

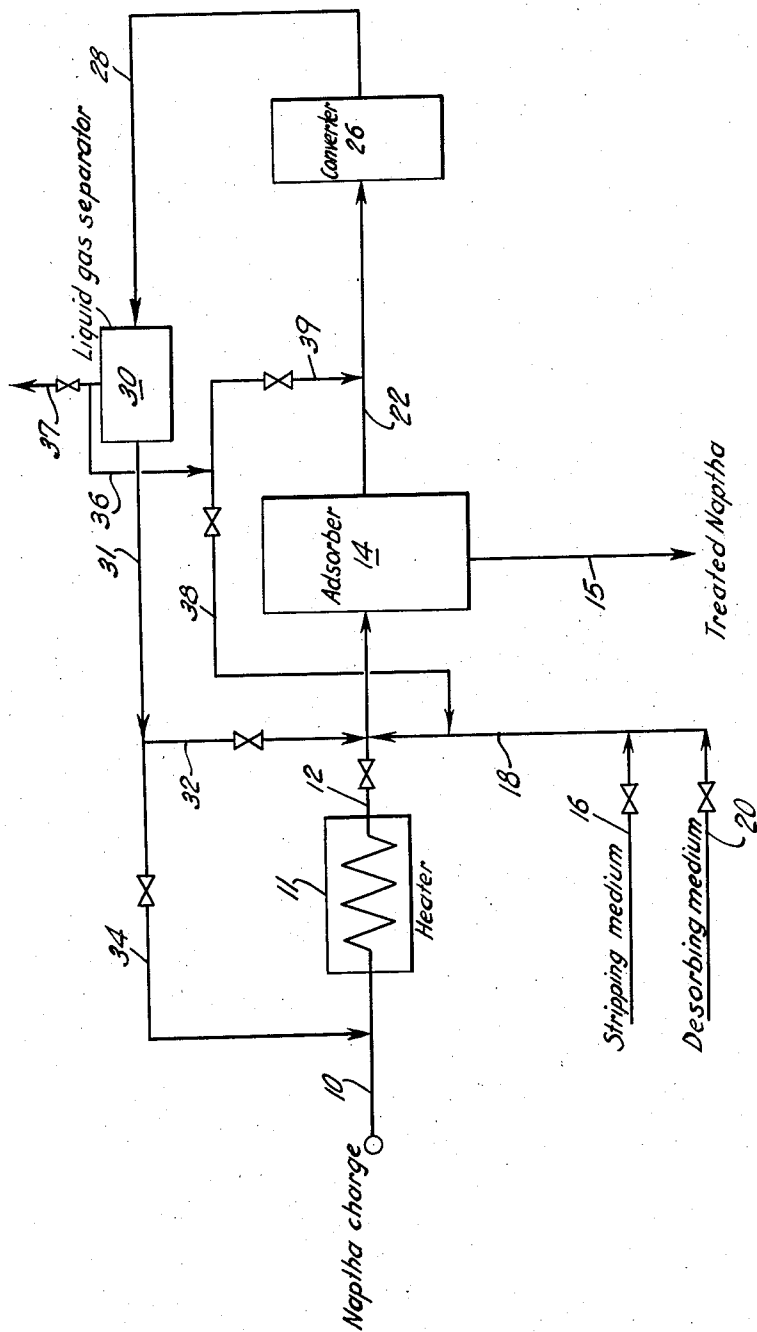
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NAPHTHA TREATING PROCESS

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2,886,509

NAPHTHA TREATING PROCESS

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This invention relates to a process for the treatment and conversion of petroleum fractions. More particularly, the invention relates to the treatment of light naphthas boiling in the range 40–225° F., more or less, and containing straight chain and non-straight chain hydrocarbons, such as light straight run naphthas and light catalytic reformed (Platformate) naphthas.

Light naphthas are generally characterized by having relatively low octane numbers. This is due to the high proportion of low octane normal paraffins, such as n-pentane, n-hexane and n-heptane, in such naphthas. Because of their relatively low octane number, light naphthas are not well suited for blending in high octane fuels.

Various processes have been proposed for upgrading or improving the octane rating of light naphthas. Generally, these processes have as a major purpose the conversion of low octane straight chain hydrocarbons (n-paraffins) into branched chain or cyclic hydrocarbons which have substantially higher octane ratings. Such conversions are quite difficult, however, due to the refractory nature of the relatively low molecular weight, C₉ and lower, straight chain hydrocarbons. The low molecular weight straight chain hydrocarbons may be converted to higher octane branched or cyclic hydrocarbons only under relatively severe treating conditions. Under certain conditions suitable for the conversion of straight chain hydrocarbons to non-straight chain cyclic hydrocarbons the straight chain hydrocarbons are subject to cracking with resultant formation of gas (methane, ethane and propane) and carbon. The formation of gas and carbon during these treating processes substantially reduces the amount of liquid hydrocarbons recoverable and therefore adversely affects the commercial attractiveness of such processes.

A principal object of this invention is to provide an improved hydrocarbon conversion process. Another object is to provide a process for the conversion of hydrocarbon fractions containing substantial amounts of straight chain hydrocarbons. Still another object is to provide a process for upgrading light naphthas boiling in the range 40–225° F., and containing a substantial amount of straight chain hydrocarbons. A further object is to provide a process wherein the normal paraffin content of light naphthas is converted to higher octane products in a scheme effective to substantially eliminate straight chain hydrocarbons from the final product. How these and other objects of the invention may be accomplished will become more obvious from the accompanying detailed description and the drawing which schematically illustrates an embodiment of the practice of this invention.

In accordance with our invention, a light naphtha is contacted with a solid adsorbent, which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons, to adsorb straight chain hydrocarbons from said naphtha followed by desorption of the adsorbed straight chain hydrocarbons from the adsorbent, conversion of the desorbed straight chain hydrocarbons into a mixture of straight

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chain and non-straight chain hydrocarbons and recycle of this mixture to the adsorption step for the removal of straight chain hydrocarbons from the mixture.

A petroleum fraction suitable for use in the practice of this invention might have an initial boiling point of about 40° F. and an end point of about 225° F., more or less. Furthermore, such a petroleum fraction must contain both straight chain and non-straight chain hydrocarbons and might have the following composition:

Hydrocarbon type:	Percent by vol.
Naphthenes	0–90
Aromatics	0–90
Saturates (including normal paraffins and iso-paraffins)	3–90
Unsaturates (including normal olefins and iso-olefins)	0–50

Any solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons can be employed in the practice of this invention. It is preferred, however, to employ as the adsorbent certain natural or synthetic zeolites or aluminosilicates such as a calcium aluminosilicate which exhibit the property of a molecular sieve, that is adsorbents made up of porous matter or crystals wherein the pores are of molecular diameter and are of uniform size. A particularly suitable solid adsorbent for the adsorption of straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons is a calcium aluminosilicate manufactured by Linde Air Products Company and designated Type 5A molecular sieve. The crystals of this particular calcium aluminosilicate, apparently actually a sodium calcium aluminosilicate, have a pore size or diameter of about 5 Angstrom units, a pore size sufficient to admit straight chain hydrocarbons, such as the n-paraffins, to the substantial exclusion of the non-straight chain hydrocarbons, such as the naphthenic, aromatic, iso-olefinic and iso-paraffinic hydrocarbons, e.g., isobutane and higher. This particular selective adsorbent is available in various sizes such as 1/16" and 1/8" diameter pellets as well as in a finely-divided powder form.

Other selective adsorbents may be employed in the practice of this invention. For example, it is contemplated that selective adsorbents having the property of selectively adsorbing straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons in the manner of a molecular sieve may be obtained by suitable treatment of various oxide gels, especially metal oxide gels of the polyvalent amphoteric metal oxides.

Other suitable selective adsorbents are known and include the synthetic and natural zeolites which, when dehydrated, may be described as crystalline zeolites having a rigid three dimensional anionic network and having interstitial dimensions sufficiently large to adsorb straight chain hydrocarbons but sufficiently small to exclude the non-straight chain hydrocarbons. The naturally occurring zeolite, chabazite, exhibits such desirable properties. Another suitable naturally occurring zeolite is analcite (NaAlSi₂O₆·H₂O) which, when dehydrated, and when all or part of the sodium is replaced by an alkaline earth metal, such as calcium, yields a material which may be represented by the formula (CaNa)Al₂Si₄O₁₂·2H₂O and which, after suitable conditioning, will adsorb straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons. Naturally occurring, or synthetically prepared phacolite, gmelinite, harmotome, and the like or suitable modifications of these products by base exchange, are also applicable in the practice of this invention.

Other solid adsorbents which selectively adsorb straight chain hydrocarbons such as n-paraffins and n-olefins to

the substantial exclusion of non-straight chain hydrocarbons, including the aromatic and naphthenic hydrocarbons, are known.

The naphtha undergoing treatment for the removal of straight chain hydrocarbons therefrom may be present either in the liquid phase or gas or vapor phase. The capacity of the solid adsorbent as a selective adsorbent for straight chain hydrocarbons is substantially unaffected by the phase condition of the hydrocarbons in contact therewith, provided, of course, sufficient time is allowed to substantially saturate the adsorbent. It is preferred in the practice of the invention to maintain the naphtha in a vapor phase while in contact with the solid adsorbent. Contact of the naphtha with the adsorbent may be effected by any suitable means for effecting gas-solid or liquid-solid contacting and the selective adsorbent may be maintained as a fixed bed, a moving bed or a fluent or fluid bed of finely divided particles.

When liquid phase contacting is carried out for the removal of straight chain hydrocarbons from the naphtha, it is preferred to conduct the adsorption operation at a temperature in the range 50–500° F. or higher, sufficient pressure being applied, if necessary, to maintain the naphtha in the liquid phase. In vapor phase adsorption it is preferred to carry out the adsorption operation at a temperature at least sufficient to maintain substantially all of the naphtha undergoing treatment in the vapor phase, such as a temperature in the range 250–700° F.

The naphtha undergoing treatment is desirably maintained in contact with the selective adsorbent until substantially all of the straight chain hydrocarbons have been removed therefrom or until the selective adsorbent has become substantially saturated with respect to straight chain hydrocarbons. When the adsorbent is substantially saturated, so that straight chain hydrocarbon adsorption is no longer possible, the naphtha fraction is contacted with fresh or regenerated adsorbent. The straight chain hydrocarbons are desorbed from the adsorbent, thereby regenerating the adsorbent, by contacting the adsorbent with a stripping medium which displaces or purges the adsorbed straight chain hydrocarbons from within the pores of the selective adsorbent. Exemplary of a suitable gaseous stripping medium are nitrogen, methane, hydrogen, flue gas, carbon dioxide, natural gas, propane, n-butane, isobutane, and steam, preferably superheated steam, or mixtures thereof. In general, any vaporized or gaseous material is suitable as a stripping medium provided it is readily separable by suitable means, as by fractionation, from the desorbed straight chain hydrocarbons. Desirably, when superheated steam is employed as the stripping medium, it is followed by another gaseous stripping medium such as an inert purge gas, e.g. methane, in order to sweep the steam from within the pores of the adsorbent.

The desorption operation can be carried out at any suitable temperature. A desorption temperature in the range 500–1100° F. has been found to be satisfactory. Although the desorption temperature is usually 100–300° F. higher than the adsorption temperature, such as a temperature in the range 700–1000° F., the desorption operation may be carried out at substantially the same temperature as the adsorption temperature. Desorption of the straight chain hydrocarbons may also be effected in the liquid phase by contacting the adsorbent with a polar liquid, e.g. water which is preferentially adsorbed over the straight chain hydrocarbons, at a suitable elevated temperature as indicated above.

After the straight chain hydrocarbons have been desorbed, they are recovered and subjected to a suitable conversion operation. Suitable conversion operations include catalytic reforming, aromatization, dehydrocyclization, isomerization and thermal cracking or reforming in order to upgrade the desorbed straight chain hydrocarbons into more valuable higher octane hydrocarbons. Preferably, the conversion operation is an isomerization

operation employing an isomerization catalyst, such as a platinum-containing catalyst or an aromatization operation employing a chromia-containing catalyst.

Isomerization of the desorbed straight chain hydrocarbons is desirably effected by contacting the desorbate with a platinum-containing catalyst, such as a U.O.P. platforming catalyst. Isomerization may be conducted over a wide range of operating conditions. Suitable conversion temperatures range from 200–900° F. more or less, preferably in the range 400–800° F. The pressure may vary from 0–2000° F. p.s.i.g., a pressure in the range 50–750 being preferred. The space velocity of the hydrocarbon feed in the isomerization may range between 0.25 to 10 v./hr./v. and the hydrogen recycle rate from 500 to 10,000 cu. ft./bbl. of feed.

Isomerization or conversion of the desorbed straight chain hydrocarbons produces an upgraded mixture of straight chain and non-straight chain hydrocarbons. The mixture so produced is further upgraded by recycling it back to the adsorption step for the removal of straight chain hydrocarbons from the mixture. In this manner, the straight chain hydrocarbons are continuously removed and the treated and upgraded product issuing from the adsorber is substantially free of straight chain hydrocarbons.

Referring now to the drawing, there is schematically illustrated an embodiment of the practice of this invention. Referring to the drawing in detail, a light straight run naphtha boiling in the range 40 to 225° F. is introduced via line 10 to heater 11. In heater 11, the naphtha is brought up to a suitable temperature preparatory to the adsorption operation. From heater 11, the naphtha is passed via line 12 to adsorber 14. Adsorber 14 contains a bed of solid selective adsorbent, Linde Type 5A molecular sieve, for the adsorption of straight chain hydrocarbons. Conditions within the adsorber to effect the adsorption of straight chain hydrocarbons may range between temperatures of 200 to 700° F. and pressures from 0 to 600 p.s.i.g. After a suitable residence time within adsorber 14 to effect the adsorption of straight chain hydrocarbons, the naphtha, substantially free of straight chain hydrocarbons, is recovered via line 15 as a finished or treated product. To completely remove the treated naphtha from adsorber 14, the adsorber is purged with a stripping medium (which desirably is the same as the desorbing medium) to displace the treated naphtha from the adsorber. Effective stripping mediums include gases such as nitrogen, carbon dioxide, methane, hydrogen and the like. The stripping medium is introduced to adsorber 14 via lines 16, 18 and 12, as indicated in the drawing.

Following completion of the adsorption phase, the adsorbent is subjected to desorption to effect the removal of straight chain hydrocarbons therefrom, i.e. to regenerate the adsorbent. Suitable desorption conditions include temperatures in the range 500–1100° F., generally 100–300° F. above adsorption temperatures, and pressures in the range 0–600 p.s.i.g. usually lower than the adsorption pressure. Isobaric and/or isothermal adsorption desorption conditions may be employed if desired.

Desorption is materially aided by the introduction of a gaseous desorbing medium which may consist of hydrogen, nitrogen, carbon monoxide, carbon dioxide, methane, flue gas, steam and others to strip the normal paraffins from the adsorbent. The desorbing medium is introduced via lines 20, 18 and 12 into adsorber 14 and the resulting desorbed straight chain hydrocarbons admixed with the gaseous desorbing medium is carried via line 22 into converter 26.

Converter 26 may consist of any converter unit suitable for transforming straight chain hydrocarbons into branched chain or cyclic hydrocarbons. Converter 26 is desirably an isomerization unit packed with a fixed bed of platinum-containing isomerization catalyst. In converter 26, the straight chain hydrocarbons are contacted with the isomerization catalyst under isomerizing condi-

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tions of temperature and pressure. The straight chain hydrocarbons are converted into branched chain hydrocarbons of substantially the same carbon content but of higher octane value. The effluent from converter 26, which contains a mixture of straight chain and non-straight chain hydrocarbons is passed via line 28 to liquid-gas separator 30 to effect the removal of gaseous products formed within or carried into converter 26. Gaseous products are removed via line 37. The gaseous effluent removed via line 37 when containing a substantial amount of hydrogen, greater than 50 vol. percent, if desired, is advantageously employed as the stripping or desorbing medium for adsorber 14 via lines 36, 38, 18 and 12, or recycled directly to converter 26 via lines 36, 39, and 22. The mixture of straight chain and non-straight chain hydrocarbons separated in liquid-gas separator 30 is passed via lines 31, 32 and 12 into adsorber 14 to effect the adsorption of the straight chain hydrocarbons from the treated product. By operating in this manner, it is possible to substantially completely remove straight chain hydrocarbons from the treated product. If desired, the mixture of straight chain and nonstraight chain hydrocarbons may be recycled to heater 11 via lines 31 and 34 in order to bring the mixture to the proper temperature prior to introduction into adsorber 14.

The following example illustrates the practice of this invention.

EXAMPLE I

A light straight run naphtha having a research clear octane number of about 69 and a boiling range of 46–226° F. was contacted with a sodium calcium aluminosilicate adsorbent, Linde Type 5A molecular sieve, in the following manner in accordance with our invention. The naphtha was vaporized and maintained in the vapor phase at a temperature about 250° F. These vapors were passed over a fixed bed of adsorbent at a space velocity of about 0.5–1.0 v./hr./v. Following the adsorption step,

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Blending of the treated naphtha and the treated isomate gives a blend having a research clear octane number of about 83.

Another mixture of straight chain hydrocarbons comparable to the hydrocarbons desorbed from the solid adsorbent and having a research clear octane number of about 39 was contacted with a U.O.P. dehydrogenation catalyst consisting of chromic oxide, magnesium oxide and aluminum oxide. The mixture of straight chain hydrocarbons was contained at a pressure of 40 p.s.i.g. and a space velocity of 0.4 v./hr./v. in the presence of hydrogen at a recycle rate of 1200 cu. ft./bbl. Contacting temperatures and the results obtained are given in Table I below:

Table I

Temperature, °F	920	943
Wt. Percent Recovery	93.8	81.3
Bromine No.	20	22
Vol. Percent Aromatics	15	13
ASTM Res. Cl. Oct. Prod.	60.6	57.6
+3 cc. TEL/gal	80.4	80.2

Other mixtures of straight chain hydrocarbons comparable to the straight chain hydrocarbons recovered during the desorption operation having compositions of about 23% by volume n-pentane, 56% by volume n-hexane and 21% by volume n-heptane and exhibiting a research clear octane number of 39 were contacted with various catalysts under isomerizing conditions including a pressure of 500 p.s.i.g., a space velocity of 1.0 v./hr./v. and a hydrogen recycle rate of 4000 cu. ft./bbl: The catalysts, reaction temperatures, and research clear octane numbers of the converted products and of the finished products, i.e. converted products after having been contacted with adsorbent for the removal of straight chain hydrocarbons, are set out in Table II below:

Table II

Temp., °F	800			850			900		
	Plat.	Baker	Ultra	Plat.	Baker	Ultra	Plat.	Baker	Ultra
Catalyst									
Liq. Rec., Wt. Percent	95.9	99.3	90.1	95.0	99.0	88.2	67.6	70.1	72.7
Converted Product, Octane No.	60.0	51.0	54.0	75.4	74.0	77.1	89.6	70.0	78.9
Product Finished by Selective Adsorption, Octane No.	78.0	61.0	72.0	84.0	82.0	82.6		80.3	

Plat.—UOP platforming catalyst.

Baker—Sinclair-Baker RD 150 catalyst.

Ultra—Standard of Indiana Ultraforming catalyst.

the treated naphtha, now substantially free of straight chain hydrocarbons, was tested and found to have a research clear octane number of about 83.7. The adsorbed hydrocarbons were recovered and found to be substantially normal paraffinic having a low octane number.

A mixture of straight chain hydrocarbons, comparable to the aforesaid straight chain hydrocarbons recovered during the desorption operation, having a composition of about 23% by volume normal pentane, 56% by volume normal hexane and 21% by volume normal heptane and exhibiting a research clear octane number of 39 was contacted with a platinum isomerization catalyst at a temperature about 850° F., a pressure of 500 p.s.i.g. and a space velocity of 1 v./hr./v. employing a hydrogen recycle rate of about 4000 standard cubic feet per barrel of charge. The resulting isomate was produced in 99 weight percent yield and consisted of a mixture of straight chain and nonstraight chain hydrocarbons having a research clear octane number of about 74. This isomate was vaporized and contacted with the solid selective adsorbent for the removal of straight chain hydrocarbons under conditions similar to those employed in treating the feed naphtha. The thus treated isomate exhibited a research clear octane number of about 82.0.

The foregoing example illustrates how a light naphtha may be treated to produce an upgraded light naphtha blending stock. The advantages of this process are apparent. Only the straight chain hydrocarbons are subjected to the hydrocarbon conversion step thereby increasing the branched chain hydrocarbon content of the total naphtha. Another advantage due to the recycle adsorption step from the converting operation is that the upgraded product is substantially free of the relatively low octane straight chain hydrocarbons.

This application is a continuation-in-part of our co-pending patent application Serial No. 478,426, filed December 29, 1954.

Obviously, many modifications and changes may be made in the process of this invention without departing from the spirit or scope thereof, and therefore only those limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for treating a hydrocarbon fraction boiling in the range 40–225° F., said fraction containing straight chain and non-straight chain hydrocarbons, said straight chain hydrocarbons including n-hexane, n-heptane and n-octane, said non-straight chain hydrocarbons com-

prising isoparaffinic, naphthenic and aromatic hydrocarbons, which comprises contacting said fraction in the gaseous phase with a solid alumino-silicate molecular sieve adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb only the straight chain hydrocarbons from said fraction, desorbing the adsorbed straight chain hydrocarbons from said adsorbent by contact with gaseous hydrogen, isomerizing the resulting desorbed straight chain hydrocarbons in the presence of said hydrogen to form a mixture of straight chain and non-straight chain hydrocarbons, separating said mixture from said hydrogen and recycling said mixture to contact said adsorbent for the removal of straight chain hydrocarbons from said mixture.

2. A process for treating a hydrocarbon fraction boiling in the range 40-225° F., said fraction containing straight chain and non-straight chain hydrocarbons, which comprises contacting said fraction in the gaseous phase with a solid alumino-silicate molecular sieve adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb only the straight chain hydrocarbons from said naphtha, desorbing the adsorbed straight chain hydrocarbons from said adsorbent with gaseous hydrogen catalytically converting the resulting desorbed straight chain hydrocarbons in contact with said hydrogen into a mixture of straight chain and non-straight chain hydrocarbons, separating said mixture from said hydrogen, recycling said mixture of straight chain and non-straight

chain hydrocarbons to contact said adsorbent and recycling said hydrogen to said catalytic converting operation and to the aforesaid desorption operation.

3. A process for treating a hydrocarbon fraction boiling in the range 40-225° F., said fraction containing straight chain and non-straight chain hydrocarbons, said straight chain hydrocarbons including n-hexane, n-heptane and n-octane, said non-straight chain hydrocarbons comprising isoparaffinic, naphthenic and aromatic hydrocarbons which comprises contacting said fraction in the gaseous phase with a solid alumino-silicate molecular sieve adsorbent which selectively adsorbs straight chain hydrocarbons to adsorb only the straight chain hydrocarbons from said naphtha, desorbing the adsorbed straight chain hydrocarbons from said adsorbent with gaseous hydrogen, catalytically converting said straight chain hydrocarbons in the presence of said hydrogen into a mixture of straight chain and non-straight chain hydrocarbons, separating said mixture from said hydrogen, recycling said mixture of straight chain and non-straight chain hydrocarbons to contact said adsorbent and recycling said hydrogen to said desorption operation.

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