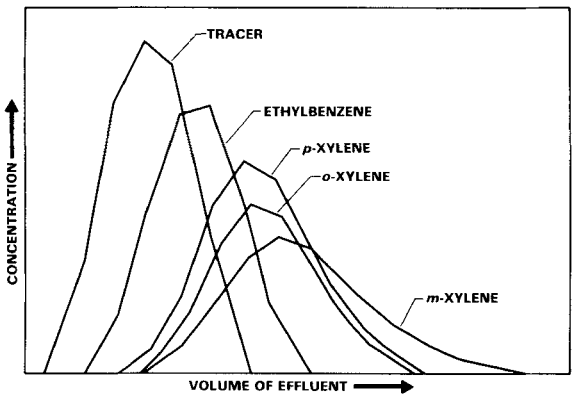


FIGURE 7. Test of Adsorbent Having High Selectivity but Poor Rates for Ethylbenzene Separation



## PRELIMINARY PROCESS STUDIES

When the adsorbent and desorbent whose selectivity test is shown in Figure 5 were tested in a small continuous Sorbex pilot plant, the performance was well below expectations. Although high purity ethylbenzene could be obtained, the yield was only about 30%. Any increase in the yield resulted in a substantial loss of purity. Also, at the high yield and low purity the only impurity in the ethylbenzene was para-xylene. When high purity ethylbenzene was obtained through a reduction of the reflux rate in the desorption zone, a considerable amount of the ethylbenzene was carried into the extract, reducing the yield to a low value. This type of operation indicates that the selectivity for the desorbent with respect to para-xylene is greater than 1. Selectivity measurements carried out in the laboratory with the adsorbent indicated that this was indeed the case.

From the results of these tests it was found that the selectivity of the chosen adsorbent for the $C_8$ aromatics and desorbent followed the order meta-xylene > ortho-xylene > desorbent > para-xylene > ethylbenzene. It was further concluded that for optimum

performance for this type of Sorbex process, the selectivity for the desorbent and para-xylene should be reversed, i.e., para-xylene > desorbent > ethylbenzene. Under these conditions all of the xylenes can be extracted as a class and the ethylbenzene cleanly rejected into the raffinate.

The selectivity test of an adsorbent/desorbent combination that meets these requirements is illustrated in Figure 8. This system performed well when tested in the small Sorbex pilot plant. Perhaps the most conspicious difference between the selectivity test of this adsorbent and that of Figure 5 is the small difference in the selectivity values for the three xylenes with respect to ethylbenzene, especially for those of meta and para-xylene. Unfortunately, the selectivity for para-xylene with respect to the desorbent cannot be determined directly from the test and must be determined by means of another method. The selectivity of para-xylene/desorbent was found to be greater than unity. Consequently, the selectivities of the $C_8$ aromatics and



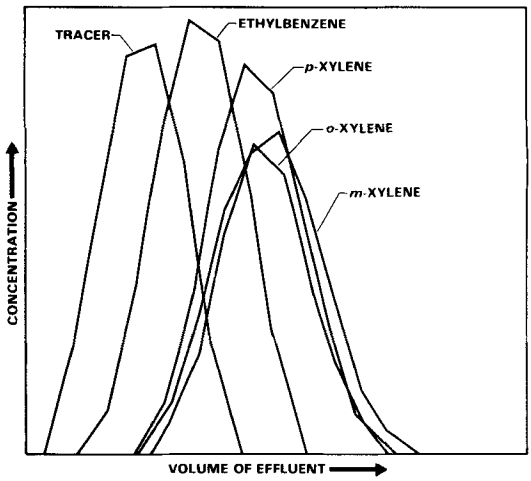


FIGURE 8. Test of Adsorbent That Gave Best Performance in the Sorbex Process for Ethylbenzene Separation

desorbent on this adsorbent followed the desired order of meta-xylene > ortho-xylene > para-xylene > desorbent > ethylbenzene.

## PROCESS VARIABLE STUDIES

The purpose of this third stage of development was to accumulate data necessary for the design of a commercial Ebex unit. To accomplish this it was necessary to operate a continuous pilot plant using a commercial feedstock and to find the best values of the process variables.

Two feedstock samples of widely different composition were obtained from a commercial source of mixed $C_8A$ isomers. Feedstock A contained about 50% ethylbenzene and about 20% para-xylene + ortho-xylene. Feedstock B contained about 25% ethylbenzene and about 30% para-xylene + ortho-xylene. The critical selectivity is between ethylbenzene and para-xylene + ortho-xylene and so the separation with feedstock B is more difficult.



The adsorbent was prepared in a manner such that the sample loaded into the pilot plant would be representative of a commercially prepared material. Although relatively small in size, the pilot plant can closely simulate operation of a larger diameter plant. This is because the diameter of the adsorbent particles is small compared to the diameter and depth of the adsorbent beds in the pilot plant. Thus, wall and end effects are minimal and plug flow is closely approached. Larger commercial units can be visualized then as merely a collection of small pilot plant beds operating in parallel. Indeed, these small pilot plants have been used extensively in the development of other commercial Sorbex processes.

The performance of the pilot plant was excellent. Purities of better than 99.5 wt-% ethylbenzene were obtained at over 99 wt-% recovery of the feed ethylbenzene in the raffinate. The

separation of the ethylbenzene from the xylenes was almost complete. Small amounts of non-aromatics species present in the feed remained as impurities in the ethylbenzene product. The results were equally good with either feedstock.

Figure 9 is a typical steady state liquid composition profile measured in the pilot plant. In this case the purity was 99.5 wt-% ethylbenzene with 99.7 wt-% of the ethylbenzene in the feed recovered in the raffinate. The feedstock contained 50 wt-% ethylbenzene. The profiles show efficient adsorption of the xylenes in the adsorption zone as shown by the drop in xylenes concentration at the top of the zone. The desorption of the ethylbenzene in the desorption zone proceeds almost to completion without significantly affecting the xylenes. In the desorption



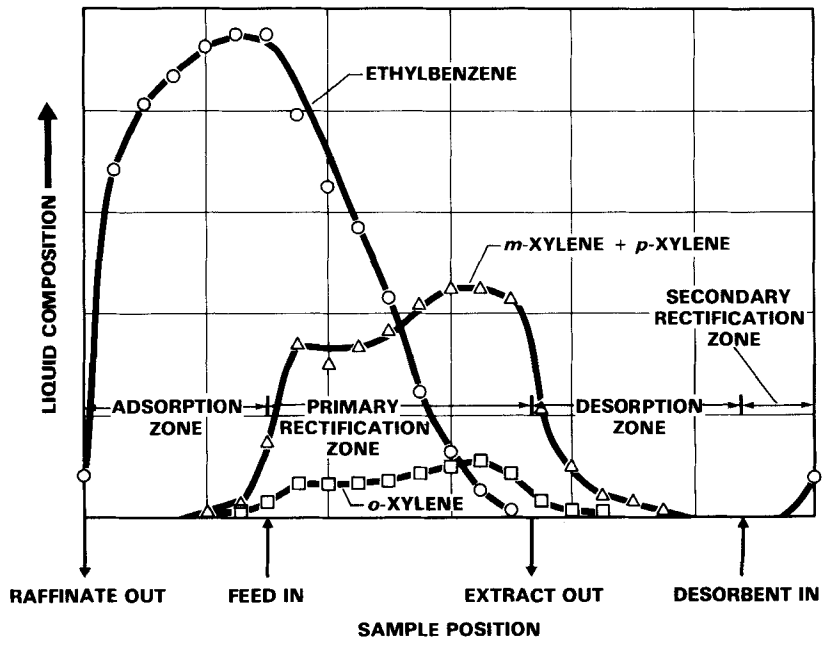


FIGURE 9. Steady State Column Concentration Profiles for Ebex Pilot Plant

zone the xylenes are desorbed completely by the time that the desorbent point is reached. Thus, there is no carryover of xylenes into the secondary rectification zone where they might contaminate the raffinate. In addition, the ethylbenzene concentration in the secondary rectification zone drops rapidly and it can be seen that there is no ethylbenzene carryover in the liquid into the desorption zone and thus no loss of recovery by this route. In summary, the liquid flows in the zones are close to optimal in this case.

## ENERGY CONSIDERATION

An economic comparison has been made between Ebex and superfractionation for production of high purity ethylbenzene from mixed xylenes. The basis is an extracted $C_8A$ feedstock containing 25% ethylbenzene. Superfractionation requires about 33% more

TABLE 2. - Comparison of Ebex and Superfractionation

| | | Ebex | | Superfractionation | |
|---|---|---|---|---|---|
| I. | Feedstock | BPSD | MM Lb/Yr | BPSD | MM Lb/Yr |
| | Ethylbenzene | 1250 | 129.5 | 1250 | 129.5 |
| | Xylenes | 3750 | 388.5 | 3750 | 388.5 |
| | Total | 5000 | 518.0 | 5000 | 518.0 |
| | EB Product (99.7%) | 1191 | 123.4 | 1128 | 116.9 |
| | EB Recovery, Wt-% | | 95.3 | | 90.3 |
| II. | Capital Investment (MM$) | | | | |
| | Total | | 16.4 | | 22.0 |
| III. | Utilities (MM$/Yr) | | | | |
| | Fuel Fired (at $2.50/MM Btu) | | 1.82 | | 5.13 |
| | Steam, 150 psig (at $3.00/M lb) | | 0.22 | | |
| | Power (at 3¢/kWh) | | 0.18 | | 0.26 |
| | Total | | 2.22 | | 5.39 |
| | Utility Cost, ¢/lb EB | | 1.8 | | 4.6 |

capital investment than Ebex for this case. The utility savings for Ebex are even more dramatic, as shown in Table 2. The bulk of the utilities requirements is for fuel for fired heaters used on fractionator reboilers. In the case of superfractionation this requirement is much greater than for Ebex. This is because of the high reflux ratio necessary in superfractionation. In the case of Ebex, although two fractionation columns are needed to separate the desorbent from the $C_8A$ in the extract and raffinate, the desorbent has a much lower boiling point than the $C_8A$'s. The relative volatility difference between desorbent and the $C_8A$'s is substantial and so the reflux rate in either Ebex column is of the order of 1, whereas in superfractionation the reflux ratio is of the order of 18.