

PATENT SPECIFICATION

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(54) ADSORPTION PROCESS FOR SEPARATING PARA-XYLENE FROM MIXTURES OF C₈ AROMATIC HYDROCARBONS

(71) We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Ten UOP Plaza, Algonquin & Mt. Prospect Roads, Des Plaines, Illinois, 60016, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the separation of para-xylene from a mixture of C₈ aromatic hydrocarbons using a solid crystalline aluminosilicate adsorbent which selectively removes para-xylene from the feed. The selectively absorbed para-xylene is then recovered from the adsorbent through a desorption step with a desorbent.

It is known in the separation art that certain adsorbents, generally comprising crystalline aluminosilicates, can separate certain hydrocarbons from mixtures thereof. It is generally recognized that certain crystalline aluminosilicates containing selected cations at the cationic sites within the zeolite enhance the selectivity of the zeolite for given C₈ aromatic hydrocarbon.

In selecting a desorbent for use in a C₈ aromatic hydrocarbon separation process it is necessary that a desorbent material be able to displace the selectively adsorbed C₈ aromatic from the feed so that the selectively adsorbed aromatic can be recovered from the adsorbent, and thereafter separated from the desorbent, as a relatively rich product. In certain processes iso-thermal and isobaric operations are used. Then the desorption step is generally carried out with a desorbent material which can physically displace the adsorbed feed components from the adsorbent.

In C₈ aromatic separation processes in which the displacement technique is used, the

desorbent material must be able to displace adsorbed feed hydrocarbons. The desorbent itself must also be displaceable by the selectively adsorbed components of the feed stock so that the adsorbent may be continuously used. Generally, the hydrocarbons used in the past as desorbent materials for xylenes were aromatic hydrocarbons. Aromatic desorbents were able to displace the C₈ aromatic hydrocarbons from the zeolitic type adsorbents. Paraffins and naphthenes were generally not able to desorb adsorbed C₈ aromatics from the zeolite adsorbents and consequently were not used as desorbents but were at times included in a desorbent as an inert diluent.

The desorbents used generally fall into two categories, namely, desorbents having boiling points lower than feed components and higher than feed components. To separate desorbent from desorbed feed stock components fractionation techniques are generally used so boiling points must differ to allow a separation by fractionation.

Higher boiling desorbents are generally used when an adsorptive separation unit is coupled with an isomerization unit. The isomerization forms naphthene components which boil within the boiling range of toluene and eventually contaminate the desorbent.

With desorbents which boil at temperatures higher than the feed stock, the desorbent boiling point should not be so high as to require excessive temperatures in the fractionation facility. Further, higher molecular weight materials are adsorbed and desorbed from zeolites at slower rates than the lower molecular weight materials so a higher operating temperature is needed in the adsorbent bed to increase the rate of adsorption and desorption. If the desorbent has a boiling point only a little higher than any component in the feed stock no increase in operating temperature is needed.

[Price 25p]

Price 75p

Certain higher molecular weight desorbents are superior to others. The higher boiling aromatic components which can be used for desorbents include aromatics having up to 10 carbon atoms per molecules. These desorbents include those selected from the group of isopropylbenzene, n-propylbenzene, 1-methyl-3-EB (ethylbenzene), 1-methyl-4-EB, 1,3,5-trimethylbenzene, 1-methyl-2-EB, tert-butylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1-methyl-3-propylbenzene, 1,2-DEB (diethylbenzene), 1,3-DEB, 1,4-DEB, 1-methyl-2-propylbenzene, 1,4-dimethyl-2-EB, 1,3-dimethyl-4-EB, 1,2-dimethyl-3-EB, 1,2,4,5-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,3,4-tetrahydronaphthalene and naphthalene. Of all of the aromatic desorbent materials mentioned above, it has now been found that the DEB (diethylbenzene) materials allow the best desorbent operations and do not substantially adversely affect competitive adsorption which takes place between feed components and desorbent. Of the DEB's disclosed, it has now been discovered that p-DEB (para-diethylbenzene) is the best desorbent.

It is known that benzene and toluene are substantially equivalent desorbents in equilibrium adsorptive operations. The same holds for DEB's and many of the other aromatic components described above. However, in operations characterized as non-equilibrium there is a distinct advantage in using para-diethylbenzene as an essential desorbent component.

In equilibrium adsorption a feed stream, which does not contain any desorbent material, is passed through a zeolitic adsorbent bed until the effluent stream composition is the same as the feed. A desorbent of higher boiling point than the feed mixture is then passed through the bed of adsorbent to displace the selectively adsorbed components of the feed. There is no desorbent in contact with adsorbent when the adsorbent step is completed as any desorbent present on the adsorbent has been displaced by feed components.

In continuous simulated or actual counter-current liquid flow systems there are zones with a simultaneous contacting of adsorbent, during adsorption, with a mixture comprising desorbent and feed. There is a competitive adsorption of both desorbent and the selectively adsorbed component of the feed.

In most continuous countercurrent solid-fluid separation process, the solid adsorbent contacts the feed mixture in an adsorption zone. The feed and solid adsorbent countercurrently contact each other with the adsorbent passing out of the adsorption zone containing the selectively adsorbed component

of the feed, and some desorbent, within the adsorbent. The solid adsorbent is eventually contacted with desorbent in a desorption zone. The desorbent displaces a selectively adsorbed component of the feed from the adsorbent and allows a mixture of desorbent and a selectively adsorbed component of the feed to be removed from the process as an extract stream. The extract stream passes to a separation means wherein the desorbent is separated, giving an enriched stream of the selectively adsorbed component of the feed. The adsorbent, after being contacted with the desorbent in the desorption zone, continues to flow counter current to the fluid flow and is recontacted with additional feed in the adsorption zone. Between the adsorption zone and desorption zone are located the flushing or rectification zones which by carefully controlled pressure drops and liquid flow prevent the raffinate and extract streams from contaminating each other. In the void spaces between adsorbent particles are flushed out, in the one case residual desorbent being flushed out in preparation for raffinate withdrawal, and in the other case residual feed mixture being flushed in preparation for withdrawal of desorbent plus selectively adsorbed component. The desorbent, which contacts the adsorbent in the adsorption zone, causes competitive adsorption between desorbent and adsorbed feed components. Thus the desorbent can affect selectivity of the adsorbent.

It has now been found that by using a desorbent containing para-diethylbenzene adsorption of feed components takes place with high selectivity and efficiency.

According to the present invention there is provided in a process for separating para-xylene from a mixture of C_8 aromatic hydrocarbons using a crystalline aluminosilicate adsorbent containing a selected cation or cations, which process comprises the steps of: (i) contacting said adsorbent with said mixture of C_8 aromatic hydrocarbons and thereby selectively adsorbing para-xylene under non-equilibrium conditions while simultaneously removing from the adsorbent a raffinate which comprises the less selectively adsorbed C_8 aromatics; (ii) contacting said adsorbent with a desorbent and thereby displacing said para-xylene from said adsorbent while simultaneously removing an extract comprising desorbent and para-xylene from said adsorbent; the improvement which comprises using a desorbent containing para-diethylbenzene.

In adsorptive-separation processes an important factor used to determine the ability of a particular adsorbent to separate components of a feed mixture is the selectivity (B) of the adsorbent for one component as compared to another component. Expressed in equation form, selectivity is shown in Equation 1 below,

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$$\text{Selectivity} = B_{x/y} = \frac{[\text{Vol.}\%x/\text{vol}\%y]a}{[\text{Vol.}\%x/\text{vol}\%y]u} \quad (1)$$

x and y are two components of the feed represented in volume percent and subscripts a and u represent the adsorbed and unadsorbed phases respectively. Selectivity is measured at equilibrium, when the feed passing over the bed of adsorbent does not change composition after contacting the adsorbent.

As the selectivity becomes less than or greater than unity there is a preferential selectivity by the adsorbent of one component as compared to another.

Less-than-equilibrium or non-equilibrium adsorption conditions refer to an operation in which desorbent remains within the adsorbent while the feed is being adsorbed. Non-equilibrium conditions occur when contacting an adsorbent with a feed which contains desorbent or by contacting an adsorbent which contains desorbent with a feed stream and only displacing a portion of the desorbent from the adsorbent.

When a hydrocarbon stream, is contacted with a molecular sieve adsorbent at less than equilibrium conditions, a desorbent containing p-DEB must be used to prevent adsorbent selectivities from being substantially reduced when using a desorbent material having a higher boiling point than any of the feed components.

The effects of the correct choice of a desorbent is readily noticed in a continuous countercurrent simulated moving bed process with non-equilibrium adsorptive conditions.

To reduce the contamination of extract and raffinate streams a desorbent is used as a flushing or rectification material between the adsorption and desorption zones. In countercurrent flow processes the solid is first contacted with the feed in an adsorption zone, then the solid is removed and contacted in a rectification or flushing zone with a liquid generally comprising desorbent, to remove any feed mixture from between the particles of adsorbent. The solid, after leaving the rectification or flushing zone, then contains substantially no unadsorbed feed mixture, but does of course contain the desorbent and the selectively adsorbed component of the feed. The solid is then passed into a desorption zone where the adsorbent is contacted with desorbent which displaces the selectively adsorbed component of the feed from the adsorbent and allows recovery of an extract stream comprising desorbent and the selectively adsorbed component of the feed. The solid leaving the desorption zone contains only pure desorbent and after leaving the desorption zone passes into a second rectification or flushing zone in which the adsorbent is contacted with raffinate from the next

adsorption zone to displace desorbent from between the particles of adsorbent. The desorbent displaced is passed into the desorption zone to reduce the quantity of desorbent needed in the process. The adsorbent is then passed into an adsorption zone where the feed contacts the adsorbent and the entire cycle described above is repeated.

In such countercurrent flow operations there is generally no equilibrium adsorption taking place. This is because a quantity of desorbent is generally present within the molecular sieve adsorbent when feed is contacting the adsorbent. The feed is not able to totally remove the desorbent from the adsorbent. Consequently, the effects of desorbent on the selectivity of the adsorbent become pronounced and require selection of a desorbent which does not adversely alter the adsorbent's ability to retain or selectively adsorb a given component of the feed.

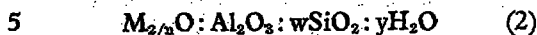
The C_6 aromatic hydrocarbons which can be used in the feed streams of the adsorptive separation process contemplated herein include ortho-xylene, meta-xylene, para-xylene and ethylbenzene. Other materials that may be included in the feed stream, but which are not necessarily detrimental include relatively small amounts of paraffins, olefins, naphthenes and other hydrocarbons possibly found in C_6 aromatic streams.

Adsorption conditions include temperatures of from 30 to 350°C. preferably 40 to 250°C. and pressures of atmospheric to 42 atm (600 psig) preferably atmospheric to 28 atm (400 psig). Both liquid phase and vapor phase operations can be used in the adsorption step; however, liquid phase operation is preferred to reduce operating temperature. Desorption conditions are similar but desorption can take place with either a reduction of pressure or increase in temperature, or both. Preferably, desorption and adsorption take place at the same temperature and in liquid phase.

The process of this invention contemplates that both the raffinate and extract stream can be passed into respective fractionating facilities in which the extract can be separated into relatively pure desorbent and relatively pure selectively adsorbed feed component stream. The raffinate stream can similarly be passed into a fractionation facility in which the raffinate material can be separated into a concentrated stream of desorbent and a stream of the less selectively retained feed components. The relatively purified desorbent from both the raffinate and extract streams can be reused in the process of this invention. The raffinate stream can if desired be passed into an isomerization zone to produce more of the selectively adsorbed component.

Adsorbents which can be used in the process of this invention are generally referred to as the crystalline aluminosilicate zeolites or molecular sieves and can comprise both

the natural and synthetic aluminosilicates. In a hydrated form the crystalline aluminosilicate is represented by the formula in equation 2 below:



where M is a cation which balances the electrovalence of the tetrahedra and is generally referred to as an exchangeable cationic site, n represents the valence of the cation, w represents the moles of SiO_2 , and y the moles of water. The cations may be any one of a number of cations.

Preferred molecular sieves are type X zeolite and type Y zeolite.

15 Adsorbents contemplated herein include not only the sodium form of the type X or Y but also crystalline materials obtained from such a zeolite by partial or complete replacement of the sodium cations with other cations.

20 The cations which may be placed upon crystalline aluminosilicate adsorbents include cations selected from the Groups IA, IIA, and IB metals. The specific cations which show a preferred selectivity for para-xylene with respect to EB include lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium, silver, manganese, cadmium, and copper. These cations could be used in an adsorptive separation process in which only p-X and EB are to be separated. The following combination of cations are particularly well suited for p-X and EB separation: potassium and barium, potassium and beryllium, potassium and magnesium, rubidium and barium, cesium and barium, copper and cadmium, copper and silver, zinc and silver, and copper and potassium.

40 Cations which show a preferred selectivity of p-X to m-X include potassium, barium, sodium, silver, alone or in combination, along with certain cation pairs including potassium and barium, potassium and beryllium, potassium and magnesium, potassium and rubidium, cesium and cesium, barium and rubidium, cesium and barium, and copper and potassium.

50 In general m-X and o-X behave similarly indicating that a sieve selective for p-X with respect to m-X would be as selective for p-X with respect to o-X. Therefore, for a p-X and o-X mixture, the above cation and cation pairs, disclosed for p-X to m-X selectivity could be used.

55 If EB is present either with m-X or o-X, the sieve should be able to separate p-X from EB, m-X, and o-X. If a single cation is used in the zeolite adsorbent, potassium, barium,

sodium and silver all show a preferential selectivity of p-X with respect to EB, m-X, and o-X. The cations recited above could also be used in combination since independently they all show a p-X selectivity as compared to all of the xylene isomers and EB.

Of course the ion-exchange step may not exchange 100% of the available cation sites, so that a small amount of cation originally on the sieve may remain on the sieve after ion exchange without great adverse effect.

The mechanics of the ion-exchange procedure are well known to those skilled in the art and need not be discussed in detail.

The desorbents which are used in the process of this invention contain p-DEB optionally together with m-DEB and o-DEB, and with small quantities of the butylbenzenes. It is preferable to use a desorbent which contains essentially p-DEB as a desorbing component of the desorbent. The concentration of p-DEB, when used as the sole DEB present in the desorbent, may vary from a few percent up to 100 LV% (liquid volume percent) of the desorbent preferably from 10 to 60 LV% and more preferable from 30 to 50 LV%. When mixed DEB's are used in a desorbent they may be present in an undiluted form and would typically contain about 60 LV% m-DEB, 7LV% o-DEB, and 26 LV% p-DEB along with approximately 7 LV% of butylbenzenes. The diluents which may be used with a desorbent include saturated hydrocarbons, including the paraffinic hydrocarbons and cyclo-paraffins, and additional the carbo-cyclic ring compounds. Typically, the diluent materials from the saturated paraffin group consist of the straight or branched chain paraffins having from 4 to 20 carbon atoms per molecule and preferably 4 to 10 carbon atoms per molecule. Cyclo-paraffins used can include cyclo-hexane, cyclo-pentanes, and branched derivatives thereof. Additional carbo-cyclic ring compounds including decalin and decalin derivatives containing branched chains may be used and are preferred diluents.

EXAMPLE I.

In this example non-equilibrium adsorption conditions were used during adsorption using a desorbent which contained p-DEB. In some instances the desorbent was p-DEB diluted in decahydronaphthalene or in iso-octane. In other instances a desorbent was used which contained p-DEB along with other DEB isomers and butylbenzene. Table I below shows the various desorbent compositions used in this example.

TABLE I

Desorbent Analysis

Desorbent Type	D	E	F
Components, LV%			
Meta-diethylbenzene	60.4		
Ortho-diethylbenzene	7.4		
Para-diethylbenzene	25.6	10.0	10.0
Butylbenzenes	6.6		
Decahydronaphthalene			90.0
Iso-octane		90.0	
	100.0	100.0	100.0

5 The equipment was used for testing the adsorbent and various desorbents was an adsorbent chamber containing approximately 70 cc of adsorbent in a 1.8 m (six-foot) long column of 0.94 cm (three-eighths inch) outside diameter copper tube. The copper column was maintained at a temperature of approximately 150°C. Gas chromatographic analysis equipment was attached to the effluent lines of the adsorbent chamber to determine its effluent composition. With flow rates and compositions known, it was possible to determine the selectivity, as defined in equation 1 above, for any two of given components.

15 The desorbent was run continuously at a nominal 1 liquid hourly space velocity (LHSV) or volume per hour of liquid feed per volume of adsorbent which amounted to about 1.17 cc per minute feed rate of desorbent. Desorbent flow is stopped and the feed is run for a ten-minute interval at 1

LHSV. Desorbent flow is then resumed at 1 LHSV and continued until all of the feed C₈ aromatics have been eluted from the column. 25

Three separate feeds were used. The feed stocks contained various quantities of individual desorbents. The three feed stocks are shown in Table II below. Feed stock B was used to show if density differences, found to have adverse effects upon the separation when using feed stock A, could be eliminated by using a diluent which more closely resembled the density of the C₈ aromatic feed stocks and the p-DEB desorbent. 30 35

Feed stock C contained a distribution of DEB isomers plus other C₁₀ materials.

Normal nonane was used in the chromatographic analyses as a tracer to determine when the elution of the feed stock had begun. The normal nonane had no adverse or beneficial affects towards the selectivity or flow rates. 40

TABLE II

Feed Stock Analysis

Feed Stock	A	B	C
Component, LV%			
Para-xylene	5.0	5.0	5.0
Meta-xylene	5.0	5.0	5.0
Ortho-xylene	5.0	5.0	5.0
Ethylbenzene	5.0	5.0	5.0
Normal-Nonane	5.0	5.0	5.0
Iso-octane	67.5		
Decahydronaphthalene		67.5	
Para-diethylbenzene	7.5	7.5	19.2
Meta-diethylbenzene			45.2
Ortho-diethylbenzene			5.6
Iso-butyl-benzene			2.2
Sec-butyl-benzene			2.8
	100.0	100.0	100.0

Four different adsorbents were used. All were type X zeolites and contained both barium and potassium cations as the exchanged cations present upon the zeolite. The major differences in the zeolites were the barium and potassium ratios and the zeolite source. Some adsorbents had been synthesized especially for production of zeolites for xylene separation and some had been purchased as commercially available materials, generally of the sodium type X configuration.

While this example is limited to barium and potassium exchanged type X zeolites the same effects would be noticed where the type Y zeolite was utilized with both barium and potassium based thereon.

All of the above disclosed cations which can

be placed upon the type X or Y zeolites would behave in a substantially similar manner as the barium and potassium exchange zeolites tested herein.

The desorbents having boiling points heavier than the feed component C₈ aromatics and having an aromatic type configuration, except DEB, are in general inferior desorbents in non-equilibrium adsorptions as they have either a reduced ability to desorb or are so tenaciously held upon the zeolite that it is extremely difficult to remove the desorbent from the zeolite. The desorbent thus may degrade the selectivity of the adsorbent during non-equilibrium operation.

Specific analysis of the four adsorbents used are shown in Table III below:

TABLE III

Adsorbents

Adsorbent	I	II	III	IV
Component, ¹ wt. %				
K ₂ O	5.6	0.9	1.5	1.7
BaO	21.1	27.7	28.2	26.7
Na ₂ O	0.9	2.0	1.7	1.3
Al ₂ O ₃	30.5	28.4	28.1	28.9
SiO ₂	40.1	40.3	39.1	39.7

¹ Adsorbent compositions given are based on volatile free basis after subjecting adsorbents to inert purge at 500°C until constant weight was achieved.

A considerable amount of testing was done with feed stock A and desorbent E. Results of this testing showed that a separation would take place, although inferior to operation using a desorbent of p-DEB and decalin. Inferior operation is thought to be due to difference in densities of iso-octane as compared to p-DEB and the C₈ aromatic hydrocarbons. Relatively low flow traces were used and the density difference between diluent and desorb-

ent and feed stock components may have masked or altered the sharp concentration gradients required for a clean separation. For these reasons these tests are not reported.

Eight other tests were run using different feed stocks and desorbents. All of the data generated for tests numbers 1 to 8 of this Example were done under non-equilibrium adsorption conditions. The results of the eight tests are shown in Table IV below:

TABLE IV

Test Data

Test Number	1	2	3	4	5	6	7	8
Adsorbent Used	I	I	II	II	III	III	IV	IV
Feed Stock	C	B	C	B	C	B	C	B
Desorbent	D	F	D	F	D	F	D	F
Test Temperature °C	150	150	150	150	150	150	150	150
Selectivity (B) for:								
P/E	1.6	1.9	2.1	2.2	2.1	2.2	1.8	2.2
P/M	2.9	4.4	3.2	3.1	3.3	3.5	3.3	4.6
P/O	2.5	4.2	2.9	3.0	3.3	3.7	3.3	5.1

From the data shown in Table IV it is clear that improved results, as far as selectivities are concerned, are seen for p-x with respect to EB, m-X, and o-X in all of the tests except for a slight reduction in the p-X to m-X selectivity in Test 4. Tests 1, 3, 5 and 7 show that mixed DEB's can be used as

desorbents during non-equilibrium operation. An improvement is seen in the overall selectivities where only p-DEB is used in admixture with decahydronaphthalene. This is unexpected as only 10 LV% p-DEB desorbent is used (Tests 2, 4, 6 and 8) compared to inferior results obtained with a desorbent

containing a larger absolute quantity of p-DEB, 25.6 LV% DEB in mixed DEB's. (Tests 1, 3, 5 and 7).

- 5 Best results were seen for the adsorbents having lower barium to potassium ratios, namely adsorbents 1 and 4.

- 10 It is anticipated that the same general results would be noticed with adsorbents were used which contain other cations described above. The effects of p-DEB as a desorbent material or component of a desorbent would necessarily give the same results.

EXAMPLE II.

- 15 In this Example three tests were run to show the improved results of using a desorbent of p-DEB and decalin compared to a desorbent of mixed DEB's.

- 20 The testing apparatus was a pilot plant simulated moving bed operation. The apparatus consisted of 24 serially connected sieve chambers of about 44 cc volume each.

- 25 Total chamber volume of the apparatus was approximately 1,056 cc. The chambers were connected with small diameter piping together with auxiliary lines leading to a rotary valve. The valve had inlet and outlet ports which connected certain of the auxiliary lines which flowed into the conduits connecting the chambers to external input or output lines.
- 30 By manipulating the rotary valve, and maintaining given pressure drops and flow rates through the various streams in and out of the chambers, a counter-current flow was produced in which the adsorbent remained stationary while fluid was flowing through the chambers.

- 35 To better understand the flow of this example, reference can be made to D. B. Broughton, et al., "The Separation of p-Xylene from C₈ Hydrocarbon Mixtures by the Parex Process," presented at the Third Joint Annual Meeting, American Institute of Chemical Engineers and Puerto Rican Institute of Chemical Engineers, San Juan, Puerto Rico, May 17, through May 20, 1970.

All experiments were conducted at about 150°C. and 7.8 atm (100 psig).

Two different adsorbents were used in this Example to illustrate the benefits of using p-DEB without other DEB isomers. The first adsorbent was identical to adsorbent III described in Table III of Example I. The second adsorbent used was labelled adsorbent V. This adsorbent had been heated to 500°C in an inert atmosphere until constant weight had been achieved. The adsorbent analysis is shown in Table V below:

TABLE V

Adsorbent Analysis

Adsorbent	V
Component, wt. %	
K ₂ O	3.2
BaO	25.6
Na ₂ O	0.7
Al ₂ O ₃	29.2
SiO ₂	41.0

The feed stock used for all tests in this Example contained about 32.6 LV% EB, 14.3 LV% p-X, 35.5 LV% m-X, and about 17.6 LV% o-X.

There were two desorbents. The first was desorbent D described in Table I of Example I while the other desorbent (labeled G) was about 32 LV% p-DEB diluted in about 68 LV% decalin.

Three tests were run to show the different efficiencies and extraction purities which resulted in the use of a diluted p-DEB desorbent. "Efficiency" is defined as (100%—% of p-X in the feed lost through the raffinate).

The tests results are shown in Table IV below. The flush stream is used to flush out the piping as the valve turns.

TABLE VI

Test	9	10	11
Adsorbent	II	II	V
<u>Flow Rates</u>			
Feed in, cc/hr.	53	49	51
Flush in	19	19	39
Desorbent in	558	589	237
Flush out	6	6	28
Extract out	75	75	57
Raffinate out	549	576	242
<u>Extract</u>			
C ₈ LV%	10.5		7.9
<u>Distribution, LV%</u>			
EB	18.7	0.9	0.2
p-X	73.4	98.0	99.4
m-X	2.4	0.4	0.2
o-X	5.5	0.6	0.2
<u>Raffinate</u>			
C ₈ LV%	5.8	7.3	16.6
<u>Distribution, LV%</u>			
EB	35.0	37.6	38.4
p-X	1.4	3.0	tr
m-X	39.5	38.4	38.1
o-X	24.1	20.9	23.5
Efficiency, %	94	82	100
Desorbent type	D	D	G

It is thought that the difference in the adsorbent of tests 9, 10 and 11 is minor. In the test 9 the pilot plant unit was operated for high recovery of p-X, i.e., 94% efficiency. This relatively high efficiency, reduced the purity of the extract p-X to about 73.4 LV%. In test 10 the pilot plant unit was operated to produce a relatively pure extract p-X 98 LV% p-X) though the efficiency dropped

to 82%. Both tests 9 and 10 used mixed DEB desorbent. Tests 9 and 10 indicate that it was not possible to obtain both high efficiency and high p-X purity with mixed DEB desorbents. The mixed DEB desorbents work but the m-DEB o-DEB and other C₁₀ aromatics present seem to degrade the adsorbent.

The results of test 11 indicate that essentially 100% extraction efficiency was possible

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with an extract p-X purity of 99.4 LV%. This indicates that p-DEB is superior to mixed DEB desorbent.

5 The test 11 desorbent contained 32 LV% p-DEB while the desorbent of test 9 and 10 contained only about 25 LV% p-DEB in admixture with the other DEB isomers. It is thought that the superior results of the operations shown in test 11 are not due to the slight increase in LV% p-DEB in desorbent 10 G as compared to desorbent D, but rather reflect the absence of o-DEB, m-DEB and butylbenzene. Additionally, a lower desorbent flow rate was used in test 11 than in tests 9 15 and 10 with improved results.

The above Examples are illustrative only and are not to be considered as limiting the scope of the attached claims.

WHAT WE CLAIM IS:—

20 1. In a process for separating para-xylene from a mixture of C₈ aromatic hydrocarbons using a crystalline aluminosilicate adsorbent containing a selected cation or cations, which process comprises the steps of: (i) contacting 25 said adsorbent with said mixture of C₈ aromatic hydrocarbons and thereby selectively adsorbing para-xylene under non-equilibrium conditions while simultaneously removing from the adsorbent a raffinate which comprises less 30 selectively adsorbed C₈ aromatics; (ii) contacting said adsorbent with a desorbent and thereby displacing said para-xylene from said adsorbent while simultaneously removing an

extract comprising desorbent and para-xylene from said adsorbent; the improvement which 35 comprises using a desorbent containing para-diethylbenzene.

2. Improved process of Claim 1 wherein the desorbent contains from 10 to 60 liquid 40 volume percent para-diethylbenzene.

3. Improved process of Claim 1 or 2 wherein the desorbent material contains para-diethylbenzene in admixture with a saturated 45 hydrocarbon.

4. Improved process of Claim 3 wherein the saturated hydrocarbon is a paraffin. 45

5. Improved process of Claim 3 wherein the saturated hydrocarbon is a cycloparaffin.

6. Improved process of Claim 3 wherein the saturated hydrocarbon is decahydronaphthalene. 50

7. Improved process of any of claims 1 to 6 wherein substantially all of the diethylbenzene in the desorbent is para-diethylbenzene. 55

8. An improved C₈ aromatic separation process according to claim 1 and substantially as hereinbefore described.

9. Para-xylene when separated by a process according to any of claims 1 to 8. 60

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with an extract p-X purity of 99.4 LV%. This indicates that p-DEB is superior to mixed DEB desorbent.

5 The test 11 desorbent contained 32 LV% p-DEB while the desorbent of test 9 and 10 contained only about 25 LV% p-DEB in admixture with the other DEB isomers. It is thought that the superior results of the operations shown in test 11 are not due to the slight increase in LV% p-DEB in desorbent 10 G as compared to desorbent D, but rather reflect the absence of o-DEB, m-DEB and butylbenzene. Additionally, a lower desorbent flow rate was used in test 11 than in tests 9 15 and 10 with improved results.

The above Examples are illustrative only and are not to be considered as limiting the scope of the attached claims.

WHAT WE CLAIM IS:—

20 1. In a process for separating para-xylene from a mixture of C₈ aromatic hydrocarbons using a crystalline aluminosilicate adsorbent containing a selected cation or cations, which process comprises the steps of: (i) contacting 25 said adsorbent with said mixture of C₈ aromatic hydrocarbons and thereby selectively adsorbing para-xylene under non-equilibrium conditions while simultaneously removing from the adsorbent a raffinate which comprises less 30 selectively adsorbed C₈ aromatics; (ii) contacting said adsorbent with a desorbent and thereby displacing said para-xylene from said adsorbent while simultaneously removing an

extract comprising desorbent and para-xylene from said adsorbent; the improvement which 35 comprises using a desorbent containing para-diethylbenzene.

2. Improved process of Claim 1 wherein the desorbent contains from 10 to 60 liquid volume percent para-diethylbenzene. 40

3. Improved process of Claim 1 or 2 wherein the desorbent material contains para-diethylbenzene in admixture with a saturated hydrocarbon.

4. Improved process of Claim 3 wherein the saturated hydrocarbon is a paraffin. 45

5. Improved process of Claim 3 wherein the saturated hydrocarbon is a cycloparaffin.

6. Improved process of Claim 3 wherein the saturated hydrocarbon is decahydronaphthalene. 50

7. Improved process of any of claims 1 to 6 wherein substantially all of the diethylbenzene in the desorbent is para-diethylbenzene. 55

8. An improved C₈ aromatic separation process according to claim 1 and substantially as hereinbefore described.

9. Para-xylene when separated by a process according to any of claims 1 to 8. 60

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