

June 13, 1961

E. E. SENSEL

2,988,577

SELECTIVE SORPTION PROCESS

Filed April 11, 1957

2 Sheets-Sheet 1

Fig. 1.

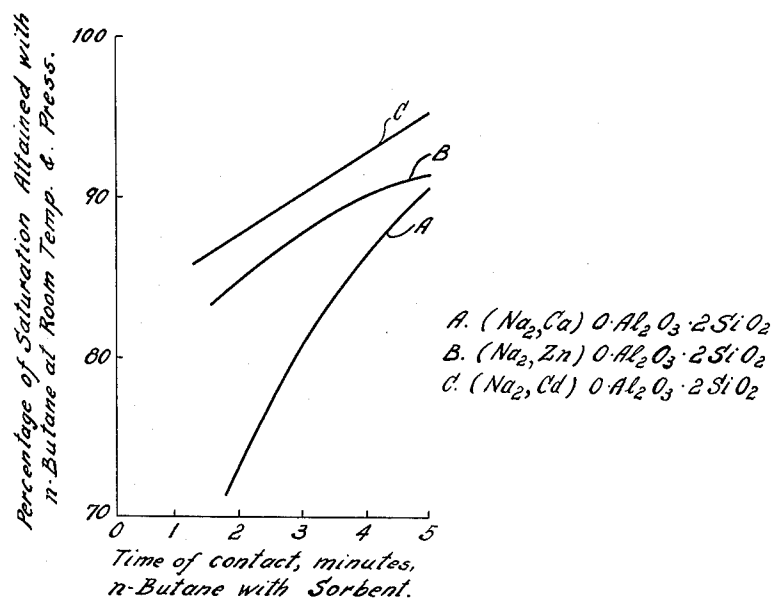
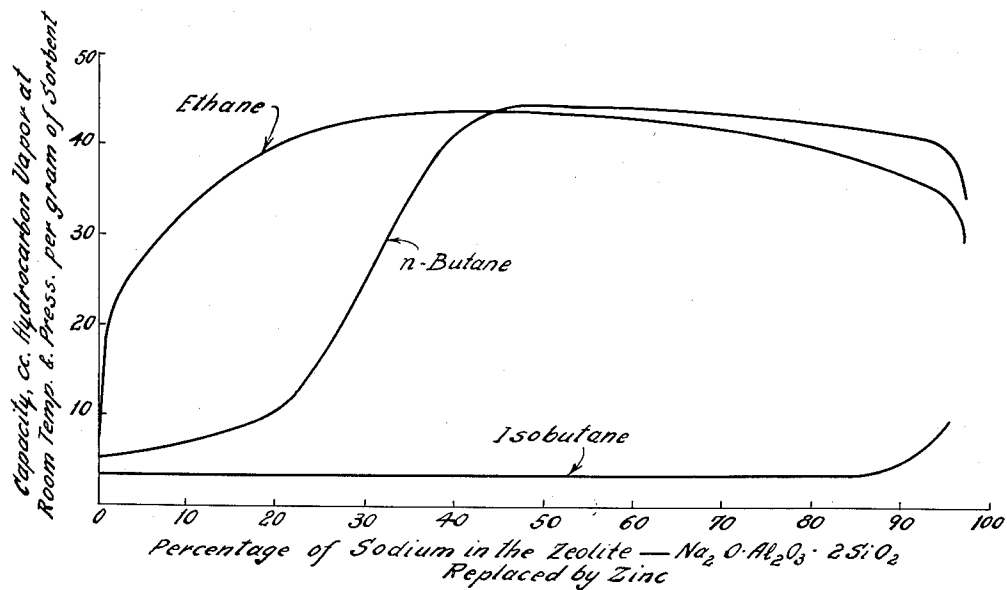


Fig. 2.



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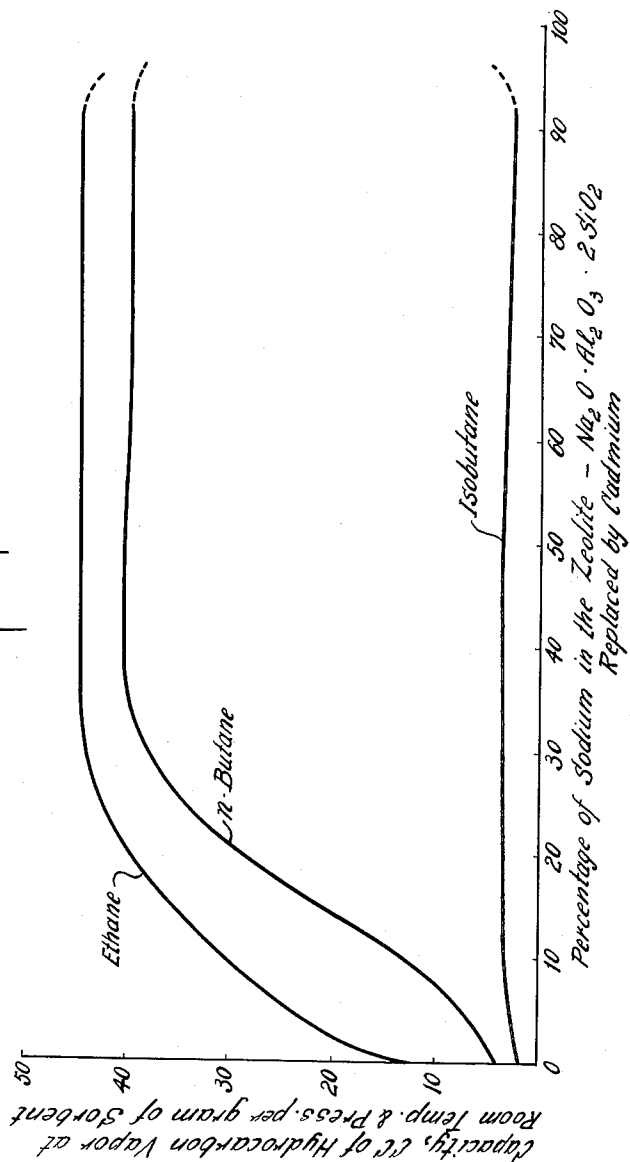
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2 Sheets-Sheet 2

Fig. 3.



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SELECTIVE SORPTION PROCESS

Eugene E. Sensel, Beacon, N.Y., assignor to Texaco Inc.,
a corporation of Delaware
Filed Apr. 11, 1957, Ser. No. 652,146
4 Claims. (Cl. 260-676)

This invention relates to an improved process for separating straight chain hydrocarbon from non-straight chain hydrocarbon in a mixture thereof, and to group 2b metal-containing zeolites effective in said process.

By straight chain hydrocarbon is meant any aliphatic or acyclic or open chain hydrocarbon which does not possess side chain branching. Representative straight chain hydrocarbons are the normal paraffins and the normal olefins, mono or polyolefins, or straight chain acetylenic hydrocarbons. The non-straight chain hydrocarbons comprise the aromatic and naphthenic hydrocarbons as well as the isoparaffins, isoolefinic hydrocarbons, and the like. Straight chain hydrocarbon-containing mixtures which are suitably treated in accordance with this invention include mixed butanes, mixtures of normal alkanes and their isomers, and various petroleum fractions such as naphtha fraction, a gasoline fraction, a diesel oil fraction, a kerosene fraction, a gas oil fraction and the like. Particularly suitable for treatment in accordance with this invention are straight chain hydrocarbon-containing fractions having a boiling point or a boiling range in the range of 40-550° F. and containing a substantial amount of straight chain hydrocarbons, e.g., 2-35% by volume. More particularly, a petroleum fraction suitable for use in practice of this invention could have an initial boiling point in the range of 40-300° F. and an end point in the range of 150-550° F. A petroleum fraction for use in the practice of this invention must contain both straight chain and non-straight chain hydrocarbons as demonstrated by the following composition:

Hydrocarbon type:	Percent by volume
Naphthenes -----	0-75
Aromatics -----	0-50
Acyclic saturates (including normal paraffins and isoparaffins) -----	2-90
Acyclic unsaturates (including normal olefins and isoolefins) -----	0-50

Typical refinery stocks or fractions which are applicable to the practice of this invention are a wide boiling straight run naphtha, a light straight run naphtha, a heavy straight run naphtha, a catalytically cracked naphtha, a thermally cracked or thermally reformed naphtha, a catalytically reformed naphtha and the like.

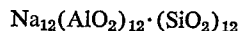
Heretofore, a synthetic sodium calcium aluminosilicate, a dehydrated crystalline zeolite, having a ratio of calcium to sodium (measured as a molecular ratio of calcium oxide to sodium oxide) between about 2:1 and about 4:1 and designated in the trade as Linde 5A Molecular Sieve, has been proposed for separating certain straight chain hydrocarbons from non-straight chain hydrocarbons in a gasiform mixture thereof. Broadly, the empirical formula for such sodium calcium aluminosilicate, in dehydrated state, can be written



This sorbent can be made by exchanging calcium for some of the sodium in the sodium form of the type A zeolite, then removing crystal water. Properties and structure of the type A zeolite are described in the articles of Breck et al. and Reed et al. which appear on pages 5963-5977 of the Journal of the American Chemical Society, No. 23, volume 78. The formula (less crystal

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water) represented for the sodium form of the type A zeolite in the above-mentioned articles is



which is a multiple of six of the empirical mineralogical oxide formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. For purposes of simplicity I prefer to use the oxide sort of formula for describing the type A zeolite structure, but it will be understood that both kinds of formulae are interchangeable for purposes of reference herein to zeolites of type A structure, and, where an oxide formula concluding with " $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ " is used herein, the material being referred to is a type A zeolite.

Capacity and selectivity of said 5A Molecular Sieve for straight chain hydrocarbons are good, e.g., approximately 40-45 cc. of normal butane per gram of this mineral sorbent at temperature of 75° F. and pressure of 760 mm. Hg as against approximately 1 to 3 cc. of isobutane per gram of the sorbent under the same conditions. At room temperature and approximately atmospheric pressure this mineral sorbent becomes, for all practical purposes, saturated (i.e., it has no more capacity for a gaseous normal paraffin such as normal butane or those of higher molecular weight) after a contact time of about 15 minutes with the straight chain hydrocarbon vapor. Furthermore, it takes almost 5 minutes to reach 90% of saturation of this sorbent with normal butane at room temperature and atmospheric pressure.

It has been proposed, for example, to separate normal butane from isobutane as one typical operation with said 5A Molecular Sieve, and to separate higher normal paraffins and olefins from non-straight chain hydrocarbons in other operations by the process which comprises: contacting the mixture of non-straight and straight chain hydrocarbons in vapor phase with said 5A Molecular Sieve, thereby selectively sorbing some of the straight chain hydrocarbon; withdrawing the resulting hydrocarbon mixture depleted of straight chain hydrocarbons; and desorbing sorbed straight chain hydrocarbon from the laden mineral sorbent to fit it for reuse. Alternating from sorption to desorption and vice-versa can be done very simply and rapidly by an essentially isothermal "pressure swing" technique. This technique is more fully described hereinafter.

Efficiency of a plant for separation of straight from non-straight hydrocarbon using the contacting process outlined above is a function of the mineral sorbents' selectivity for, and sorbing and desorbing rates for the straight chain hydrocarbons in process. This becomes particularly evident in the instance of a fixed bed contacting plant wherein a substantial shortening of the sorbing phase of the operating cycle coupled with only a small reduction in capacity of the mineral sorbent for straight chain hydrocarbons will permit a greater number of operating cycles a day and, consequently, will increase the production significantly.

I have now found, in a process for separating straight chain from non-straight chain hydrocarbons in a mixture thereof, that use of a synthetic crystalline zeolite of type A structure having about 0.3 to about 0.95 of its exchangeable cation content as at least one group 2b metal selected from the group consisting of zinc and cadmium under certain controlled operating conditions hereinafter described can shorten significantly the sorbing time without a proportional sacrifice in sorbing capacity or any significant loss in selectivity. Viewed from one aspect, my invention permits the processing of a larger quantity of particular hydrocarbon mixture to desired specification with a given weight of sorbent than has been possible

heretofore. Thus, by contacting the hydrocarbon mixture with the aforementioned group 2b metal-containing type A zeolites under vapor phase sorbing conditions, I find that I can obtain 80-95% of saturation capacity of said zeolites for a straight chain hydrocarbon or hydrocarbons present in a very short time, generally in substantially less than 4 minutes, e.g., 1-3 minutes, and usually in a time as short as 1-2 minutes, or even less.

As this sorption of the straight chain hydrocarbon is occurring, there is withdrawn from sorbing contact a hydrocarbon mixture containing a reduced amount of straight chain hydrocarbon. When 80-90% saturation of my zeolite with sorbed hydrocarbons has been effected in the aforesaid short time, the feed mixture of hydrocarbons is shut off, and the laden zeolite subjected to desorbing conditions whereby previously sorbed straight chain hydrocarbon is driven off and the zeolite made ready for another cycle.

Not only can sorbing be made materially faster using the above processing technique and said group 2b metal-containing type A zeolite (as compared to using the conventional sodium calcium aluminosilicate 5A Molecular Sieve), but also desorbing appears to proceed at a correspondingly faster rate under comparable desorbing conditions. For greatest processing throughput with a given amount of mineral sorbent, desorbing is advantageously discontinued when the zeolite contains straight chain hydrocarbon material from previous sorbing operations amounting to roughly 10-20% of saturation capacity. Thus, in preferred operation both sorbing and desorbing is only 80-90% complete, but done very rapidly with short contact time.

While the hydrocarbon contacting operations with my sorbents are conducted preferably as a cyclic process with a fixed bed of sorbent particles, it is possible also to use moving or fluidized bed contact. This is particularly true when the particles of sorbent are stabilized by methods described in the following U.S. patent applications, all of which are assigned to The Texas Company: Riordan et al., Serial No. 544,244, filed on November 1, 1955; Hess et al., Serial No. 544,185, now U.S. Patent No. 2,885,368, filed on November 1, 1955; and Ray, Serial No. 599,231, filed on July 20, 1956, now U.S. Patent No. 2,947,709.

The preferred group 2b containing sorbents of my invention are most conveniently prepared by exchanging zinc and/or cadmium for sodium in the hydrated sodium form of the type A zeolite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4.5\text{H}_2\text{O}$, for example, by agitating such hydrated parent zeolite for $\frac{1}{2}$ to 12 hours in a 0.1 to 5 N aqueous zinc and/or cadmium salt solution, discarding the salt solution, and repeating the treatment with fresh solution until the necessary proportion of the sodium originally present in the structure has been replaced by the group 2b metal or metals. Operating at room temperature and pressure five changes of aqueous 1 N cadmium chloride or zinc chloride are usually adequate to obtain sufficient group 2b metal substitution for purposes of practicing my invention. After calcining or otherwise ridding the resultant sorbent of water, it is receptive to straight chain hydrocarbons.

Alternatively, a hydrated sodium-calcium form of the type A zeolite, e.g., the Linde 5A Molecular Sieve, or a hydrated sodium-lithium or hydrated sodium-potassium form of the type A zeolite, can be treated with a zinc and/or cadmium salt solution in a similar manner to produce a similarly useful type A zeolite having about 0.3-about 0.95 of its exchangeable cation content of zinc and/or cadmium. The fraction of exchangeable cation content referred to herein is computed as the ratio of the number of equivalents of the group 2b metal to the sum of the equivalents of all the exchangeable metals, e.g., Zn^{++} , Cd^{++} , Na^+ , Li^+ , K^+ , Ca^{++} etc., in the resulting type A structure.

Among the zinc salts useful in the ion exchanging are the nitrate, chloride, bromide, acetate, and sulfate. Among the cadmium salts useful in the ion exchanging are the nitrate, chloride, bromide, sulfate, acetate, and formate. The parent sodium form of the type A zeolite can be made by the processes shown in the following U.S. patent applications, both of which are assigned to The Texas Company: Sensel, Serial No. 617,734, now U.S. Patent No. 2,841,471 and Estes, Serial No. 617,735, now U.S. Patent No. 2,847,280, both filed on October 23, 1956.

FIGURE 1 of the drawing shows curves plotted from experimental results finding the percentage of saturation (ultimate capacity) obtained with n-butane at room temperature and pressure for various contact times of the n-butane with two selective mineral sorbents of my invention and one conventional selective mineral sorbent. Thus, curve A is for the conventional type A zeolite ($\text{Na}_2\text{Ca} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, i.e., the Linde 5A Molecular Sieve wherein the ratio of Ca to Na_2 was about 3:1. Curve B is for a typical sodium-zinc form of the type A zeolite of this invention wherein about 53% of the exchangeable cation content in the structure was zinc. Curve C is for a typical sodium-cadmium form of type A zeolite of this invention wherein about 40% of the exchangeable cation content in the structure was cadmium. Inspection of the figure shows that the conventional zeolite attained only about 73% of saturation with the normal hydrocarbon in two minutes, whereas the novel zeolites of my invention attained about 85% and 87½% of saturation in two minutes. Ultimately capacity of these three mineral sorbents for n-butane under the test conditions was practically the same.

N-butane sorbing characteristics for group 2b metal-containing type A zeolites having broadly 0.3 to 0.95 of their exchangeable cation content as zinc and/or cadmium and corresponding to the above test zeolites are about the same. However, for economy and efficiency of preparation, those having about 0.4-0.7 of the exchangeable cation content consisting of at least one group 2b metal selected from the group consisting of zinc and cadmium are preferred.

FIGURE 2 shows curves plotted from experimental results finding straight and non-straight chain hydrocarbon capacity and selectivity characteristics at about room temperature (75° F.) and atmospheric pressure for type A zeolites wherein the content of zinc in the zeolite was varied over a wide range. As the zinc-containing type A zeolites are made most conveniently and preferably by exchanging a portion of Na^+ ions for Zn^{++} ions in the sodium form of the type A zeolite, the test zeolites were made that way and the x axis indicates the percentage of sodium replaced by zinc in the type A structure. The capacities of the zinc-containing type A zeolites for the non-straight chain hydrocarbon, isobutane, and the straight chain hydrocarbons, normal butane and ethane, are indicated on the y axis.

FIGURE 3 shows curves plotted from experimental results finding straight and non-straight chain hydrocarbon capacity and selectivity characteristics at about room temperature (75° F.) and atmospheric pressure for type A zeolites wherein the content of cadmium in the zeolite was varied over a wide range. As these cadmium-containing type A zeolites are made most conveniently and preferably by exchanging a portion of Na^+ ions for Cd^{++} ions in the sodium form of the type A zeolite, the test zeolites were made that way and the x axis indicates the percentage of sodium replaced by cadmium in the type A structure. The capacities of the cadmium-containing type A zeolites for the non-straight chain hydrocarbon, isobutane, and the straight chain hydrocarbons, normal butane and ethane, are indicated on the y axis.

While the foregoing experimental work was done mainly with butane and isobutane, it will be understood that

these two hydrocarbons are representative of the two broad classes of hydrocarbons for purposes of this invention, namely straight chain and non-straight chain hydrocarbons, and that hydrocarbons of higher molecular weight, e.g., up to about 550° F. normal boiling point, can be treated similarly except with the reservation that temperature and/or pressure conditions must be such that the hydrocarbons are in vapor phase for sorption.

A convenient and rapid way to change from sorbing conditions to desorbing conditions in the practice of my process is to operate essentially isothermally at a temperature from about 50° to about 800° F. and to sorb under a pressure of 100 to 2000 p.s.i.g. then to desorb at lower pressure in the range from 0 to 100 p.s.i.g. or even sub-atmospheric pressure. Such operation is described in United States patent application Serial No. 484,833 of January 28, 1955, of Hess et al., also assigned to The Texas Company.

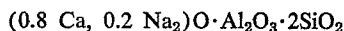
The process of my invention can also be operated wherein temperature of sorbing contact is between 50 and 500° F. and is raised for desorption. Alternatively, desorption can be done at a temperature substantially above, and at a pressure substantially below the sorbing temperature and pressure to drive off sorbed straight chain hydrocarbons. Desorbing can be done advantageously by using a subatmospheric pressure, e.g., 10 to 25 inches of Hg absolute, and/or a sweep of low molecular weight gas, e.g., hydrogen, nitrogen, isopentane, or methane to help drive off desorbed straight chain hydrocarbon vapors from the mineral sorbent.

The following examples show how type A zeolites having zinc and cadmium as a portion of their exchangeable cation content have been prepared and how such zeolites can be used in a refinery, but should not be construed as limiting the invention.

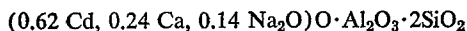
A type A zeolite in which 52.9% of the exchangeable cation content was zinc was made as follows: 30 grams of pelleted and dehydrated sodium form of the type A zeolite, marketed as Linde 4A Molecular Sieve, was allowed to soak for 36 hours at 200° F. in 70 cc. of 2.1 N aqueous ZnCl_2 solution. The exchanged zeolite was washed with water and dehydrated at 575° F. to prepare it for sorption of straight chain hydrocarbons.

A type A zeolite in which 40.4% of the exchangeable cation content was cadmium was made as follows: 30 grams of pelleted and dehydrated sodium form of the type A zeolite, marketed as Linde 4A Molecular Sieve, was allowed to soak for 36 hours at 200° F. in 70 cc. of 1.5 N aqueous CdCl_2 solution. The exchanged zeolite was washed with water and dehydrated at about 575° F. to prepare it for sorption of straight chain hydrocarbons.

A cadmium-calcium-sodium form of type A zeolite was made as follows: 30 grams of granular dehydrated calcium-sodium form of type A zeolite,

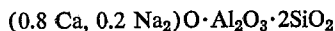


was allowed to soak in 72 cc. of 4.5 N aqueous CdCl_2 solution at 200° F. for 84 hours. The granules were washed thoroughly with water and dehydrated to remove zeolitic water. Chemical analysis of the product zeolite indicated a formula (dehydrated state) as follows:



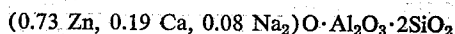
Capacity of the product at 75° F. and atmospheric pressure, found by test, was 41 cc. of ethane per gram, 37 cc. of n-butane per gram, and 4 cc. of isobutane per gram.

A zinc-calcium-sodium form of the type A zeolite was made as follows: 30 grams of granular dehydrated calcium-sodium form of type A zeolite,



was allowed to soak in 72 cc. of 4.5 N aqueous ZnCl_2 solution at 200° F. for 84 hours. The granules were

washed thoroughly with water and dehydrated to remove zeolitic water. Chemical analysis of the product zeolite indicated a formula (dehydrated state) as follows:



Capacity of the product at 75° F. and atmospheric pressure, found by test, was 31 cc. of ethane per gram, 32 cc. of n-butane per gram, and 5 cc. of isobutane per gram.

The four foregoing products were capable of attaining from 80–90% saturation (ultimate capacity) with normal butane at room temperature and atmospheric pressure in substantially less than four minutes.

A typical hydrocarbon separation contemplated with my group 2b metal-containing form of type A zeolite is the removal of straight chain hydrocarbons from stabilized, catalytically reformed motor naphtha, such naphtha having characteristics, for example, of API gravity, 48.8°; refractive index

$$\left(\frac{20^\circ \text{ C.}}{4^\circ \text{ C.}} \right)$$

about 1.444; ASTM distillation I.B.P., 126° F. and E.P., 377° F.; and ASTM research clear octane rating, 87.1.

The naphtha in vapor form is passed through a first bed of my type A zeolite in pelleted form at temperature of about 750° F., and under pressure of about 350 p.s.i.g., for 2 minutes. The zeolite has 40–70% of its exchangeable cation content a group 2b metal selected from the group consisting of cadmium and zinc with balance of sodium. Saturation of the pellets with straight chain hydrocarbon components is then about 85% complete. The unsorbed naphtha vapors emerge from the bed low in the straight chain hydrocarbon content which detracts from the octane rating of the feed stock. At this point the naphtha feed is shunted to another similar sorbent bed. A stream of recycle hydrogen from catalytic reforming of the feed naphtha is passed through the first bed, briefly under elevated pressure to purge the vessel of unsorbed material. Then the pressure on the first bed is reduced to 0 p.s.i.g. and the hydrogen is continued for about 2 minutes to desorb all but approximately 15–20% of the straight chain hydrocarbons in the laden sorbent pellets. The effluent vapors from the desorbing operation are used as part of the recycle feed to the naphtha reforming process.

I claim:

1. In a process for the separation of straight chain hydrocarbons from a mixture of straight chain and non-straight chain hydrocarbons wherein the mixture is contacted under vapor phase hydrocarbon sorbing conditions with a dehydrated crystalline zeolite of type A structure having at least a part of its exchangeable cation content replaced with a divalent metal ion for a period of time sufficient to effect sorption of said straight chain hydrocarbon by said zeolite, and thereafter desorbing straight chain hydrocarbon from the laden zeolite, the improvement which comprises contacting said mixture with a type A zeolite wherein about 0.3 to about 0.95 of the exchangeable cation content is divalent cadmium for a period within the range of 1 to 4 minutes sufficient to effect about 80 to 95 percent saturation of said zeolite with the straight chain hydrocarbon present in the mixture.

2. A process according to claim 1 wherein from about 0.4 to about 0.7 of the exchangeable cation content of the zeolite is cadmium.

3. A process according to claim 1 wherein the contact period is from 1 to 2 minutes.

4. A process according to claim 1 wherein the exchangeable cation content of said zeolite is cadmium, calcium and sodium.

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