

March 12, 1963

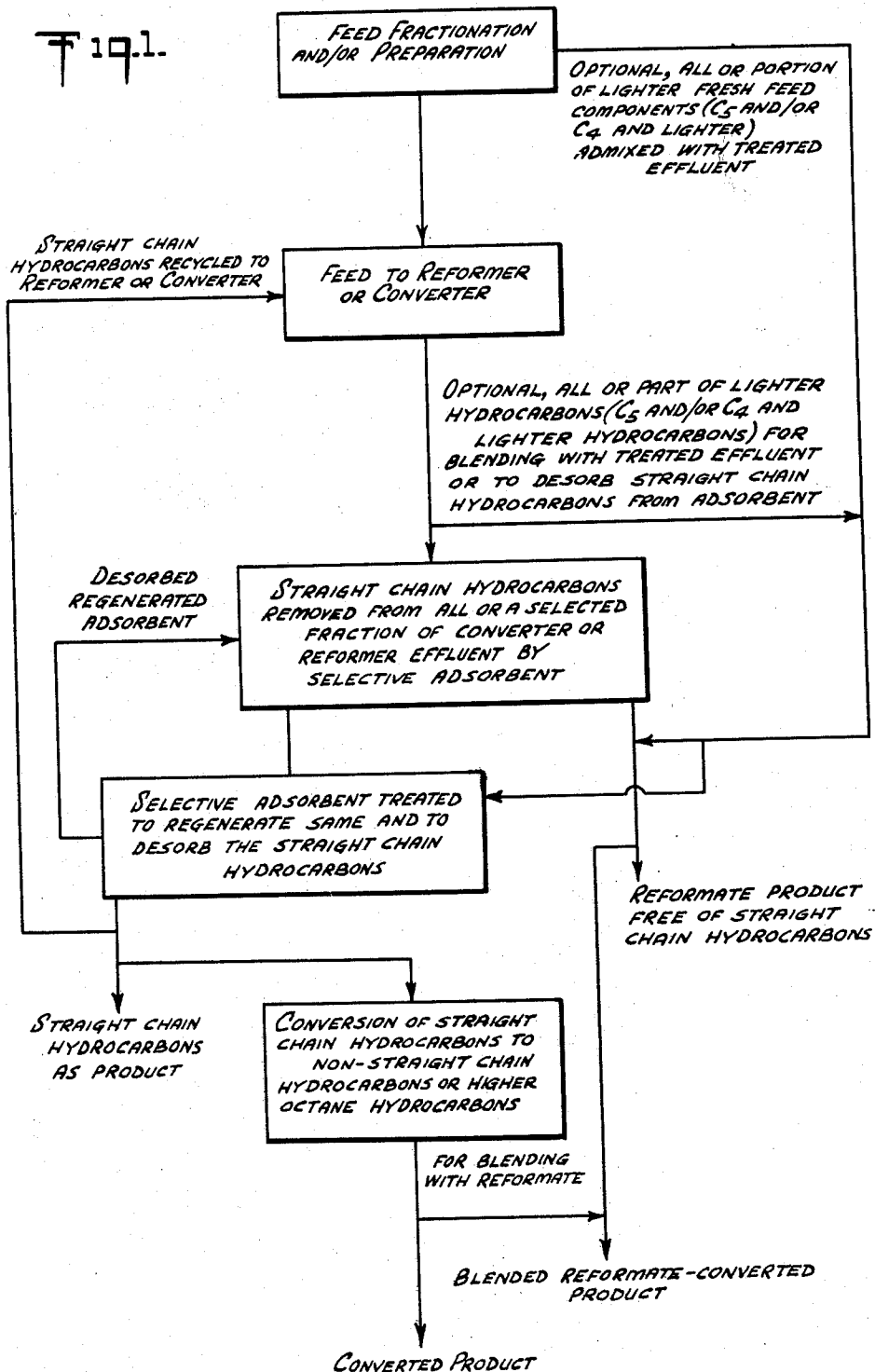
H. V. HESS ET AL
METHOD OF TREATING A PETROLEUM FRACTION USING
MOLECULAR SIEVE ALUMINO-SILICATE
SELECTIVE ADSORBENTS

3,081,255

Filed May 18, 1959

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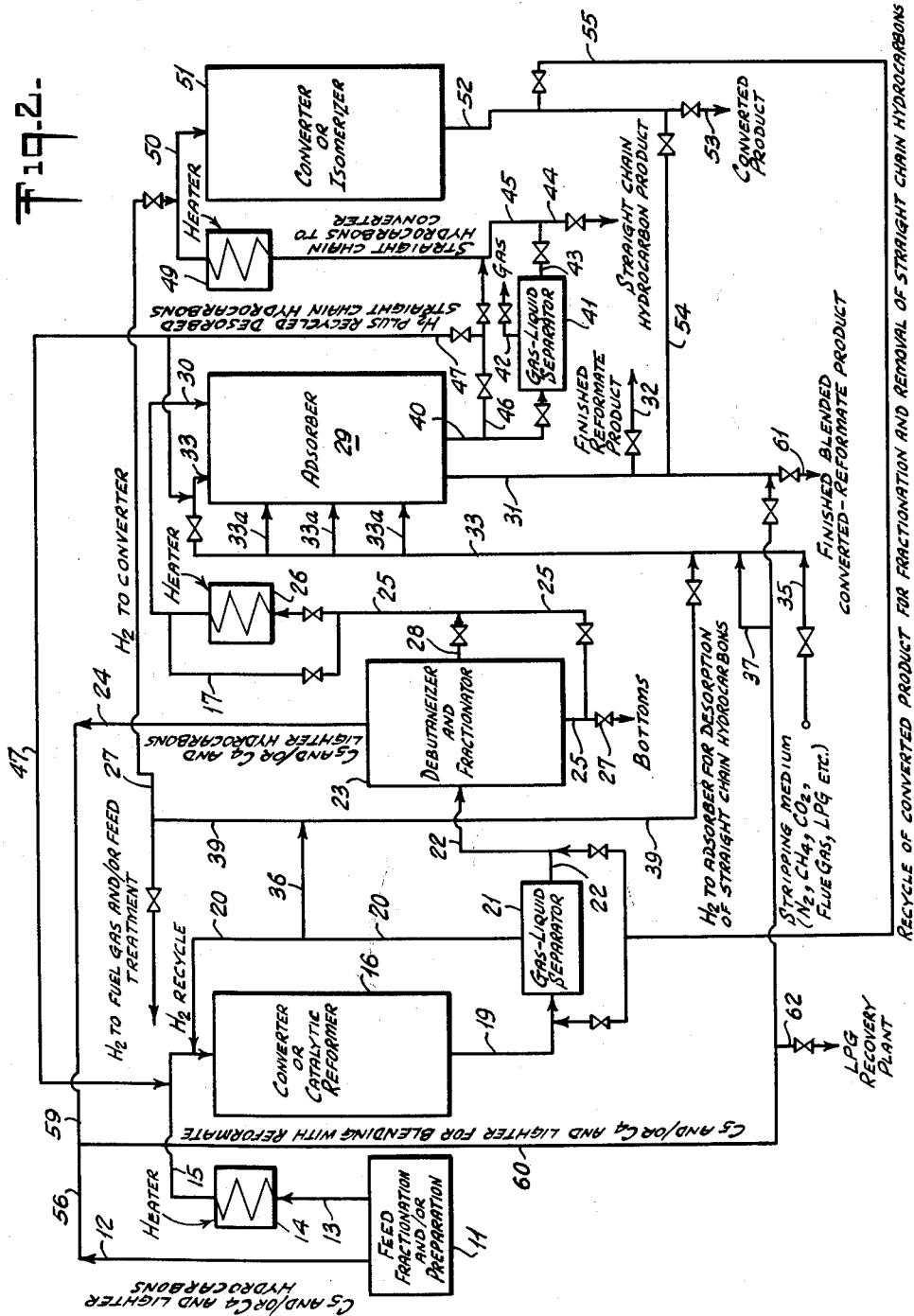
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METHOD OF TREATING A PETROLEUM FRACTION USING MOLECULAR SIEVE ALUMINO-SILICATE SELECTIVE ADSORBENTS**Howard V. Hess, Glenham, and Edward R. Christensen, Wappingers Falls, N.Y., assignors to Texaco Inc., New York, N.Y., a corporation of Delaware**

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5 Claims. (Cl. 208—88)

This invention relates to a method of treating petroleum fractions. More particularly, this invention relates to an improved hydrocarbon conversion process. In accordance with one embodiment this invention relates to the treatment of petroleum fractions in the naphtha or gasoline boiling range to improve their quality. Still more particularly, this invention is directed to the treatment of petroleum fractions containing straight chain hydrocarbons and non-straight chain hydrocarbons, especially naphtha stocks wherein the amount of straight chain hydrocarbons is substantial, i.e., in the range 3–30% by volume and higher.

Various converting and catalytic reforming 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 petroleum fractions in the gasoline boiling range by contact with an active converting catalyst such as a platinum-containing catalyst, a chromia-alumina catalyst, a molybdena-alumina catalyst or the like. During treatment of these selected petroleum fractions, a number of reactions take place substantially simultaneously. For example, in a catalytic reforming operation employing a platinum-containing catalyst in contact with a naphtha fraction containing aromatics, naphthenes, isoparaffins and n-paraffins, dehydrogenation of the naphthenes to aromatics occurs. Substantially at the same time isomerization and dehydrogenation of the paraffinic hydrocarbons take place. Additionally, under these conditions aromatization or dehydrocyclization of the paraffinic hydrocarbons also takes place. Concurrently with these reactions, particularly under the more severe treating or conversion conditions, a certain amount of cracking and gas formation (C_4 and lighter) takes place together with deposition of carbon upon the catalyst thereby resulting in a reduction in the recoverable yield of the more valuable normally liquid hydrocarbons. Cracking, as evidenced by gas formation and carbon deposition, is particularly noticeable when the aforesaid conversion or catalytic reforming reactions are carried out under the more severe catalytic reforming conditions in order to produce a high octane motor fuel or motor fuel component.

The platinum-containing treating catalysts employed in present day commercial catalytic reforming operations are expensive. Some of these platinum-containing catalysts are regenerable and some are non-regenerable. An important factor in the determination of the useful life of a treating or a catalytic reforming catalyst, particularly a platinum-containing catalyst, is the amount of carbon deposited or laid down upon a catalyst. Carbon deposition in turn is usually governed or dependent upon the severity of the converting or reforming conditions in which the catalyst is employed. The replacement of a spent treating catalyst, particularly a platinum-containing catalyst, is expensive. Moreover, the regeneration of a spent regenerable catalyst is an expensive operation and time consuming, all the more so in a refinery operation when for purposes of regeneration it is necessary to take a catalyst case off stream for catalyst regeneration.

Accordingly, it is an object of this invention to provide

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an improved process for treating petroleum fractions containing straight chain hydrocarbons.

It is another object of this invention to provide a flexible petroleum converting operation which is capable of handling a wide variety of petroleum fractions containing straight chain hydrocarbons and non-straight chain hydrocarbons.

Still another object of this invention is to provide a treating process wherein the useful on-stream life of a treating catalyst, especially a platinum-containing catalyst, is substantially increased, particularly when compared with the useful catalyst life of the same catalyst employed in the same catalytic conversion operation in the conventional manner to produce a petroleum fraction or gasoline component having the same octane number as produced by the combination treating process in accordance with this invention.

Yet another object of this invention is to provide a combination treating operation employing a catalytic converting or catalytic reforming operation for the production of a high octane motor fuel not otherwise obtainable save at the expense of a prohibitively shortened catalyst life.

Yet another object of this invention is to provide a combination process for increasing the yield of a given high octane number motor fuel obtainable from a given naphtha fraction as compared to the yield obtainable by employing a conventional operation.

Yet another object of this invention is to provide a petroleum product particularly useful as a motor fuel.

Still another object of this invention is to provide a process for the production of a petroleum product particularly useful as a jet fuel.

In at least one embodiment of this invention at least one of the foregoing objects will be achieved.

How these and other objects in this invention are achieved will become apparent with reference to the accompanying disclosure and drawing wherein:

FIG. 1 is a block flow diagram broadly outlining the process of this invention, and

FIG. 2 is a schematic flow diagram illustrating various embodiments of the practice of this invention.

In accordance with this invention we have provided an improved process for treating or converting a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises subjecting the petroleum fraction to a treating or converting operation, such as a catalytic reforming or isomerization operation, to produce a petroleum fraction of improved quality, such as an improved or higher octane product, and subjecting the resulting improved petroleum fraction 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 fraction, thereby producing a further improved petroleum fraction. The practice of this invention is particularly applicable to any petroleum fraction suitable for use in a catalytic reforming or isomerization operation or suitable for the production of aromatics or improved naphthas or motor fuels in the gasoline boiling range, provided, of course, said petroleum fraction contains straight chain hydrocarbons and non-straight chain hydrocarbons.

By straight chain hydrocarbons 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, 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 50–300° F. and an end point in a range 200–475° F., more or less. Furthermore, a petroleum fraction suitable for use in the practice of this invention contains 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 normal paraffins and iso-paraffins) -----	3-90
Unsaturates (including normal olefins and iso-olefins, etc.) -----	0-50

The straight chain hydrocarbons, e.g., the n-paraffin content of petroleum fractions suitable for use in the practice of this invention is frequently in the range 3–50% by volume. 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 catalytic cracked naphtha, a thermally cracked or thermally reformed naphtha. This invention, however, is particularly applicable to the treatment of catalytic reformates in the naphtha boiling range.

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 dimension and are of uniform size. A particularly suitable solid molecular sieve adsorbent for the adsorption of straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons is a calcium aluminosilicate, apparently actually a sodium calcium aluminosilicate, having 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 and the isoparaffins and iso-olefinic hydrocarbons, e.g. isobutane and higher. This particular selective adsorbent is commercially available in various sizes such as 1/16" or 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 permit the entry of and 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 $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ 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 $(\text{Ca}, \text{Na})\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ 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 the n-olefins to the substantial exclusion of the non-straight chain hydrocarbons, including the aromatic and naphthenic hydrocarbons, are known.

Referring now to FIG. 1 of the drawing which sets forth in a block flow diagram various embodiments of the practice of this invention, a fresh feed petroleum fraction which may have a wide or narrow boiling range, containing straight chain hydrocarbons (n-paraffins and/or n-olefins) in admixture with non-straight chain hydrocarbons (aromatic and/or naphthenic and/or isoparaffinic and/or isoolefinic hydrocarbons), is supplied from a suitable source to a suitable feed fractionation and/or preparation unit. Should the fresh feed contain substantial amounts of undesirable polar or polarizable compounds such as sulphur-containing compounds, oxygenated hydrocarbons, nitrogen-containing compounds and the like, it is sometimes desirable, although not necessary, to remove these materials from the feed prior to the special subsequent treatment in accordance with this invention. The removal of these polar or polarizable materials may be accomplished by solvent extraction, extractive distillation, hydrogenation, dehydrogenation, acid or caustic washing and the like or by any suitable combination thereof. Processes for removal of or neutralization of the above-mentioned polar and polarizable materials in a petroleum fraction are well known.

Advantageously, preferably prior to feed preparation, the fresh feed is subjected to fractionation to produce a petroleum fraction having the boiling point range most suitable for subsequent treatment in accordance with this invention. If the fresh feed contains components which have a boiling point below about 100° F., it is usually desirable to remove substantially all of these feed components. Hydrocarbons which have a boiling point below 100° F. are n-butane, isobutane, isopentane and neopentane, all of which possess a rather high octane number and for this reason alone would be desirable components in a motor fuel or gasoline. Normal pentane, having a boiling point of about 97° F., however, has a lower octane number (about 61) and accordingly its presence in a motor fuel is less desirable.

The removal of these low boiling hydrocarbons is desirable since these low boiling hydrocarbons are refractory and do not readily undergo catalytic reforming. When these low boiling hydrocarbons are passed to a catalytic reforming operation they pass through substantially unchanged and in effect act as a diluent. Accordingly, the low boiling, C_3 or C_4 and lighter, hydrocarbons are advantageously fractionated from the feed undergoing treatment in accordance with this invention. All or a portion of these low boiling hydrocarbons, however, may advantageously be blended back into the final treated petroleum fraction or otherwise employed, e.g., as a desorbing agent, in the practice of this invention.

Following the feed fractionation and/or preparation operations as indicated in FIG. 1, the naphtha feed is sent to a conversion operation, such as a catalytic reformer, which might also be an isomerization unit, wherein it is contacted with an active reforming catalyst under reforming conditions of temperature and pressure to upgrade the feed into a converted product or reformate as an improved motor fuel or high octane motor fuel component.

Various converting and catalytic reforming or isomerizing operations particularly suitable for upgrading a petroleum fraction in a naphtha boiling range may be employed in the combination treating process in accordance with this invention. Generally, reforming or isomerization processes, the words "reforming" and "isomerizing" being used herein interchangeably, may be described as processes for upgrading relatively low octane naphthas or petroleum fractions in the gasoline boiling range to high octane motor gasolines, or as processes for producing high octane motor fuel components from selective naphthas or petro-

leum fractions, or as processes for producing a high yield of aromatic hydrocarbons or high octane motor fuel components.

These catalytic reforming operations may be carried out by employing a fixed bed of catalyst, a moving bed of catalyst or a fluidized catalyst, or any combination thereof, and are generally operated at a temperature in the range 400–1000° F., more or less, and a pressure in the range 25–900 p.s.i.g., more or less, depending upon the severity or extent of reforming desired or the reforming catalyst employed or the quality or composition of the petroleum fraction undergoing reforming and/or the product desired. Various catalysts suitable for reforming hydrocarbons may be employed, e.g., platinum-containing catalysts, molybdena-alumina catalysts, chromia-alumina catalysts and cobalt-molybdate catalysts; the particular reforming or isomerizing process is sometimes adequately defined merely by describing the particular catalyst employed therein. As a result of the reforming operation, there is produced and recovered a reformat having improved qualities as a motor fuel.

Depending upon the composition of the fresh feed other converting processes, in place of catalytic reforming, may be employed, e.g. thermal cracking, thermal reforming (essentially non-catalytic processes), etc., particularly when the fresh feed contains a substantial amount, in the range 10–50 and higher percent by volume straight chain hydrocarbons.

The effluent from the reforming or converting operation is treated to separate the normally gaseous materials therefrom, e.g. hydrogen, methane, ethane, propane and C₄ hydrocarbons. At least a portion of the separated and recovered hydrogen is usually desirably recycled to the reforming or converting operation.

The remaining normally liquid components of the effluent are then contacted with the solid selective adsorbent material in powdered, beaded, microspheroidal, granular or pelleted form to selectively adsorb the straight chain hydrocarbons therefrom. Although it is preferred to remove substantially all of the straight chain hydrocarbons from the effluent it is realized that it is not necessary in the practice of this invention to adsorb or separate all of the straight chain hydrocarbons. The extent or degree of straight chain hydrocarbon removal, especially for octane number improvement, in order to produce a high octane gasoline is governed by various factors, economic and otherwise, including capacity of the available equipment, the quality desired in the finished treated product, yield considerations, the composition of the effluent and the like.

The effluent undergoing treatment for the removal of the straight chain hydrocarbons therefrom may be present either in the liquid phase or in a gas or vapor phase. The capacity of the solid adsorbent material as a selective adsorbent for straight chain hydrocarbons is substantially unaffected by the phase condition of the material to be treated (reformer effluent) in contact therewith, provided sufficient time is allowed to substantially saturate the adsorbent. Contact of the effluent with the solid adsorbent may be effected by any suitable means for effecting gas-solid or liquid-solid contacting. For example, in contact with the reformer effluent the selective adsorbent may be maintained as a fixed bed, a moving bed or a fluid bed.

When liquid phase contacting is carried out for the removal of the straight chain hydrocarbons from the effluent, it is preferred to carry out the adsorption operation at a temperature in a range 50–500° F. or higher, sufficient pressure being applied, if necessary, to maintain the effluent 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 effluent undergoing treatment in the vapor phase, such as a temperature in the range 300–700° F. or higher. Satisfactory liquid phase or vapor phase adsorption operations have been carried out at temperatures in the range 200–650° F.

The effluent undergoing treatment is 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 petroleum fraction or effluent undergoing treatment is contacted with additional 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, purges, desorbs or sweeps out the adsorbed straight chain hydrocarbons from within the pores of the selective adsorbent. Preferably the stripping medium is readily separable, as by distillation, from the desorbed straight chain hydrocarbons. Exemplary of a suitable stripping medium are nitrogen, methane, hydrogen, flue gas, carbon dioxide, substantially dry natural gas and the normally gaseous hydrocarbons such as ethane, propane, n-butane and isobutane. Liquids are also useful as a stripping medium, such as the liquefied normally gaseous hydrocarbons, including propane, n-butane, isobutane, n-pentane, isopentane and higher and lower molecular weight hydrocarbons or mixtures thereof. Desirably, the molecules of the stripping medium thereof are sufficiently small to enter the pores of the adsorbent.

The desorption operation may be carried out at any suitable temperature, higher or lower, or, if desired, isothermal with respect to the adsorption operation. Similarly the desorption operation may be carried out at a pressure greater than or less than or isobaric with respect to the adsorption operation. A desorption temperature in the range 200–1000° F. has been found to be satisfactory and the desorption temperature may be in the range 100–300 degrees Fahrenheit higher than the adsorption temperature, such as a temperature in the range 300–700° F.

After the straight chain hydrocarbons have been desorbed, the straight chain hydrocarbons are recovered and, if desired, are subjected to a suitable conversion operation such as catalytic reforming or isomerization, or thermal cracking in order to upgrade the desorbed straight chain hydrocarbons into more valuable materials, e.g. normal paraffins to normal olefins and/or to their corresponding branched chain isomers. The resulting converted product can be directly blended with the straight chain hydrocarbon-free effluent from the adsorber or, if desired, may be contacted with selective adsorbent to remove the straight chain hydrocarbons therefrom and the remaining straight chain hydrocarbon-free converted product blended with the above-mentioned effluent. Also, the desorbed straight chain hydrocarbons may be separately recovered and utilized as such, as an industrial solvent, jet fuel, etc.

In FIG. 2 of the drawing there are schematically illustrated various embodiments of the practice of this invention. Referring now in greater detail to FIG. 2 a fresh feed petroleum fraction, such as a petroleum fraction in the naphtha boiling range, from a source not shown, is subjected to fractionation and/or preparation by feed preparation unit 11. During fractionation and/or preparation of the fresh feed therein to yield a petroleum fraction having a suitable boiling point range for subsequent treating in accordance with this invention, the lighter components of the fresh feed, such as the hydrocarbons having a molecular weight in the range C₅ and lower, especially substantially all of the isopentane and butane contained in the fresh feed, are advantageously removed overhead as a separate fraction via line 12. The remaining fresh feed, substantially free of C₅ and lower molecular weight hydrocarbons, and having the desired boiling point range, such as a boiling range in the range 150–450° F., is subjected to a feed preparation operation which might involve a mild hydrogenation or hydrogen refining operation to saturate

the unsaturated hydrocarbons therein, for removal of the more polar compounds therefrom, e.g. sulfur-containing compounds and the like. Application of the above-described operations of fresh feed fractionation and/or preparation to a straight run naphtha fraction would produce a heavy straight run naphtha fraction which might have the composition set forth in accompanying Table I. A naphtha fraction possessing these properties would be suitable for subsequent treatment in accordance with this invention.

TABLE I

Naphtha, A.P.I. -----	53.9
A.S.T.M. distillation, ° F.:	
I.B.P. -----	177
10% -----	218
50% -----	264
90% -----	329
E.P. -----	392
A.S.T.M. octane number:	
Clear -----	56.5
+3 cc. TEL -----	73.4
Aromatics, volume percent -----	13.5
Naphthenes, volume percent -----	44.0
Paraffins (include n-paraffins and isoparaffins) -----	42.5
R.V.P., lbs. -----	1.5

Following suitable feed fractionation and preparation treatment the prepared feed issues from unit 11 via line 13 into heater 14 where it is brought up to a sufficiently high temperature, such as a temperature in the range 400–1000° F., for introduction via line 15 into catalytic reforming unit 16. Catalytic reforming unit 16 is suitably provided with an active reforming catalyst such as a platinum-containing catalyst which may be regenerable or non-regenerable, or a chromia-alumina catalyst or a molybdena-alumina catalyst or a cobalt-molybdate catalyst. Typical operating conditions for catalytic reformer 16 when employing a platinum-containing catalyst are as follows: inlet temperature 875° F., pressure 250 p.s.i.g., space velocity 3 v./hr./v. with a recycle of 8000 cu. ft./bbl. of prepared feed of a gas containing at least about 90 mol percent hydrogen. Two or more of catalytic reforming units 16 may be employed in series or in parallel.

Within catalytic reforming unit 16 hydrocarbon components present in the treated feed are upgraded into higher octane hydrocarbons with a resulting net production of hydrogen. For example, the naphthenic hydrocarbons are dehydrogenated to form a corresponding aromatic hydrocarbon. Substantially simultaneously therewith the isoparaffinic and normal paraffinic hydrocarbons undergo isomerization, dehydrocyclization and a certain amount of cracking with resulting gas formation (C₄ and lower molecular weight hydrocarbons) depending upon the severity of the reforming operation. In any event the effluent issuing from reformer 16 has an increased aromatic hydrocarbon content and/or improved qualities as a motor fuel and/or a higher octane rating, as compared to the feed supplied to reforming unit 16.

The effluent issuing from reforming unit 16 via line 19 is passed to a gas-liquid separator 21 wherein the hydrogen produced during the reforming operation is separated. At least a portion of this separated hydrogen is usually recycled via line 20 to reformer 16 to provide the desired hydrogen therein. The remaining reformer effluent or reformat is advantageously passed from gas-liquid separator 21 via line 22 into fractionator 23 wherein an overhead fraction comprising substantially all of the C₅ and/or C₄ and lighter hydrocarbons are removed overhead as a separate fraction via line 24. The remaining higher molecular weight, higher boiling effluent, comprising substantially all of the normally liquid hydrocarbons in the reformer effluent, are passed via line 25 to heater 26 wherein the effluent, if desired, is heated to a suitable temperature for introduction into adsorber 29. The resulting effluent is introduced from heater 26 into adsorber 29 by

means of line 30. If heater 26 is unnecessary, especially if it is desired to carry out liquid phase adsorption, it may be bypassed via line 17.

If desired, the reformer effluent in fractionator 23, after removal of the C₅ and/or C₄ and lighter hydrocarbons is further fractionated to procure a side cut via line 28 having a boiling point not greater than about 250° F. It has been observed that the remaining higher boiling fraction, such as a reformat having a boiling point range in the range 250–450° F., more or less, is less susceptible to upgrading as regards octane number increase by subsequent treatment in accordance with this invention. This higher boiling fraction accordingly may be separately removed from fractionator 23 as a bottoms fraction via lines 25 and 27 for subsequent blending, by means not shown, with the blended product in line 61.

Adsorber 29 is provided with a fixed bed of solid particle molecular sieve selective adsorbent. As disclosed suitable adsorbents for straight chain hydrocarbons are the alkaline earth metal aluminosilicates, more particularly the calcium aluminosilicates, e.g. sodium calcium aluminosilicate. The adsorber 29 is operated at a temperature such that substantially all of the straight chain hydrocarbons, such as the normal paraffins in the effluent introduced into adsorber 29 via line 30 in the gaseous or liquid phase, are adsorbed by the adsorbent material therein with the result that there issues from the bottom of adsorber 29 via line 31 in the gaseous or liquid phase a treated or finished reformat fraction substantially free of straight chain hydrocarbons.

The adsorption conditions within adsorber 29 are to some extent dependent upon the composition of the reformat or reformat fraction undergoing treatment or finishing therein, e.g., the greater the amount of straight chain hydrocarbons the longer the adsorption or finishing period required to effect substantially complete adsorption of the straight chain hydrocarbons. Removal of the straight chain hydrocarbons, especially the straight chain paraffinic hydrocarbons, is desirable since these hydrocarbons possess a very low octane number. For example, normal hexane has an octane number of 24, normal heptane an octane number of 0, normal octane an octane number of -17. The removal of the normal paraffins from the reformer effluent therefore is desirable when it is desired to produce a high octane motor fuel. The branched chain hydrocarbons, such as the branched chain isomeric paraffinic hydrocarbons, in a motor fuel are not undesirable since branched chain hydrocarbons in general possess a relatively high octane number. For example, isohexane has an octane number of about 73.

Processing or finishing periods for the effluent undergoing treatment in adsorber 29 in the range 2 minutes up to about 1½–2 hours at throughputs in the range ¼ v./hr./v. up to about 20 v./hr./v. are satisfactory and suitable in order to effect the desired removal of the straight chain hydrocarbons or before the adsorbent material within adsorber 29 is substantially saturated with straight chain hydrocarbons. The finished effluent issuing from adsorber 29 via line 31 may be withdrawn as a separate reformat product via line 32 or blended with additional hydrocarbons in a manner to be described hereinafter.

After a suitable period of time and when the adsorbent material within adsorber 29 becomes substantially saturated with respect to straight chain hydrocarbons regeneration of the adsorbent by desorption of the straight chain hydrocarbons therefrom becomes necessary. The straight chain hydrocarbons are desorbed from the adsorbent by contacting the adsorbent with a desorbing fluid or stripping medium such as nitrogen, methane, natural gas, flue gas, carbon dioxide, hydrogen, gaseous hydrocarbons and gaseous or liquefied normally gaseous hydrocarbons, etc. The stripping medium is introduced into adsorber 29 via line 33 or by multi-point injection via lines 33a, having been supplied from suitable sources

via line 35. Hydrogen, if employed as a stripping medium, is advantageously supplied from gas-liquid separator 21 via lines 20, 36 and 39 and if gaseous and liquefied C₃ and C₄ hydrocarbons and the like are employed as stripping medium these materials may be supplied from fractionator 23 via lines 24, 59, 60, 37 and 33.

The desorption operation, as previously stated, may be carried out at substantially the same temperature as the adsorption operation. Although liquid phase adsorption and desorption are suitable and the various combinations of liquid and gaseous adsorption and desorption are useful, it is sometimes desirable to employ a desorption temperature sufficient to maintain the materials being treated or desorbed in the vapor phase, e.g. temperature in the range 300–700° F. during adsorption and a temperature in the range 400–900° F. during desorption. Usually in these instances the desorption temperature is about 100–300 degrees Fahrenheit higher than the adsorption temperature, generally in the range 500–1000° F. As a general rule the desorption temperature should be such that the adsorbed straight chain hydrocarbons are relatively quickly desorbed without at the same time causing destruction of the adsorbent or decomposition or cracking of the adsorbed-desorbed hydrocarbons. The desorbed straight chain hydrocarbons together with the accompanying stripping medium issue from adsorber 29 via line 40 and are introduced into gas-liquid separator 41. When a normally gaseous stripping medium, such as hydrogen, flue gas, nitrogen and the like is employed as the stripping medium the separation of these normally gaseous materials and the desorbed straight chain hydrocarbons is effected within separator 41, the normally gaseous stripping medium being removed via line 42 and recovered for further use as a stripping medium by means not shown and the straight chain hydrocarbons are removed via line 43.

The desorbed straight chain hydrocarbons issuing from separator 41 via line 43 may be recovered as a separate product via line 44 or sent to a subsequent conversion operation, to be described, via line 45. Advantageously when hydrogen is employed as a stripping medium and when the aforesaid subsequent conversion operation is a catalytic conversion operation or isomerization operation or the like wherein the presence of hydrogen during the conversion of the desorbed straight chain hydrocarbons is desirable, the vaporized desorbed straight chain hydrocarbons together with the hydrogen stripping medium are recycled within adsorber 29 via lines 40, 46 and 47, gas-liquid separator being by-passed, until the desired hydrocarbon concentration has been reached at which time a portion of the hydrogen and hydrocarbon mixture in line 46 is introduced into line 45, heater 49 and line 50 into converter 51. Fresh hydrogen may be supplied as additional stripping medium from separator 21 via lines 20, 36, 39 and 33 and then, as indicated, eventually into line 45 via lines 40 and 46, by-passing the gas-liquid separator 41. The desorbed straight chain hydrocarbons move via line 45 to heater 49 where they are brought up to the desired conversion temperature and introduced via line 50 into converter 51 wherein the desorbed straight chain hydrocarbons are converted into higher octane or improved motor fuel components. If desired, as indicated in FIG. 2 the desorption effluent containing hydrogen and straight chain hydrocarbons may be recycled to reformer 16 via lines 47, 17 and 15.

The conversion operation carried out within converter 51 may be thermal cracking, thermal reforming, catalytic cracking, catalytic reforming, isomerization and the like, depending upon the properties and composition of the desorbed straight chain hydrocarbons. Preferably the conversion operation within converter 51 is an isomerization operation employing an isomerization catalyst such as a platinum-containing catalyst. The upgraded effluent issuing from converter 51 via line 52, now possessing

a higher octane number and now containing straight chain hydrocarbons and non-straight chain hydrocarbons, may be removed as a separate converted product via line 53, or blended with the substantially straight chain hydrocarbon-free effluent issuing from adsorber 29 via line 31 by means of line 54 or all or a portion of the effluent from converter 51 may be returned via lines 52 and 55 and line 22 to fractionator 23 and adsorber 29 for additional treatment as previously described.

The overhead fractions in lines 12 and 24 containing C₅ and/or C₄ and lighter hydrocarbons, from feed preparation unit 11 and fractionator 23, respectively, preferably containing substantially all of the isopentane and the C₄ hydrocarbons present in the fresh feed and the effluent issuing from catalytic reformer 16, are combined by lines 56 and 59, respectively, into line 60 for blending with the combined adsorber-converter effluent in line 31 and are removed as a separate finished blended converted reformat product via line 61. If desired, all or a portion of the combined overhead fractions in line 60 may be passed via line 62 to a liquefied petroleum gas recovery plant. Further, if desired those normally gaseous hydrocarbons, C₃, C₄, etc., recovered via lines 12 and 24 may be employed via lines 60, 37 and 33 to desorb the adsorbed straight chain hydrocarbons.

Exemplary of the advantages obtainable in the practice of this invention as applied to a 20,000 bbl. a day charge catalytic reforming unit employing a platinum-containing catalyst, it has been determined that when such a unit is operated in the conventional manner, including a mild hydrogenation treatment of the feed thereto, to produce a catalytic reformed gasoline having an octane number of about 93 there is produced 16,140 barrels per day of a debutanized gasoline having a research octane number clear of 92.9. Additionally there is produced a hydrogen and hydrocarbon-containing fuel gas in an amount equal to 15,003 MM standard cu. ft. This amount of gas represents an actual loss of hydrocarbons. However, when operating in accordance with the practice of this invention employing in combination a catalytic reforming unit followed by selective finishing of the resulting reformat to remove substantially all the straight chain hydrocarbons therefrom, it was determined that the reforming unit could be operated at a lesser degree of severity, as indicated by the recovery of 17,440 barrels per day of debutanized gasoline and the recovery of a smaller amount of hydrogen and hydrocarbon-containing gas. The increased recovery of debutanized gasoline amounts to about an 8% by volume increase over the conventional operation.

The recovered debutanized catalytic reformed gasoline amounting to 17,440 barrels per day is then treated in the manner of the invention described herein with a selective adsorbent for the removal of straight chain hydrocarbons therefrom and there is produced 16,272 barrels per day of catalytic reformed gasoline having a clear research octane number of 92.9 together with 1168 barrels per day of straight chain hydrocarbons which may be recovered and employed as such as a solvent or subjected to an isomerization or catalytic reforming operation to produce additional high octane motor fuel or employed per se as a jet fuel. The advantages of employing the practice of this invention are an increased recovery of high octane gasoline since, as indicated hereinabove, less of the treated hydrocarbons are converted to butanes and lighter hydrocarbons. Additionally since the platforming operation operated in the combination treating process in accordance with this invention is carried out under less severe conditions the useful catalyst life is extended at least twofold, 150 days vs. 70 days.

Further indicative of the advantages obtainable in the practice of this invention an 85.9 CFRR (clear) catalytic reformed gasoline (catalytic reformat) was upgraded in accordance with the practice of this invention by vapor phase contact with a molecular sieve selective adsorbent

for the removal of the straight chain hydrocarbons therefrom. The results are summarized below in Table II:

TABLE II

Adsorption temperature, ° F:	
390	93.4
425	93.3
450	93.4
500	92.3
550	91.8
600	90.8
650	89.7
700	89.0

The above operations were carried out employing a finishing or adsorption time of about thirty minutes, a space velocity of about 1 v./hr./v. and a desorption or regeneration temperature, following adsorption, of about 700° F. employing natural gas as the stripping medium.

Further indicative of the practice of this invention a catalytic reformed gasoline having a research octane number clear of 86.8 was upgraded by vapor phase contact with a solid molecular sieve selective adsorbent for straight chain hydrocarbons employing a space velocity of about 1 v./hr./v., for the removal of straight chain hydrocarbons therefrom. The adsorption and desorption was carried out at various temperatures, desorption being effected by natural gas comprising substantially one methane. The operating conditions and results obtained are set forth in Table III.

TABLE III

Run No.	Adsorption		Desorption		Product Octane Research, Clear
	Temp., ° F.	Time, Min.	Temp., ° F.	Time, Min.	
1	425	30	700	107	93.3
2	525	30	525	42	90.8
3	525	15	525	42	93.3
4	525	15	535	57	93.3
5	525	15	525	72	93.5
6	425	30	700	117	92.8

Since the straight chain hydrocarbons removed from the effluent undergoing finishing, such as a catalytic reformer effluent, represent a substantial fraction thereof it is desirable in accordance with the practice of this invention to upgrade the straight chain hydrocarbons with respect to octane number or otherwise to improve their quality as a motor fuel or motor fuel component or petrochemical. Accordingly in accordance with the practice of this invention a straight chain hydrocarbon fraction, comparable to the desorbed straight chain hydrocarbons which are recovered during the desorption operation, and 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 in the range 700-900° F., at a pressure of about 500 p.s.i.g., at a space velocity of about 1.0 v./hr./v., employing a hydrogen recycle rate of about 4000 standard cu. ft. per bbl. charge. The resulting isomates were subsequently finished by removal of the straight chain hydrocarbons. The results obtained are set forth in Table IV.

TABLE IV

Run No.	1	2	3	4
Temp., ° F.	750	800	850	900
Liquid Recovery Isomate, wt. percent	98.8	95.9	95.0	67.6
Do.	98.9	96.0	96.7	---
Isomate Oct. No., Res. Clear	45.0	60.0	75.4	89.6
Isomate Oct. No., Res. Clear after finishing to remove straight chain hydrocarbons	66	78.0	84	---

By operating in the above-indicated manner substantially all of the straight chain hydrocarbons in the initial

feed fraction are charged to an improved high octane material or to branch chain hydrocarbons.

The practice of this invention is particularly applicable to catalytic reforming followed by finishing of the reformer effluent or reformat for the removal of straight chain hydrocarbons therefrom. Petroleum fractions in the naphtha boiling range, e.g. having an initial boiling point in the range 45-250° F. and an end point in the range 175-475° F. and containing a substantial amount of naphthenic hydrocarbons, for example containing at least about 5-50% by volume naphthenic hydrocarbons, are particularly suited for treatment in accordance with this invention.

In accordance with another embodiment of the invention the catalytic reforming operation is carried out under relatively mild conditions of temperature, pressure and throughput such that substantially only the naphthenic hydrocarbons contained in the naphtha fraction undergoing treatment are dehydrogenated during the catalytic reforming operation whereas the remaining straight chain and non-straight chain (branched acyclic and/or aromatic) hydrocarbons pass through the catalytic reforming operation substantially unchanged. By operating in accordance with this embodiment of the invention the catalyst life of the catalyst employed in the catalytic reforming operation can be extended for an indefinite period of time. This is particularly advantageous when the catalytic reforming operation employs an expensive platinum-containing non-regenerable catalyst.

Further exemplary of the practice of this invention a catalytic reformed naphtha was finished in accordance with the practice of this invention by the removal of the straight chain hydrocarbons therefrom. There was produced a high octane finished gasoline having an octane number substantially greater than the initially charged naphtha and having a value higher than that which could be economically reached by catalytic reforming alone. The results are indicated in Table V.

TABLE V

	Reformat Charge	Finished Naphtha
° API	50.3	47.5
ASTM Research Octane: Clear	85.9	92.9
+3 cc. TEL	95.5	100.0
RVP, lbs.	2.9	3.0
ASTM Distillation, °F:		
IBP	132	130
5%	177	176
10	191	195
20	211	217
30	226	230
40	230	246
50	252	258
60	265	270
70	279	284
80	296	298
90	316	310
95	335	354
EP	368	353
Percent Rec.	98.0	98.0
Yields, Vol. Percent:		
Finished Naphtha	94.6	
Desorbed Material	5.0	

Still further exemplary of the practice of this invention a catalytic reformed gasoline was separated into ten (10) close boiling fractions and finished by the removal of the straight chain hydrocarbons therefrom. The results set forth in Table VI indicate that fractions of a catalytic reformed gasoline having a boiling point above about 250° F. exhibit a smaller octane number increase than the lower boiling fractions. Accordingly it is advantageous to finish only the more responsive lower boiling fractions of a reformat, leaving the relatively less responsive high boiling fractions untreated, rather than to finish the whole reformat.

TABLE VI

SELECTIVE FINISHING OF CLOSE BOILING FRACTIONS
FROM A CATALYTIC REFORMATE

[87.1 clear research oct.]

Cut No.	Boiling Range, ° F.	Vol. Per- cent Cu- mulative	ASTM Res. Oct. Clear		ASTM Res. Oct. +3 cc. TEL	
			Raw	Finished	Raw	Finished
1.-----	75-138	10.6	78.9	89.2	95.4	101.1
2.-----	138-171	20.6	71.0	82.2	89.4	96.6
3.-----	171-186	30.7	60.6	73.1	84.9	91.3
4.-----	186-209	40.7	78.1	91.0	94.4	100.8
5.-----	209-225	50.7	82.0	90.0	96.0	99.8
6.-----	225-249	60.8	86.6	94.3	97.3	100.7
7.-----	249-254	70.8	95.6	99.6	101.7	102.7
8.-----	254-311	80.9	97.6	100.9	102.7	103.3
9.-----	311-350	86.1	101.1	102.3	103.8	104.1
10.-----	350-440	97.9	103.8	104.6	105.1	106.0

For purposes of simplicity and clarity, conventional control equipment, valves, pumps, compressors, heaters, coolers, gas-liquid separators, fractionators, etc. have for the most part not been illustrated in the drawing. The location and employment of these auxiliary pieces of equipment and the like in the practice of this invention are well known to those skilled in the art. Furthermore the above-described operations of catalytic reforming, straight chain hydrocarbon adsorption and desorption and isomerization or reforming or converting of the desorbed straight chain hydrocarbons can be carried out substantially continuously by employing a plurality of catalytic reforming units 16 and adsorbers 29 and converters 51, one or more adsorbers 29 undergoing desorption-regeneration at the same time. For purposes of simplicity and clarity only one reformer unit 16, one adsorber 29 and one converter 51 have been shown. The employment of one or more of these units in the manner to effect substantially continuous operation is well known to those skilled in the art.

As is evident to those skilled in the art many modifications, substitutions and changes are possible in the practice of this invention without departing from the spirit or scope thereof.

This application is a continuation-in-part of copending application Serial No. 483,998, filed January 25, 1955 (now Patent No. 2,917,449), which in turn is a continuation-in-part of application Serial No. 478,426, now Patent No. 2,886,508, filed December 29, 1954.

We claim:

1. A petroleum treating process which comprises catalytically reforming a petroleum naphtha to yield a reformat, subjecting said reformat to fractionation to separate therefrom a C₄ fraction, a light reformat fraction having a boiling range in the range 75-250° F. and a heavy reformat fraction, contacting said light reformat fraction in the liquid phase with a 5 Angstrom unit alumino-silicate molecular sieve adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said light reformat and to yield a treated light reformat substan-

tially free of straight chain hydrocarbons, blending the resulting treated light reformat with said heavy reformat and at least a portion of said C₄ fraction to yield a product having improved qualities as a motor fuel.

2. A petroleum treating process which comprises catalytically reforming a heavy naphtha to yield a catalytic reformat, fractionating said catalytic reformat to separate therefrom a C₄ fraction, a light reformat fraction and a heavy reformat fraction, contacting said light reformat fraction with a 5 Angstrom unit alumino-silicate molecular sieve adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons therefrom, subsequently desorbing the adsorbed straight chain hydrocarbons from said adsorbent, recovering from the aforesaid adsorption a treated light reformat fraction and blending said treated light reformat fraction with said heavy reformat fraction.

3. A petroleum treating process which comprises pre-treating a broad boiling range sulfur-containing petroleum naphtha having light hydrocarbon material boiling below 100° F. and an end point in the range 392 to 475° F. to remove light hydrocarbon material boiling below 100° F. and to reduce the sulfur content of the remaining broad boiling range naphtha, catalytically reforming the pre-treated broad boiling range naphtha, fractionating the reformat and separating hydrogen and light hydrocarbons including C₁ to C₅ hydrocarbons therefrom, recycling a portion of said separated hydrogen to said reforming step, further fractionating and separating from the remaining reformat a light reformat fraction having a boiling point not above about 250° F., and a heavy reformat fraction having a boiling point range of about 250 to 450° F., contacting said separated light reformat fraction with a 5 Angstrom unit alumino-silicate molecular sieve adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons therefrom, recovering from said adsorption operation a treated light naphtha fraction now substantially free of straight chain hydrocarbons, blending said treated light naphtha fraction with said heavy reformat to yield a product having improved qualities as a motor fuel.

4. A method in accordance with claim 3 wherein said light reformat fraction is contacted with said molecular sieve alumino-silicate adsorbent in the liquid phase.

5. A method in accordance with claim 3 wherein said light reformat fraction is contacted with said alumino-silicate molecular sieve adsorbent in the gaseous phase.

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