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(19)

(54) 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. 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 field of art to which this invention pertains is hydrocarbon separation, more specifically, hydrocarbon separation using crystalline aluminosilicates to selectively adsorb and separate aromatic isomer mixtures.

Prior art exists relating to the use of type X or type Y zeolites to separate xylenes. For brevity, the following abbreviations are used: o-X is ortho-xylene, p-X is para-xylene, m-X is meta-xylene and EB is ethylbenzene. It is known to use particular cations on type X or type Y zeolites to selectively adsorb a particular xylene. It is also known to use barium and potassium, both base-exchanged upon a type X or Y crystalline aluminosilicate, to render a sieve selective towards p-X with respect to all other xylene isomers including EB. It appears that a barium and potassium combination renders a sieve superior to that obtainable using either barium by itself or potassium by itself.

The prior art has not recognized the use of water to selectively alter the selectivity of a zeolite for para-isomers as compared to the other isomers. Water does modify the rates at which molecules pass into and out of a zeolite and water has been used with 4 or 5 Angstrom zeolite sieves to separate normal paraffins from isoparaffins. Water has not been used for xylene separation to modify the selectivity of an adsorbent for a particular feed component. It has now been discovered that water can be placed upon a crystalline aluminosilicate, especially one which contains barium cations, to modify the selectivity of a sieve. Water and barium give effects similar to those obtained with potassium and barium upon the zeolite. The theory proposed for the effects of water on the zeolite is not known.

Accordingly, the present invention provides a process for separating an aromatic hydrocarbon para-isomer from a feed containing a mixture of aromatic hydrocarbon isomers including a para-isomer, which process comprises contacting said feed with an adsorbent selected from type X and type Y zeolites containing from 1 to 8 wt % water as measured on a volatile-free basis (as hereinafter defined), and which may contain barium cations at, for example, over 75% of the base exchangeable sites within the zeolite, and thereby selectively adsorbing said para-isomer with said adsorbent.

Feed stocks which can be used in the process of this invention include C_8 aromatic isomers, C_9 aromatic isomers, C_{10} aromatic isomers and C_{11} aromatic isomers, such as the xylene isomers—p-X, m-X, o-X and EB—the diethylbenzenes and the cymenes.

Feed stocks can be derived from many areas within petro-chemical or petroleum processing plants. Specifically, xylene can be derived from treated reformate streams. The feed may also include minor amounts of paraffins or olefins or other aromatic hydrocarbons. It is preferred to reduce the quantity of non-xylene materials passed as feed into the process of this invention to prevent damage to the adsorbent from reactive feed components and to prevent the reduction of the selectivity of the adsorbent for the xylenes. In many instances, the presence of other type hydrocarbon compounds severely restricts the maximum attainable selectivity to an extent which renders the absorbent almost totally unselective with respect to any feed stock component.

Specific feed streams which can be used in the process of this invention contain at least two xylene isomers with possible inclusions of some straight and branched chain paraffins,

[Price 33p]
Price 75p

cyclo-paraffins and aromatics including benzene, toluene and naphthalenes. Feeds of 80 to 100 LV% (liquid volume percent) xylene isomers are preferred. The feed may come from a xylene isomerizer.

Other feed stocks such as the cymenes, the diethyl-benzenes or any other single range aromatic hydrocarbon with ortho, meta and para-isomers may also be used. Specifically included are the ortho, meta and para-diethylbenzenes along with butylbenzene, and the ortho-, meta- and para-cymene isomers along with butylbenzene.

Desorbents are those materials which are capable of displacing para-isomers from the adsorbent. The desorbent should itself be easily displaced by para-isomers or else once a sieve had been contacted by the desorbent the adsorbent would thereafter be useless.

Desorbents used may vary depending upon the feed stock or the particular processing sequence used in the process. When using a relatively constant temperature process, in liquid or vapor phase, it is possible to use benzene or toluene or higher aromatic hydrocarbons such as the C_8 aromatics or the diethylbenzenes. Other possible desorbents are paraffins, cycloparaffins, olefins or chlorinated or sulfonated hydrocarbons.

If desorption takes place using increased temperatures and/or vacuum, gaseous materials such as air, oxygen, nitrogen and light hydrocarbons can be utilized to purge paraisomer for the adsorptive sites of the adsorbent. High temperature and vacuum alone may be enough to completely purge the para-isomer from the adsorbent.

The selectively adsorbed component is commonly referred to as the extract component of the feed stock and for purposes of this specification is referred to as the para-isomer since that isomer is selectively adsorbed when utilizing adsorbent described herein. In some instances there may be two or more para-isomers adsorbed by the adsorbent such as in cases where there rae mixtures of different molecular weight feed stocks. The raffinate is what remains after the para-isomer has been selectively adsorbed from the feed by the adsorbent.

Adsorption temperatures suitably range from ambient up to 232°C (450°F) but higher temperatures may be used. Pressures suitably range from atmospheric up to 69 atm (1000 psig) but higher pressures may be used. Pressures of from 2.4 to 14.6 atm (20 to 200 psig) are preferred to reduce equipment cost in commercial installations. Temperatures should be high enough so that feed and desorbent can pass into and out of the selective adsorption sites of the adsorbent without undue delay. The process may be conducted in either liquid or vapor phase.

Desorption conditions can include the temperature and pressure limitations described for adsorption. A purge stream may also be used to help remove para-isomers from the adsorbent.

The flow schemes which can be utilized to effect the process of this invention include batch-type fixed bed processes, the continuous simulated moving-bed systems and the moving bed systems. A simulated moving bed is preferred.

The term "volatile-free basis" as used herein and in the claims means the zeolite has been heated at about 500°C until the zeolite reached a constant weight.

Some zeolites contain a binder. In determining water content of these adsorbents, it is presumed that the water is evenly dispersed between the binder and the zeolite.

To measure the water content of a zeolite on a volatile-free basis, the sieve is first heated to drive off a certain percentage of volatile materials. After a certain period of time the only material being driven off is water. The drying procedure is stopped short of the condition when the adsorbent contains no water. The adsorbent is removed from the furnace and placed in a desiccator to cool. A portion of this material is removed for use as adsorbent, and a portion is retained. Material retained is then further dried at 500°C until it reaches a constant weight. From the difference in weight the wt % water on the adsorbent may be calculated.

Adsorbents which can be used in the process of this invention are generally referred to as crystalline aluminosilicates or molecular sieves and can comprise both the natural and synthetic aluminosilicates.

Both type X and type Y zeolites may be used. These zeolites include crystalline aluminosilicates having a three dimensional interconnected cage structure as defined by U.S. Patents 2,882,244 and 3,130,007.

Adsorbents contemplated herein include not only the sodium form of the type Y zeolite but also crystalline materials obtained from such a zeolite by partial or complete replacement of the sodium cation with other individual cations or groups of cations. Similarly, the type X zeolite also may be ion-exchanged.

Cations or base exchange methods are generally known to those familiar with the field or crystalline aluminosilicate production. They are generally performed by contacting the zeolite with an aqueous solution of the soluble salts of the cation or cations desired to be placed upon the zeolite.

To improve the zeolite's selectivity for para-isomers, the zeolite may contain Group IA, Group IIA and Group IB metals. Specific cations which show a preferential selectivity for p-X with respect to EB include lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium, silver, manganese, cadmium and

copper. These cations should be used in an adsorptive separation process in which p-X and EB are to be separated. If the above cations are used, p-X is the preferentially adsorbed component of the feed mixture.

The following combination of cations are particularly well suited for p-X and EB separation. These combinations include potassium and barium, potassium and beryllium, potassium and manganese, rubidium and barium, cesium and barium, copper and cadmium, copper and silver, zinc and silver, and copper and potassium.

Cations which have shown a preferential selectivity of p-X with respect to m-X and o-X include potassium, barium, sodium, silver along with the cation pairs including potassium and barium, potassium and beryllium, potassium and magnesium, potassium and rubidium, potassium and cesium, barium and rubidium, cesium and barium, and copper and potassium.

When single cations are base exchanged upon a zeolite the cations can comprise anywhere from 5 to 75 wt %, on a volatile-free basis, of the zeolite depending upon the molecular weight of the material exchanged upon the zeolite. Single ions may be on the zeolite in concentrations of from 1% to 100% of the cations present (generally sodium or calcium) on the zeolite prior to ion-exchange. From the silica to alumina ratio of the type of zeolite used, its water content and the percentage of binder used, if any, it is possible to calculate the percentage of ion exchange that has taken place.

When more than one type of cations are placed upon the zeolite, there are two things to consider: the extent of ion-exchange and the ratio of individual cations placed on the zeolite. If the cation pairs comprise a group IIA metal and a group IA metal the weight ratio of these components may vary from less than one up to eighty depending upon the molecular weight of the Group IIA or Group IA metal. A particular useful zeolite is one which contains barium and potassium cations having a weight ratio of barium to potassium or from 1:1 to 40:1, preferably from 1:1 to 30:1. A ratio of from 5:1 to 25:1 is especially preferred. When using Group IIA and Group IA metals the cations can occupy from 20 up to 100% of the ion-exchangeable sites located upon the zeolite. Cations other than Group IA or IIA metals generally occupy from 10 to 100% of the sites available.

In testing the various adsorbents, two properties are of particular importance. The "selective volume" of the adsorbent is the volume of the adsorbent which selectively adsorbs extract from the feed. The "non-selective volume" is the volume in the adsorbent which is dead space, e.g., the cavities of the adsorbent which contain no selective adsorptive sites and the interstitial spaces between adsorbent particles.

The accompanying drawing shows a graphical representation of the effect on selectivity of water. The abscissa is the wt % H_2O on an adsorbent, on a volatile-free basis, and the ordinate is the selectivity.

The solid lines indicate essentially totally barium exchanged type X zeolite adsorbent. The broken lines indicate a barium and potassium exchanged type X zeolite.

The squares represent the selectivity, B, of adsorbents for p-X with respect to m-X. Triangles represent the B of p-X with respect to o-X. Circles represent the B of p-X with respect to EB.

In general the two different adsorbents showed very similar change in selectivity with changes in water content. The barium exchanged type X zeolite produced higher overall selectivities than the barium-potassium exchange zeolite at similar water contents.

As can be seen from the graph, the B of p-X with respect to the other C_8 aromatic isomers reaches a maximum. For the B of p-X with respect to m-X and o-X around 2 to 3 wt % H_2O is optimum. However, the B of p-X with respect to EB (which in this case is the limiting B) reaches a maximum at around 1.2 to 2.0 wt % H_2O. Depending on the feed composition, the water content can be varied anywhere from 1 up to 5. If ethylbenzene is absent the water concentration can vary even more; from less than 1 up to 8 or more wt %. At the upper limit of water concentrations the adsorbent contains less adsorptive capacity because of the high water loading, and this may make operation of the process uneconomical.

The same results are expected for para-cymene with respect to the ortho-cymene, meta-cymene and isobutylbenzene isomers, for para-diethylbenzene with respect to ortho-diethylbenzene, meta-diethylbenzene and butylbenzene isomers, and for other feed stock isomers having para-, meta- and ortho-configurations along with a single alkyl substituted isomer analogous to the ethylbenzene isomer.

In this example two adsorbents containing varying water contents were tested to illustrate the necessity of selecting the proper amount of water on the adsorbent to enhance selectivity of a barium containing zeolite.

The feed contained 5 LV% each of o-X, m-X, p-X, EB and normal nonane, 19.2 LV% para-diethylbenzene, 45.2 LV% meta-diethylbenzene, 5.6 LV% ortho-diethylbenzene, and 5 LV% butyl-benzenes. The feed is basically C_8 aromatic hydrocarbons diluted in a desorbent of mixed diethylbenzenes. Normal nonane acts as a tracer to indicate, via gas chromatographic analysis,

when the feed is being eluted from the adsorbent by desorbent.

The desorbent mixed diethylbenzenes, 60.4 LV% meta-diethylbenzene, 7.4 LV% ortho-diethylbenzene, 25.6 LV% para-diethylbenzene and 6.6 LV% butylbenzenes. This material was also used to dilute the feed.

The adsorbents were two type X zeolites. One was totally barium exchanged type X crystalline aluminosilicate. The zeolite was about 40.1 wt % silica, 29.4 wt % alumina, 1.1 wt % sodium oxide and about 29.4 wt % barium oxide. This zeolite contained approximately 20 wt % clay binder, comprising a mixture of silica and alumina. The other adsorbent was a similar type X structured crystalline aluminsilicate which contained both barium and potassium cations. The zeolite was about 41.0 wt % silica, 29.2 wt % alumina, 0.7 wt % sodium oxide, 3.2 wt % potassium oxide and about 25.6 wt % barium oxide. Both adsorbents contained water. Water contents ranged from 1/2 to 7 wt %.

The equipment used for testing consisted of a 1.5 meter (5 foot) coiled copper column holding about 70 cc of adsorbent. The column was maintained at a constant temperature of about 150°C. Sufficient pressure was maintained in the coil to maintain liquid phase operation. The coil contained about 70 cc of adsorbent, ground to a particle size of from 0.4 to 1.2 mm (14 to 40 mesh). The coil was connected to a gas chromatograph which analyzed the effluent stream composition.

Pure desorbent was passed through the adsorption coil at about a 1 liquid hourly space velocity, LHSV, (70 cc/hr) until all of the adsorbent located within the coil had contacted desorbent. A 10 minute pulse of feed is then injected into the coil at a 1 LHSV. After this 10 minute feed pulse, desorbent flow is resumed at a 1 LHSV and continued until all of the feed aromatics are eluted from the coil. The gas chromatograph gives the varying composition of the effluent stream and from this the selectivity of an adsorbent for the various C_8 isomers can be calculated.

Slectivity is defined by the following equation:

$$\text{Selectivity}=B_{x/y}=\frac{(x/y)a}{(x/y)b} \qquad (5)$$

where the letters x and y represent the volume % of the two feed components being tested, and subscripts a and b refer to the adsorbed and unadsorbed phases, respectively.

The results of this testing are shown in Table I below:

TABLE I

Adsorbent Description	Wt % Water*	Selectivity P/E	P/M	P/O
Ba type X	0.5	1.98	2.29	1.81
Ba type X	2.4	2.13	3.70	3.40
Ba type X	3.6	1.77	3.63	3.37
Ba type X	5.5	1.66	3.06	2.94
Ba type X	7.1	1.54	2.38	2.38
Ba-K type X	0.6	1.69	2.45	2.60
Ba-K type X	1.9	1.71	2.87	2.69
Ba-K type X	2.4	1.57	3.67	3.13
Ba-K type X	3.5	1.50	3.68	3.26
Ba-K type X	5.5	1.45	3.16	2.99

* Wt % water based on a volatile-free basis.

As can be seen from the data shown above there is a certain water content in which all of the selectivities of para-xylene with respect to ethylbenzene, meta-xylene, ortho-xylene show a maximum value.

WHAT WE CLAIM IS:—

1. A process for separating an aromatic hydrocarbon para-isomer from a feed containing a mixture of aromatic hydrocarbon isomers including a para-isomer, which process comprises contacting said feed with an adsorbent selected from type X and type Y zeolites containing from 1 to 8 wt % water as measured on a volatile-free basis (as hereinbefore defined) and thereby selectively adsorbing said para-isomer with adsorbent.

2. The process of Claim 1 wherein the feed is selected from C_8 aromatic isomers, C_9 aromatic isomers, C_{10} aromatic isomers and C_{11} aromatic isomers.

3. The process of Claim 1 or 2 wherein the zeolite contains barium cations at the base exchangeable sites within the zeolite.

4. The process of Claim 3 wherein the zeolite contains barium cations at over 75%

when the feed is being eluted from the adsorbent by desorbent.

The desorbent mixed diethylbenzenes, 60.4 LV% meta-diethylbenzene, 7.4 LV% ortho-diethylbenzene, 25.6 LV% para-diethylbenzene and 6.6 LV% butylbenzenes. This material was also used to dilute the feed.

The adsorbents were two type X zeolites. One was totally barium exchanged type X crystalline aluminosilicate. The zeolite was about 40.1 wt % silica, 29.4 wt % alumina, 1.1 wt % sodium oxide and about 29.4 wt % barium oxide. This zeolite contained approximately 20 wt % clay binder, comprising a mixture of silica and alumina. The other adsorbent was a similar type X structured crystalline aluminsilicate which contained both barium and potassium cations. The zeolite was about 41.0 wt % silica, 29.2 wt % alumina, 0.7 wt % sodium oxide, 3.2 wt % potassium oxide and about 25.6 wt % barium oxide. Both adsorbents contained water. Water contents ranged from 1/2 to 7 wt %.

The equipment used for testing consisted of a 1.5 meter (5 foot) coiled copper column holding about 70 cc of adsorbent. The column was maintained at a constant temperature of about 150°C. Sufficient pressure was maintained in the coil to maintain liquid phase operation. The coil contained about 70 cc of adsorbent, ground to a particle size of from 0.4 to 1.2 mm (14 to 40 mesh). The coil was connected to a gas chromatograph which analyzed the effluent stream composition.

Pure desorbent was passed through the adsorption coil at about a 1 liquid hourly space velocity, LHSV, (70 cc/hr) until all of the adsorbent located within the coil had contacted desorbent. A 10 minute pulse of feed is then injected into the coil at a 1 LHSV. After this 10 minute feed pulse, desorbent flow is resumed at a 1 LHSV and continued until all of the feed aromatics are eluted from the coil. The gas chromatograph gives the varying composition of the effluent stream and from this the selectivity of an adsorbent for the various C_8 isomers can be calculated.

Slectivity is defined by the following equation:

$$\text{Selectivity} = B_{x/y} = \frac{(x/y)a}{(x/y)b} \qquad (5)$$

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Ba type X	5.5	1.66	3.06	2.94
Ba type X	7.1	1.54	2.38	2.38
Ba-K type X	0.6	1.69	2.45	2.60
Ba-K type X	1.9	1.71	2.87	2.69
Ba-K type X	2.4	1.57	3.67	3.13
Ba-K type X	3.5	1.50	3.68	3.26
Ba-K type X	5.5	1.45	3.16	2.99

* Wt % water based on a volatile-free basis.

As can be seen from the data shown above there is a certain water content in which all of the selectivities of para-xylene with respect to ethylbenzene, meta-xylene, ortho-xylene show a maximum value.

WHAT WE CLAIM IS:—

1. A process for separating an aromatic hydrocarbon para-isomer from a feed containing a mixture of aromatic hydrocarbon isomers including a para-isomer, which process comprises contacting said feed with an adsorbent selected from type X and type Y zeolites containing from 1 to 8 wt % water as measured on a volatile-free basis (as hereinbefore defined) and thereby selectively adsorbing said para-isomer with adsorbent.

2. The process of Claim 1 wherein the feed is selected from C_8 aromatic isomers, C_9 aromatic isomers, C_{10} aromatic isomers and C_{11} aromatic isomers.

3. The process of Claim 1 or 2 wherein the zeolite contains barium cations at the base exchangeable sites within the zeolite.

4. The process of Claim 3 wherein the zeolite contains barium cations at over 75%

of the base exchangeable sites within the zeolite.

5. The process of any of Claims 1 to 4 wherein the zeolite contains from 1 to 5 wt % water as measured on a volatile-free basis.

6. The process of any of Claims 1 to 5 wherein the feed is xylene isomers and ethylbenzene.

7. The process of any of Claims 1 to 5 wherein the feed is diethylbenzene isomers.

8. The process of any of Claims 1 to 5 wherein the feed is cymene isomers.

9. A process for separating an aromatic hydrocarbon para-isomer as claimed in claim 1 substantially as hereinbefore described.

10. An aromatic hydrocarbon para-isomer when separated from isomer mixtures by a process according to any of claims 1 to 9.

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