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PATENT SPECIFICATION

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(54) IMPROVED HYDROCARBON SEPARATION PROCESS

(71) We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of No. 30, Algonquin Road, Des Plaines, Illinois, 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 present invention relates to an improved process for the separation of aromatic hydrocarbons using a solid adsorbent which selectively removes at least one aromatic component from the feed. The selectively adsorbed aromatic component is recovered from the solid adsorbent through a desorption step.

Our Patent *Appln. No. 30561/69* (Serial No. 1,236,369) describes and claims a process for separating a C_8 aromatic isomer from a feed stock containing a mixture of C_8 aromatic isomers which comprises: (a) contacting said feed stock with a bed of crystalline aluminosilicate adsorbent comprising faujasite containing at least one cation selected from potassium, rubidium, cesium, barium and silver, together with at least one different cation selected from lithium, potassium, barium, magnesium, strontium, beryllium, cadmium, cobalt, nickel, copper, manganese, silver and zinc; (b) adsorbing the selectively more adsorbable C_8 aromatic isomer of said feed stock on said adsorbent; (c) withdrawing from said bed of adsorbent a raffinate stream comprising selectively less absorbed C_8 aromatic isomer or isomers; (d) contacting the adsorbent bed with a desorbent material, and desorbing the selectively adsorbed C_8 isomer from the adsorbent; and (e) withdrawing from said adsorbent bed a product stream comprising desorbent and said selectively adsorbed C_8 aromatic isomer. The above mentioned application disclosed that a number of metal cation pairs, including the cation pair potassium and barium, increase the selectivity of the adsorbent material. Recent studies have shown that the use of specified weight ratios of barium and potassium give particularly good adsorbent selectivity.

Accordingly, the present invention provides a process for the separation of a C_8 aromatic hydrocarbon from a hydrocarbon feed mixture comprising at least two C_8 aromatic hydrocarbons which process comprises the steps of: (a) contacting said feed mixture with an adsorbent comprising a crystalline aluminosilicate zeolite which selectively retains a major portion of one of said C_8 aromatic hydrocarbons; (b) withdrawing from said bed of adsorbent a raffinate stream comprising at least one C_8 aromatic hydrocarbon less selectively retained by said adsorbent; (c) contacting said adsorbent with a desorbent material to remove from the adsorbent selectively retained C_8 aromatic hydrocarbon and; (d) withdrawing from the adsorbent a stream comprising desorbent material and selectively retained C_8 aromatic hydrocarbon; and which includes the improvement of employing as said adsorbent a type X or type Y structured crystalline aluminosilicate containing barium and potassium cations in a weight ratio of barium to potassium within the range of from 1:1 to 100:1, desirably 1:1 to 50:1, preferably 5:1 to 35:1, especially 5:1 to 17:1.

Preferably at least 75% of the exchangeable cationic sites within said zeolite are occupied by barium or potassium ions.

The improved results of using a specified weight ratio of Ba to K will now be illustrated by the following examples.

A first series of experiments was conducted as described in the earlier application. The dynamic tester adsorbent chamber contained 40 cc of adsorbent and was maintained at 150° C. The feed was 75 LV% (liquid volume %, iC8 (150-octane) and 25 LV% C8A (aromatics). The C8A was comprised of 8 ⅓ LV% p-X (para-xylene), 8 ⅓ LV% m-X (metra-xylene) and 8 ⅓ LV%

[Price 25p]

Price 75p

EB (ethylbenzene). The desorbent was 25 LV% T (toluene) and 75 LV% iC_8 diluent.

The selectivities in either liquid or vapor phase measured at the same temperature are about the same, but the vapor phase operations show slightly higher selectivities because of the influence of the difference in relative volatilities of the components tested.

Type Y structured zeolite having SiO_2/Al_2O_3 mole ratios of about 3.3 were used as adsorbents. The zeolites tested were all air-equilibrated before testing. The air-equilibration procedure consisted of contacting the zeolites with air in a muffle furnace at a temperature of about 500° C until the zeolite reached a constant weight indicating equilibrium between the hot gas and the zeolites.

Six different adsorbents were tested.

Adsorbent I was Na form zeolite which contained primarily Na at the cationic exchangeable sites within the zeolite. Adsorbent II was a 100% Ca exchanged zeolite. Adsorbent III was a Ba exchanged form of adsorbent I and contained about 18.7 wt % Ba and about 1.9 wt % residual Na. Adsorbent IV was a K exchanged form of adsorbent I and contained about 18.0 wt % K with practically no residual Na. Adsorbents V and VI were Ba and K exchanged forms of adsorbent I and contained about 12.0 wt % Ba, 4.7 wt % K and 0.6 wt % Na and 10.0 wt % Ba, 4.3 wt % K and 1.4 wt % Na respectively. The slight difference in the cation composition for adsorbents V and VI was thought to be the result of slight differences in the ion exchange techniques used in preparing the adsorbents. All wt % measurements are on air-equilibrated adsorbent.

The selectivities of the adsorbents were determined and are shown in Table I below.

TABLE I

Adsorbent Selectivities

Adsorbent	Description	Selectivity (B)	
		Bp/m[1]	Bp/EB[2]
I	Na form	0.75	1.32
II	Ca form	0.35	1.17
III	Ba form	1.27	1.85
IV	K form	1.83	1.16
V	Ba+K form	3.35	2.32
VI	Ba+K form	3.76	2.10

[1] Bp/m = Selectivity of para-xylene with respect to meta-xylene.

[2] Bp/EB = Selectivity of para-xylene with respect to ethylbenzene.

Adsorbent V was also tested for the selectivity of p-X to o-X by replacing m-X in the feed with o-X. The results of this test confirmed the similar behaviour expected between m-X and o-X. The selectivity of adsorbent V for p-X with respect to o-X (Bp/o) was about 3.11.

The zeolites exchanged with both Ba and K were superior to any of the other zeolites tested including the Ba exchanged and K exchanged zeolites. The Ba and K give a synergistic effect which results in unexpectedly improved selectivities for p-X.

While the adsorbents tested were type Y zeolites, the same synergistic effect should occur for type X zeolites.

In this Example type X structured zeolites were tested to show the effects of Ba and K. These zeolites were dried at 200° C in a nitrogen atmosphere.

The description of the six adsorbents tested in this Example is shown in Table II below.

TABLE II

Adsorbent Description	Weight % Component A			Wt. Ratio Ba/K	Total g. equivalent or cationic sites per 100 g. of adsorbent	% of total g. equivalent cationic sites occupied by given component		
	K	Ba	Na			K	Ba	Na
VII	6.1	13.5	1.4	2.22	0.415	37.6	47.7	14.7
VIII	5.5	15.3	1.4	2.80	0.426	33.1	52.4	14.5
IX	3.5	18.6	1.3	5.30	0.428	21.0	63.6	15.4
X	14.1	—	1.4	0	0.423	85.1	—	14.9
XI	—	24.7	1.4	∞	0.427	—	85.1	14.0
XII	—	—	18.4	—	0.420	—	—	100.0

A adsorbents contained small portions of binder material.

The degree of ion-exchange was the percentage of the exchangeable cationic sites (g. equivalents) of the total g. equivalents that were occupied by Ba and K cations. For example, in adsorbent VII Ba and K were present at about 85.3% of the total exchangeable cationic sites within the adsorbent.

Sieves VII through XII were each tested for selectivity in the dynamic testing apparatus at about 3.7 atm (40 psig) pressure and about 125° C. The selectivities are reported below in Table III.

TABLE III

Adsorbent Description	Weight Ratio Barium/Potassium	Selectivities	
		Bp/m	Bp/EB
VII	2.22	3.4	2.1
VIII	2.80	3.3	2.1
IX	5.30	3.5	2.3
X	0	1.8	1.2
XI	∞	1.3	1.8
XII	—	0.8	1.3

Adsorbent XII of Table III is only slightly selective for p-X as compared to EB (Bp/EB=1.3) and is not all selective for p-X as compared to m-X (Bp/m=0.8). Adsorbent XII was essentially totally exchanged with Ba cations and tested as adsorbent XI. The presence of Ba improved selectivities for adsorbent XI as compared to adsorbent XII. Adsorbent X which was essentially a totally K exchanged type X zeolite showed an improvement only in Bp/m selectivity as compared to the Na form zeolite.

Adsorbent VII, VIII and IX, however, showed an improvement in all respects over adsorbent X, XI and XII. The presence of both Ba and K on a zeolite resulted in a synergistic effect on both Bp/m and Bp/EB selectivity.

In Table IV below three adsorbents were tested which had various weight ratios of

Ba/K. The sieves were approximately 85% ion-exchanged (about 15% of the cationic sites contained sodium cations) and were dried at 300° C in nitrogen.

TABLE IV

Adsorbent Description	Weight Ratio Barium/Potassium	Selectivities	
		Bp/m	Bp/EB
XIII	0.84	1.9	1.3
XIV	1.32	2.4	1.5
XV	2.22	3.0	2.0

As can be seen from the data presented in Table IV that as the weight ratio of Ba/K increases the selectivities also increase. The difference in the selectivities for adsorbents VII and XV, which have identical weight ratios of Ba/K (2.22), is probably due to differences in drying temperatures of the absorbents (200° C versus 300° C).

In this example, various type X structured zeolitic adsorbents were used with varying weight ratios of Ba to K to study selectivity of p-X with respect to the other C8 aromatic hydrocarbons. These adsorbents were all equilibrated at 500° C in an inert atmosphere.

Ion-exchange was used to place Ba and K upon the zeolite. The analysis of the adsorbents is shown in Table V below.

TABLE V

Adsorbent Analysis

Adsorbent	XVI	XVII	XVIII	XIX
Component[1], wt %				
K_2O	5.6	1.7	1.5	0.9
BaO	21.1	26.7	28.2	27.7
Na_2O	0.9	1.3	1.7	2.0
Al_2O_3	30.5	28.9	28.1	28.4
SiO_2	40.1	39.7	39.1	40.3
Ba/K wt %/wt %	4.1	17.0	20.1	33.3

In this example the feed stock contained approximately 5 LV% each of p-X, m-X, o-X and EB along with 5 LV% normal nonane used as a tracer component. 67.5 LV% decalin and 7.5 LV% para-diethylbenzene were used as diluent material. The desorbent was 90 LV% decalin and 10 LV% para-diethylbenzene.

In this example the adsorbent chamber contained approximately 70 cc of adsorbent in a 1.83 m (six-foot) long copper tube with an outside diameter of 0.95 cm ($\frac{3}{8}$ inch).

The tube was maintained at temperature of approximately 150° C. Feed and desorbent streams were pre-heated to maintain isothermal operation. Gas chromatographic (GC) analysis equipment was attached to the effluent stream to determine the composition of the effluent stream at given time intervals. Knowing the feed rate into and out of the adsorbent chamber, the temperature, the feed and desorbent composition, and the particular chromatograph pattern shown by the effluent materials leaving the column, it was possible to determine concentrations of the components in the adsorbed and unadsorbed phases. Knowing this data the selectivity was determined for any of the two given feed components.

The operations taking place were as follows. The desorbent flow was at a 1 liquid hourly space velocity (LHSV) of volume per hour of liquid feed at 15° C per volume of adsorbent about 1.17 cc per minute. Desorbent flow is stopped. The feed is then run for ten minutes at 1 LHSV flow rate. Desorbent flow is then resumed at 1 LHSV and continued until all of the feed C8A is eluted from the column as determined by GC analysis of the column effluent. The sequence of operations usually takes about an hour.

To evaluate the performance of the adsorbents, the distance between the mid-point of the normal nonane tracer peak envelope and the mid-point of the C8A peak envelope was measured. The selectivity of p-X with respect to the other C8 aromatics is the ratio of distance between the centre of the p-X peak envelope and the C8 tracer peak envelope to the corresponding distances for EB, m-X, and o-X. The test date for the various adsorbents tested is shown in Table VI below.

TABLE VI

Selectivity Data

Adsorbent	Weight Ratio Ba/K	Selectivities		
		Bp/EB	Bp/m	Bp/o
XVI	4.1	1.9	4.4	4.2
XVII	17.0	2.2	4.6	5.1
XVIII	20.1	2.2	3.5	3.7
XIX	33.3	2.2	3.1	3.0

The above data indicate that the Ba and K weight ratio effects the selectivities of a zeolitic adsorbent for p-X with respect to the various C8 aromatic hydrocarbons.

The examples given above are specific embodiments of the process of the claimed invention and are not presented to limit the scope of the invention.

In Example II of the parent Patent Application No. 30561/69 (Serial No. 1,236,369) reference is made to the use, for separation of para-xylene from C_8 aromatic hydrocarbon mixtures, of type X and type Y zeolites which have been ion-exchanged with a mixture of barium and potassium ions to give a barium to potassium mole ratio of about 3:1, and a chemical analysis is given of one such zeolite, based on volatile-free adsorbent, showing a barium: potassium weight ratio of about 5.2:1. We make no claim herein to the use of the zeolites containing potassium and barium disclosed in Example II of the parent patent application. Subject to this disclaimer,

WHAT WE CLAIM IS:—

1. A process for the separation of a C_8 aromatic hydrocarbon from a hydrocarbon feed mixture comprising at least two C_8 aromatic hydrocarbons which comprises the steps of:

(a) contacting said feed mixture with an adsorbent comprising a crystalline aluminosilicate zeolite which selectively retains a major portion of one of said C_8 aromatic hydrocarbons;

(b) withdrawing from said bed of adsorbent a raffinate stream comprising at least one C_8 aromatic hydrocarbon selectively less retained by said adsorbent;

(c) contacting said adsorbent with a desorbent material to remove from the adsorbent selectively retained C_8 aromatic hydrocarbon; and

(d) withdrawing from the adsorbent a stream comprising desorbent material and selectivity retained C_8 aromatic hydrocarbon;

and which includes the improvement of employing as said adsorbent a type X or type Y structured crystalline aluminosilicate containing barium and potassium cations in a weight ratio of barium to potassium within the range of from 1:1 to 100:1.

2. A process according to Claim 1 wherein the hydrocarbon feed contains para-xylene which is selectively retained by the adsorbent and at least one C_8 aromatic hydrocarbon selected from ortho-xylene, meta-xylene and ethylbenzene.

3. A process according to Claim 1 or 2 wherein at least 75% of the exchangeable cationic sites within said zeolite are occupied by barium or potassium cations.

4. A process according to any of Claims 1 to 3 wherein the weight ratio of barium to potassium is within the range of 1:1 to 50:1.

5. A process according to Claim 4, wherein the weight ratio of barium to potassium is 5:1 to 35:1.

The operations taking place were as follows. The desorbent flow was at a 1 liquid hourly space velocity (LHSV) or volume per hour of liquid feed at 15° C per volume of adsorbent about 1.17 cc per minute. Desorbent flow is stopped. The feed is then run for ten minutes at 1 LHSV flow rate. Desorbent flow is then resumed at 1 LHSV and continued until all of the feed C8A is eluted from the column as determined by GC analysis of the column effluent. The sequence of operations usually takes about an hour.

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XVII	17.0	2.2	4.6	5.1
XVIII	20.1	2.2	3.5	3.7
XIX	33.3	2.2	3.1	3.0

The above data indicate that the Ba and K weight ratio effects the selectivities of a zeolitic adsorbent for p-X with respect to the various C8 aromatic hydrocarbons.

The examples given above are specific embodiments of the process of the claimed invention and are not presented to limit the scope of the invention.

In Example II of the parent Patent Application No. 30561/69 (Serial No. 1,236,369) reference is made to the use, for separation of para-xylene from C_8 aromatic hydrocarbon mixtures, of type X and type Y zeolites which have been ion-exchanged with a mixture of barium and potassium ions to give a barium to potassium mole ratio of about 3:1, and a chemical analysis is given of one such zeolite, based on volatile-free adsorbent, showing a barium:potassium weight ratio of about 5.2:1. We make no claim herein to the use of the zeolites containing potassium and barium disclosed in Example II of the parent patent application. Subject to this disclaimer,

WHAT WE CLAIM IS:—

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(a) contacting said feed mixture with an adsorbent comprising a crystalline aluminosilicate zeolite which selectively retains a major portion of one of said C_8 aromatic hydrocarbons;

(b) withdrawing from said bed of adsorbent a raffinate stream comprising at least one C_8 aromatic hydrocarbon selectively less retained by said adsorbent;

(c) contacting said adsorbent with a desorbent material to remove from the adsorbent selectively retained C_8 aromatic hydrocarbon; and

(d) withdrawing from the adsorbent a stream comprising desorbent material and selectivity retained C_8 aromatic hydrocarbon;

and which includes the improvement of employing as said adsorbent a type X or type Y structured crystalline aluminosilicate containing barium and potassium cations in a weight ratio of barium to potassium within the range of from 1:1 to 100:1.

2. A process according to Claim 1 wherein the hydrocarbon feed contains para-xylene which is selectively retained by the adsorbent and at least one C_8 aromatic hydrocarbon selected from ortho-xylene, meta-xylene and ethylbenzene.

3. A process according to Claim 1 or 2 wherein at least 75% of the exchangeable cationic sites within said zeolite are occupied by barium or potassium cations.

4. A process according to any of Claims 1 to 3 wherein the weight ratio of barium to potassium is within the range of 1:1 to 50:1.

5. A process according to Claim 4, wherein the weight ratio of barium to potassium is 5:1 to 35:1.

* C L M S *

6. A process according to Claim 5 wherein the weight ratio of barium to potassium is 5:1 to 17:1.

7. An improved hydrocarbon separation process according to Claim 1 and substantially as hereinabove described.

8. Para-xylene when separated from a feed mixture comprising at least two C_8 aromatic hydrocarbons by a process according to any of claims 1 to 7.

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