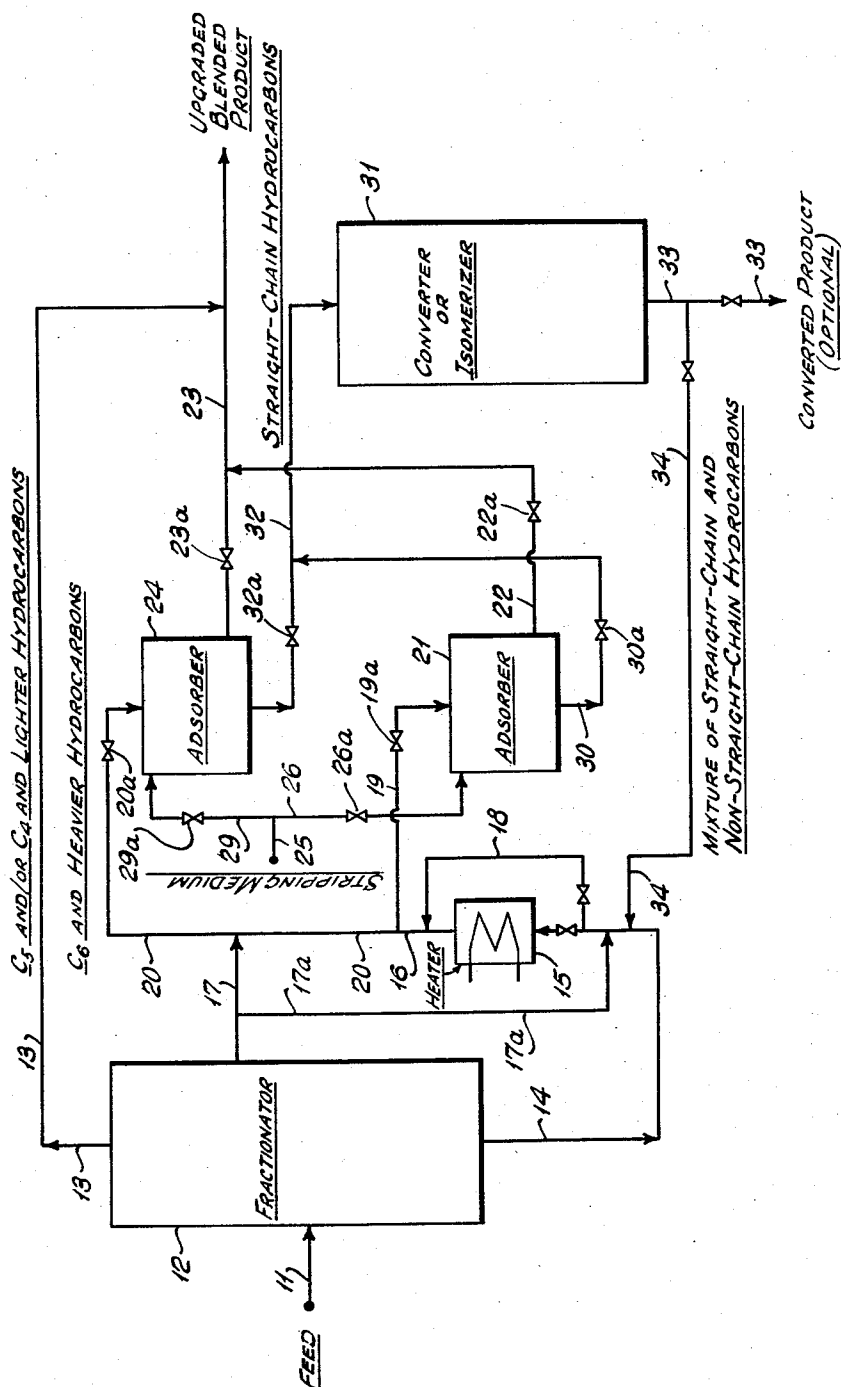


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METHOD OF TREATING A PETROLEUM FRACTION WITH MOLECULAR SIEVE ADSORBENTS

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This invention relates to a method of treating petroleum fractions. More particularly, this invention relates to a method of treating petroleum fractions containing relatively low molecular weight hydrocarbons such as C_4 hydrocarbons and/or C_5 hydrocarbons in admixture with relatively high molecular weight straight chain and non-straight chain hydrocarbons, such as hydrocarbons having a molecular weight in a range C_6 – C_{10} and higher. In accordance with one embodiment of this invention there is provided an improved non-catalytic method for upgrading a petroleum fraction in the naphtha boiling range, such as a naphtha fraction having an initial boiling point (I. B. P.) in a range 35–80° F. and an end point (E. P. in a range about 150–425° F., e. g. a light straight run naphtha.

Various processes have been proposed for the treatment of naphtha stocks to produce a high quality, high octane motor fuel. These processes call for the vapor phase treatment of selected petroleum fractions in the gasoline boiling range by contact with an active converting, reforming or isomerizing catalyst, such as a platinum-containing catalyst, (e. g. so-called platforming catalyst), a chromia-alumina catalyst, a cobalt molybdate, a molybdena-alumina catalyst or the like.

During the treatment of these selected petroleum fractions a number of reactions may take place simultaneously, e. g. isomerization, dehydrogenation, cyclization, dehydrocyclization and the like. At the same time some of the higher molecular weight hydrocarbons are converted to lower molecular weight hydrocarbons such as the normally gaseous hydrocarbons, butane, propane and the like with the result that the yield of recoverable normal liquid hydrocarbons is substantially lower than the amount of normally liquid hydrocarbons charged to the catalytic conversion operation.

Accordingly, it is an object of this invention to provide an improved process for treating a petroleum fraction in the naphtha boiling range.

It is another object of this invention to provide an improved process for upgrading petroleum fractions in the naphtha boiling range, said fractions containing straight chain hydrocarbons and non-straight chain hydrocarbons in admixture with relatively low boiling, low molecular weight hydrocarbons, such as hydrocarbons in a molecular weight range C_5 and/or C_4 and lower.

Another object of this invention is to provide a non-catalytic method for upgrading a hydrocarbon fraction such as a light straight run naphtha fraction whereby a relatively improved, high octane, high quality motor fuel is produced.

Yet another object of this invention is to provide a method of treating a light straight run naphtha containing butane and/or isopentane and/or normal pentane in admixture with higher molecular weight straight chain and non-straight chain hydrocarbons whereby there is produced after treatment, in accordance with this inven-

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tion, a naphtha fraction having an improved quality as a motor fuel.

Another object of this invention is to provide an integrated combination process for treating a naphtha fraction, such as a light straight run naphtha, whereby there is produced a substantially increased amount of high octane normally liquid hydrocarbons as compared with conventional processes operated at the same octane product level for upgrading such fractions into a high octane motor fuel.

How these and other objects of this invention are achieved will become more apparent with reference to the accompanying disclosure and drawing which schematically illustrates an embodiment of the practice of this invention.

In accordance with our invention, we have provided an improved operation for treating or converting a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises fractionating said fraction to produce overhead a selected fraction containing relatively low boiling, low molecular weight hydrocarbons, and subjecting the remaining fraction (now containing a reduced amount of low molecular weight hydrocarbons) to contact 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 remaining fraction and subsequently blending the aforementioned overhead fraction with the effluent from the aforesaid adsorption operation, which effluent is substantially free of straight chain hydrocarbons, to produce a blended product having improved qualities as motor fuel.

By straight chain hydrocarbon is meant any aliphatic or acyclic or open chain hydrocarbon which does not possess side chain branching or cyclic structure. Representative straight chain hydrocarbons are, of course, the normal paraffins and the normal olefins, mono- or polyolefins, including the straight chain acetylenic hydrocarbons. The non-straight chain hydrocarbons comprise the aromatic and naphthenic hydrocarbons as well as the isoparaffinic and isoolefinic hydrocarbons and the like.

A petroleum fraction suitable for use in the practice of this invention might have an initial boiling point in the range 35–100° F. and an end point in the range of 150–425° F., more or less. A petroleum fraction suitable for use in the practice of this invention must contain both straight chain and non-straight chain hydrocarbons and might have the following composition:

Hydrocarbon type:	Percent by volume
Naphthenes	0–75
Aromatics	0–50
Paraffins (including n-paraffins and isoparaffins)	5–90
Unsaturates (including n-olefins and isoolefins)	0–50

The straight chain hydrocarbons, e. g. n-paraffin content of a petroleum fraction particularly suitable for use in the practice of this invention is usually in the range 5–75% by volume. Typical refinery stocks or fractions, such as a total or wide boiling straight run naphtha, a light straight run naphtha, a thermally cracked or thermally reformed naphtha may be upgraded to produce an improved motor fuel by employing the practice of this invention. Exemplary of a petroleum fraction suitable for use in the practice of this invention is a light straight run naphtha having a boiling range in the range 45–225° F., and an octane number, clear, in the range 45–85.

Any solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-

straight chain hydrocarbons may be employed in the practice of this invention. It is preferred, however, to employ as the selective adsorbent certain natural or synthetic zeolites or aluminosilicates such as a calcium aluminosilicate e. g. sodium calcium aluminosilicate, which exhibit the property of a molecular sieve, i. e. materials made up of porous crystals or containing pores wherein the pores are of molecular dimension and of uniform size, sufficiently large to permit the entry of straight chain hydrocarbons to the exclusion of the non-straight chain hydrocarbons.

A particularly suitable selective adsorbent for straight chain hydrocarbons is a calcium aluminosilicate manufactured by the Linde Air Products Company and designated Linde 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, sufficiently large to admit straight chain hydrocarbons such as the n-paraffins and the n-olefins up to at least C_{14} in chain length to the substantial exclusion of the naphthenic, aromatic hydrocarbons as well as isoparaffins, isobutanes and higher and the isoolefinic hydrocarbons. This particular selective adsorbent is available in various sizes. Any suitable selective adsorbent for straight chain hydrocarbons may be employed in the practice of this invention. It is contemplated that selective adsorbents having the property of selectively adsorbing straight chain hydrocarbons to the substantial exclusion of the non-straight chain hydrocarbons in the manner of a molecular sieve may be obtained by suitably treating the various oxide gels, especially metal oxide gels of the polyvalent amphoteric metal oxides.

Other suitable solid 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 dimension sufficiently large to adsorb straight chain hydrocarbons but sufficiently small to exclude non-straight chain hydrocarbons. The natural zeolite chabazite exhibits such desirable properties. Another suitable natural zeolite is analcite $NaAlSi_3O_8 \cdot H_2O$ which, when dehydrated, and when all or part of the sodium is replaced by calcium, yields a material which may be represented by the formula $(Ca, Na_2)Al_3Si_4O_{12} \cdot 2H_2O$ and which, after suitable conditioning, will adsorb straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons. Other naturally occurring or synthetically prepared zeolites are gmelinite, harmotome, phacolite and the like, or suitable modifications of these produced by base exchange are also suitable.

Other solid adsorbents which selectively adsorb straight chain hydrocarbons such as the n-paraffins and the n-olefins to the substantial exclusion of the non-straight chain hydrocarbons are known.

The adsorption operation or the separation of the straight chain hydrocarbons from an admixture containing the same together with non-straight chain hydrocarbons is effected by direct contact between the mixture containing the straight chain hydrocarbons and the particular selective adsorbent employed. The mixture being separated or treated for the adsorption of the straight chain hydrocarbons therefrom may be in a liquid phase or in the gaseous or vaporous phase. Any suitable means or method for effecting liquid-solid contact or vapor-solid contact may be employed in the practice of this invention. For example in presumably the simplest operation a liquid mixture containing straight chain hydrocarbons to be separated therefrom may be directly contacted with solid selective adsorbent to form a slurry. After sufficient time has been allowed for the adsorption of the straight chain hydrocarbons, the liquid phase is separated from the slurry and the remaining solid ad-

sorbent is separately treated for the removal or desorption of the straight chain hydrocarbons therefrom.

The solid adsorbent may be in the form of a fixed bed, a moving bed, a fluidized bed, and the mixture undergoing treatment for the separation of the straight chain hydrocarbons therefrom may pass in a direct concurrent or counter-current contact with the selective adsorbent. The various known means and methods for effecting liquid or vapor contact with a solid material are applicable in the practice of this invention.

The adsorption operation may take place at any temperature in the range 50–700° F. and higher depending upon whether or not it is desired to maintain the mixture undergoing separation in the liquid or vapor phase and depending to some extent upon the composition of the mixture undergoing treatment, and the amount of the straight chain hydrocarbons desired to be removed therefrom. Also, any desired adsorption pressure may be employed, depending upon whether it is desired to carry out liquid or vapor phase adsorption. In a liquid phase operation it is preferred to maintain the adsorption temperature in the range 50–200° F., more or less. In a vapor phase adsorption operation, it is preferred to maintain the adsorption temperature in a temperature range 200–500° F., more or less.

After the adsorption of the straight chain hydrocarbons by the selective adsorbent employed has been carried out to the desired extent the selective adsorbent is treated to desorb and separately recover the straight chain hydrocarbons therefrom. Desorption of the straight chain hydrocarbons is conveniently effected by the application of heat and is preferably effected by contacting the adsorbent with a hot stripping medium such as flue gas, nitrogen, methane, hydrogen, carbon dioxide, air or oxygen-containing gas under controlled temperature conditions, gaseous low boiling hydrocarbons, such as dry natural gas, superheated steam and the like. Usually a temperature in the range 300–1300° F., preferably a temperature in the range 500–1000° F. is sufficient to effect substantially complete desorption of the straight chain hydrocarbons from the selective adsorbent. Although the desorption temperature may be the same as the adsorbent temperature, it is sometimes desirable to maintain the desorption temperature about 100–300° F. higher than the adsorption temperature. As a general rule the desorption temperature should be high enough so that the adsorbed straight chain hydrocarbons are relatively quickly desorbed without at the same time causing destruction of the selective adsorbent or decomposition or cracking of the adsorbed-desorbed straight chain hydrocarbons. Liquid water, such as superheated water, i. e. water at a temperature greater than 212° F. at superatmospheric pressure, may also be employed as a desorbing medium in the practice of this invention. It is preferred to employ steam or superheated steam as the desorption or stripping medium since, after the desorption of the straight chain hydrocarbons has been effected by superheated steam, the recovery of the straight chain hydrocarbons is effected by simply condensing the steam. It is advantageous to displace the steam now adsorbed to some extent by adsorption within the pores of the adsorbent, by contacting the adsorbent with a purge gas such as a flue gas, nitrogen, hydrogen, natural gas or the like in order to sweep the steam from the pores of the adsorbent.

Referring now to the drawing which schematically illustrates an embodiment of the practice of this invention, a suitable feed petroleum fraction such as a naphtha fraction, e. g. a light naphtha fraction, having an end point in the range 150–425° F. and containing a substantial amount of hydrocarbons (in the range 20–80% by vol.) in the molecular weight range C_4 – C_{12} is introduced via line 11 into fractionator 12 wherein it is fractionated to produce overhead a low boiling or relatively low molecular weight fraction containing substantially all of the C_4 and C_5 hydrocarbons present

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in the feed fraction. Desirably substantially all of the hydrocarbons present in the overhead fraction should have a boiling point below about 100° F. Preferably, in accordance with one embodiment of this invention fractionator 12 is operated under such conditions with the overhead fraction therefrom containing substantially all of the C₄ hydrocarbons and isopentane in the feed, leaving behind a bottoms fraction containing substantially all of the n-pentane and higher molecular weight hydrocarbons originally present in the feed fraction.

The overhead fraction removed from fractionator 12 via line 13 will comprise normal butane and isopentane and varying amounts of n-pentane and even higher molecular weight hydrocarbons depending upon the operation of fractionator 12. Normal butane has an octane number of about 95 and isopentane an octane number of about 92; accordingly, these materials are particularly useful as blending components in a motor fuel gasoline. Normal pentane has an octane number of about 61 and accordingly is less desirable as a motor fuel blending agent than the other aforementioned hydrocarbons.

There is recovered from fractionator 12 a liquid bottoms fraction via line 14 or a vaporous side stream fraction via lines 17 or 17a, each substantially free of C₄ and C₅ hydrocarbons. The bottoms fraction in line 14 or the side stream fraction in line 17a is introduced into heater 15 wherein it is vaporized and/or brought up to a suitable adsorption temperature such as a temperature in the range 250–500° F. Heater 15, if desired, may be bypassed via line 18. The resulting vaporized bottoms or side stream fraction issues from heater 15 via line 16 and is introduced via line 19 (valve 19a being open and valve 20a being closed) into adsorber 21 wherein it passes downwardly in direct contact with a fixed bed of selective adsorbent which selectively adsorbs the straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons. Adsorber 21 is operated at a suitable adsorption temperature, as previously indicated, and at a throughput such that the effluent issuing from adsorber 21 via line 22 (valve 22a being open) is substantially free of straight chain hydrocarbons. More particularly adsorber 21 is operated under such conditions of temperature and pressure, consistent with liquid or vapor phase contacting, and at a throughput (such as a space velocity in the range 0.25–25 v./hr./v.) such that substantially all of the straight chain hydrocarbons, e. g. straight chain hydrocarbons having a molecular weight in the range C₆–C₁₂ and higher, contained in the fraction undergoing treatment, are adsorbed. The effluent issuing from adsorber 21 through line 22 (valve 22a being open) is introduced into line 23 (valve 23a being closed) wherein it is blended or admixed with the previously separated overhead fraction flowing in line 13 to produce a blended product having a higher octane number and improved properties as a motor fuel.

When the selective adsorbent within adsorber 21 has become substantially saturated with respect to straight chain hydrocarbons or when the selective adsorbent within adsorber 21 is no longer able to adsorb straight chain hydrocarbons at the desired rate, valve 19a is closed and valve 20a is open with the result that the fraction to be treated is introduced via line 20 into adsorber 24 wherein it is contacted with fresh or regenerated selective adsorbent in accordance with this invention as previously described and illustrated in the drawing.

The straight chain hydrocarbons comprising predominantly hydrocarbons in the molecular weight range C₆–C₁₂ adsorbed by the adsorbent material within adsorber 21 are desorbed therefrom by contacting with a stripping medium introduced via lines 25 and 26 (valve 26a being open and valve 29a being closed) such as flue gas, nitrogen, hydrogen, carbon dioxide, methane and the like or superheated steam.

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The desorption temperature, preferably in the range 300–1300° F., usually in the range 500–1000° F. or 100–300° F. higher than the adsorption temperature, should be such that the adsorbed straight chain hydrocarbons are relatively quickly desorbed without at the same time causing destruction of the solid selective adsorbent or decomposition or cracking of the adsorbent hydrocarbons.

The desorbed straight chain hydrocarbons issuing from adsorber 21 via line 30 (valve 30a being open and valve 32a being closed) together with the gaseous desorbing medium, preferably hydrogen, or after suitable treatment, if desired or necessary for the separation of the straight chain hydrocarbons from the desorbing medium by conventional means such as a cooler or condenser operated in combination with a gas-liquid separator (not illustrated), are introduced via line 32 into converter 31 where they are upgraded, by isomerization, catalytic reforming, thermal reforming or cracking or the like into more valuable motor fuel components, e. g. branched chain hydrocarbons.

The treated or upgraded effluent from converter 31 preferably comprising a mixture of straight chain hydrocarbons and non-straight chain hydrocarbons, including varying amounts of unsaturated or olefinic hydrocarbons depending upon the operation of converter 31, issues via line 33. A portion or all of this effluent is recycled via line 34 into line 14 for eventual contact with the selective adsorbent, as described hereinabove and illustrated in the drawing, with the result that substantially all of the straight chain hydrocarbons separated from the fraction undergoing treatment are converted into branched chain hydrocarbons and other more valuable motor fuel components. Moreover, if desired, a portion or all of the effluent issuing from converter 31 via line 33 may be withdrawn as a separate product as indicated.

After the straight chain hydrocarbons have been desorbed from the adsorbent within adsorber 21 the adsorbent therein is now in condition to be again contacted with the bottoms and/or side stream fraction issuing from fractionator 12. Desirably at about this time the adsorbent material within adsorber 24 shall have been substantially saturated with respect to straight chain hydrocarbons. The straight chain hydrocarbons adsorbed by the adsorbent material within adsorber 24 are then desorbed therefrom by introduction of a stripping medium via lines 25 and 29 (valve 29a being open and valve 26a being closed).

By operating in the above-indicated manner it will be apparent to those skilled in the art that by manipulation of the valves and by adjustment of throughputs and operating conditions the described operations of fractionation, adsorption, desorption, conversion and blending may be carried out continuously.

Exemplary of the practice of this invention a light straight run naphtha having a boiling range 46–226° F. was fractionated to remove overhead substantially all of the C₄ hydrocarbons contained therein. The resulting bottoms fraction was contacted in the vapor phase with a solid selective adsorbent (Linde Type 5A Molecular Sieve) in order to remove substantially all of the straight run chain hydrocarbons therefrom. The naphtha charge originally had an octane number clear of about 72. After fractionation and treatment to remove substantially all the straight chain hydrocarbons therefrom there was recovered a bottoms fraction having an octane number clear of about 74. However, upon blending back the overhead fractionated C₄ hydrocarbons with the treated bottoms fraction, now substantially free of straight chain hydrocarbons, there was produced a blended product having an octane number substantially greater than 74.

Further exemplary of the practice of this invention a light straight run naphtha was distilled at a 122° F. overhead temperature and the resulting residue or bot-

toms fraction, amounting to 68.3% by volume of the original charge to the fractionator was treated with a selective adsorbent for the removal of the straight chain hydrocarbons therefrom. Prior to the removal of the straight chain hydrocarbons, the fractionator bottoms had an ASTM Research Octane Number Clear of 69.7. After the removal of the straight chain hydrocarbons the bottoms fraction had an octane number of about 72. However, upon blending back the overhead fraction with the treated bottoms fraction there was produced a blended product having an octane number substantially greater than 72.

Further exemplary of the practice of this invention a light straight run naphtha having an initial boiling point and an end boiling point in the range of 35–375° F. is fractionated to remove overhead substantially all of the C₄ hydrocarbons and the isopentane contained therein. If desired substantially all of the C₅ hydrocarbons are removed overhead with the C₄ hydrocarbons. The resulting bottoms fraction is contacted with a selective adsorbent to remove substantially all of the straight chain hydrocarbons from the bottoms fraction so as to produce a treated bottoms fraction substantially free of straight chain hydrocarbons. This resulting treated bottoms fraction is then blended with the aforesaid mentioned overhead fraction comprising C₄ hydrocarbons and isopentane to yield an upgraded fraction particularly suited as a motor fuel component.

The straight chain hydrocarbons separated from the bottoms fraction and comprising substantially only straight chain hydrocarbons in molecular weight range C₆–C₁₂ are desorbed from the adsorbent and isomerized by contact with an isomerizing catalyst, e. g. a platinum-containing catalyst under straight chain hydrocarbon isomerizing conditions of temperature and pressure, preferably in the presence of hydrogen, e. g. stripping hydrogen, to produce a mixture of straight chain and non-straight chain hydrocarbons. This resulting isomate has a substantially greater octane number as compared to the mixture of straight chain hydrocarbons supplied to the isomerizer.

Exemplary of this particular feature of applicants' invention, a mixture of straight chain hydrocarbons comparable to a mixture of straight chain hydrocarbons which would be recovered as a separate stream in accordance with the practice of this invention and containing by volume 24% n-pentane, 56% n-hexane and 20% n-heptane was charged to an isomerizing unit containing a platinum-containing isomerization catalyst, such as a UOP platforming catalyst. The conditions of isomerization are as follows: operating pressure of about 500 p. s. i. g., space velocity 1.0 v./hr./v., hydrogen recycle rate of 4,000 cubic feet per barrel of charge.

The results obtained are indicated in Table No. I.

Table No. I

Isomerization Temp., ° F.	ASTM Micro-research clear	Weight Percent liquid recovered
Charge stock	28.2	
700	43.0	97.8
750	48.6	98.8
800	58.0	98.5

The isomate product having an octane number 58.0 was then treated at a temperature of 235° F. and at substantially atmospheric pressure and at a space velocity of 1.0 v./hr./v. with a solid selective adsorbent to remove substantially all of the straight chain hydrocarbons therefrom.

The resulting finished product had an octane number of 77.1 clear and 94.0 w./3.0 cc. TEL/gallon (ASTM micro-research) at a yield of approximately 60 volume percent. This upgraded finished product is advanta-

geously adsorbed with the previously separated and blended overhead-treated fractions as indicated in the drawing.

In view of the foregoing, it is apparent that we have provided a non-catalytic method of upgrading a petroleum fraction in a naphtha boiling range whereby an improved higher octane motor fuel is obtained. The practice of this invention is particularly applicable to upgrading of light naphtha, especially light straight run naphtha which is usually not suitable for upgrading by the various catalytic reforming processes. The process of this invention is particularly applicable to the upgrading of light straight run naphthas containing acyclic, saturated hydrocarbons (normal paraffins, isoparaffins) in an amount in the range of 20–90% by volume.

This patent application is a continuation-in-part of our co-pending application Serial No. 478,426, filed December 29, 1954, which is particularly directed to a petroleum treating process involving the separation of straight chain hydrocarbons from a petroleum fraction followed by conversion of the resulting treated straight chain hydrocarbon free fraction. This parent application also discloses fractionating a petroleum fraction to remove an overhead fraction and blending the removed overhead fraction with the remaining treated-converted petroleum fraction. This application is also related to our co-pending patent application Serial No. 483,998, filed January 25, 1955, which discloses a petroleum treating operation involving converting a petroleum fraction, such as by catalytic reforming, followed by an adsorption treatment to produce a treated fraction substantially free of straight chain hydrocarbons. This application also discloses fractionating a converted or catalytic reformed petroleum fraction to remove overhead a fraction comprising C₄ hydrocarbons, treating the remaining catalytic reformed fraction to separate the straight chain hydrocarbons therefrom and blending the overhead fraction into the resulting treated catalytic reformed product.

As will be apparent to those skilled in the art many modifications, substitutions and changes are possible without departing from the spirit or scope of this invention.

We claim:

1. A method of treating a petroleum fraction having an end point in the range 100–425° F. and containing a substantial amount of C₄ and C₅ hydrocarbons which comprises fractionating said petroleum fraction to remove overhead substantially all of the C₄ and C₅ hydrocarbons, subjecting the remaining petroleum fraction to contact with a molecular sieve alumino-silicate selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said remaining petroleum fraction, recovering from the aforesaid adsorption operation a treated fraction substantially free of straight chain hydrocarbons and blending with said recovered treated fraction the C₄ and C₅ hydrocarbons separated overhead in the aforesaid fractionation operation.

2. A method in accordance with claim 1 wherein the straight chain hydrocarbons are desorbed from said adsorbent and isomerized to produce a mixture of straight chain and non-straight chain hydrocarbons.

3. A method of treating a petroleum fraction in the naphtha boiling range and containing a substantial amount of acyclic hydrocarbons in the molecular weight range C₅ and lower which comprises subjecting said petroleum fraction to fractionation to remove overhead substantially all the hydrocarbons therein having a boiling point not greater than about 100° F., subjecting the remaining petroleum fraction to contact with a molecular sieve alumino-silicate solid selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb

straight chain hydrocarbons therefrom thereby yielding a treated fraction substantially free of straight chain hydrocarbons and blending the overhead from the aforementioned fractionation operation with said treated straight chain hydrocarbon free fraction recovered from the adsorption operation.

4. A method of treating a light straight run naphtha having an end point in the range 100–225° F. said naphtha containing a major amount of saturated hydrocarbons, including a substantial amount of C₄ and C₅ hydrocarbons, which comprises fractionating said naphtha to remove overhead substantially all of the C₄ and C₅ hydrocarbons in said naphtha, subjecting the remaining naphtha fraction to contact with a molecular sieve alumino-silicate selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said remaining naphtha fraction, recovering from the aforesaid adsorption operation a treated naphtha fraction substantially free of straight chain hydrocarbons and blending with said recovered treated fraction said C₄ and C₅ hydrocarbons separated overhead in the aforesaid fractionation operation.

5. A method in accordance with claim 4 wherein the straight chain hydrocarbons are desorbed from said adsorbent and isomerized to produce an isomate mixture of straight and non-straight chain hydrocarbons, contacting said isomate with a selective adsorbent to adsorb substantially all of the straight chain hydrocarbons therefrom to produce a treated isomate substantially free of straight chain hydrocarbons and blending said treated isomate with said treated fraction and said C₄ and C₅ hydrocarbons.

6. A method of treating a light straight run naphtha having an end point in the range 100–225° F., said naphtha containing a major amount of saturated hydrocarbons, aliphatic and alicyclic hydrocarbons, including a substantial amount of C₄ and C₅ hydrocarbons, which comprises fractionating said naphtha to remove overhead substantially all of the C₄ and C₅ hydrocarbons in said naphtha, subjecting the remaining naphtha fraction to contact with a molecular sieve alumino-silicate selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain

hydrocarbons to adsorb straight chain hydrocarbons from said remaining naphtha fraction, recovering from the aforesaid adsorption operation a treated naphtha fraction substantially free of straight chain hydrocarbons, desorbing the straight chain hydrocarbons from said adsorbent and reforming said straight chain hydrocarbons to produce a reformat mixture of straight chain and non-straight chain hydrocarbons, contacting said reformat with a molecular sieve alumino-silicate selective adsorbent to adsorb substantially all of the straight chain hydrocarbons therefrom to produce a treated reformat and blending together said treated reformat, said treated naphtha fraction and said C₄ and C₅ hydrocarbons.

7. A method of treating a petroleum fraction having an end point in the range 100°–425° F. and containing a substantial amount of C₄ and C₅ hydrocarbons which comprises fractionating said petroleum fraction to remove overhead substantially all of the C₄ and C₅ hydrocarbons, subjecting the remaining petroleum fraction to contact with a molecular sieve alumino silicate selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said remaining petroleum fraction, recovering from the aforesaid adsorption operation a treated fraction substantially free of straight chain hydrocarbons, blending the recovered treated fraction with the C₄ and C₅ hydrocarbons separated overhead in the aforesaid fractionation operation, desorbing the adsorbed straight chain hydrocarbons from said adsorbent by contacting said adsorbent with gaseous hydrogen and isomerizing the resulting desorbed straight chain hydrocarbons in the presence of the hydrogen employed to desorb the adsorbed straight chain hydrocarbons from the selective adsorbent with a platinum-containing isomerization catalyst under isomerizing conditions.

References Cited in the file of this patent

UNITED STATES PATENTS

2,146,039	Whiteley	Feb. 7, 1939
2,304,187	Marschner	Dec. 8, 1942
2,425,535	Hibshman	Aug. 12, 1947
2,442,191	Black	May 25, 1948
2,522,426	Black	Sept. 12, 1950
2,602,772	Haensel	July 8, 1952