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H. V. HESS ET AL

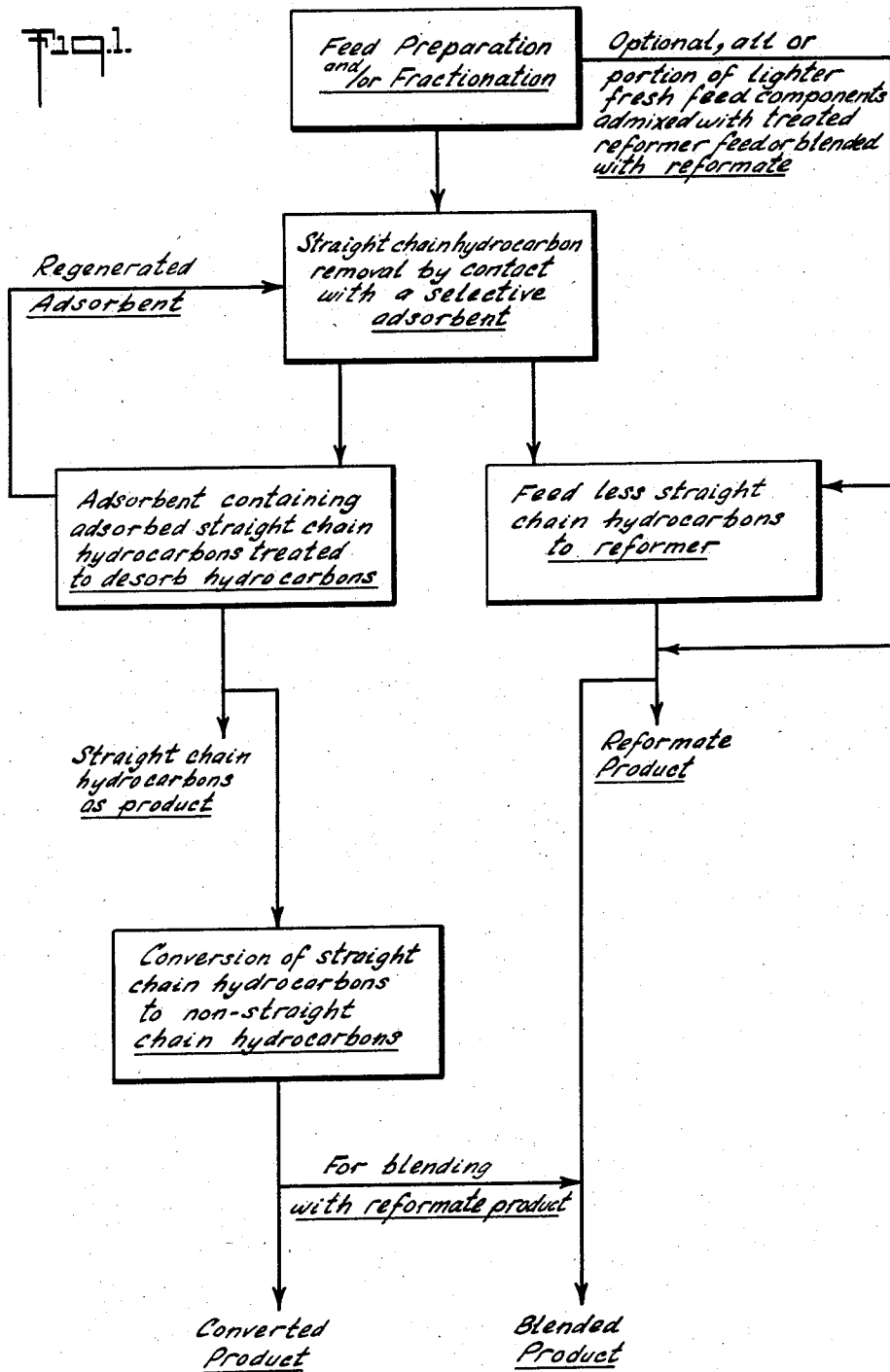
2,886,508

METHOD OF TREATING A PETROLEUM FRACTION USING MOLECULAR
SIEVE ALUMINO-SILICATE SELECTIVE ADSORBENTS

Filed Dec. 29, 1954

2 Sheets-Sheet 1

Fig. 1.



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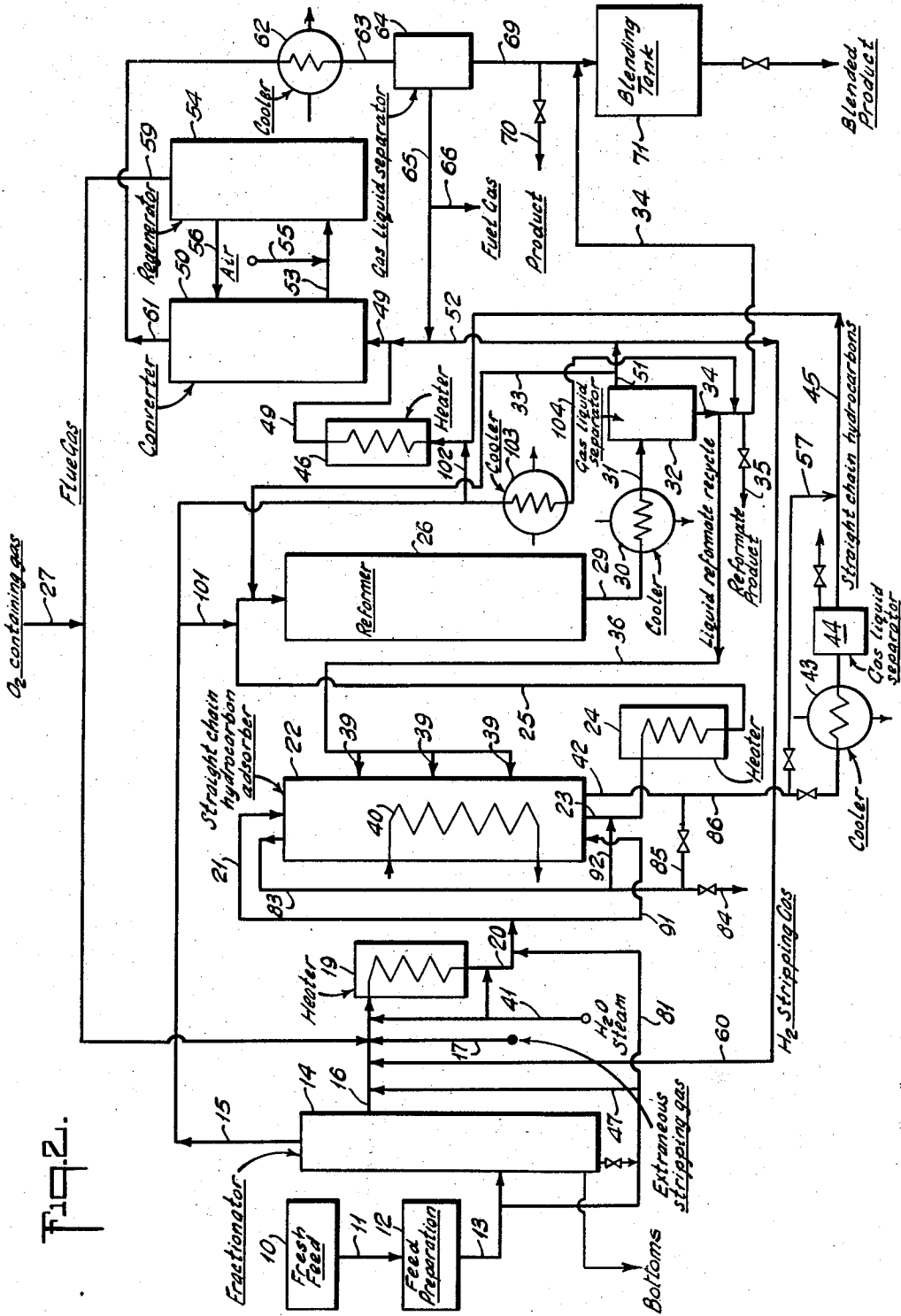
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METHOD OF TREATING A PETROLEUM FRACTION USING MOLECULAR SIEVE ALUMINO-SILICATE SELECTIVE ADSORBENTS**Howard V. Hess, Glenham, and Edward R. Christensen, Beacon, N.Y., assignors to The Texas Company, New York, N.Y., a corporation of Delaware**

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16 Claims. (Cl. 208—79)

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 naphtha or motor fuels in the gasoline boiling range to improve their quality. Still more particularly this invention is directed to the treatment of naphtha stocks 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 5-30% by volume, and higher.

Various converting 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 selective 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 selective petroleum fractions a number of reactions take place substantially simultaneously. For example, in a treating operation employing a platinum-containing catalyst in contact with a naphtha stock containing aromatics, naphthenes, isoparaffins and n-paraffins, dehydrogenation of the naphthenes to aromatics occurs. Substantially at the same time, especially when operating under more severe treating conditions, isomerization and dehydrogenation of the paraffinic components takes place. Additionally under these conditions aromatization or dehydrocyclization of the paraffinic components also takes place. Concurrently with these reactions, particularly under the more severe treating conditions, a certain amount of cracking takes place with the resulting deposition of carbon upon the catalyst. The straight chain hydrocarbons, particularly the C₈ and higher n-paraffins are susceptible to cracking with resulting carbon formation. The lighter straight chain hydrocarbons such as the C₆ and lighter n-paraffins are more refractory and exhibit less tendency to cracking and carbon deposition under a given set of reforming conditions than do the higher molecular weight straight chain hydrocarbons.

The platinum-containing treating catalysts employed in the present day commercial 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 catalyst, particularly a platinum catalyst, is the amount of carbon deposited or laid down upon the catalyst. The replacement of a spent treating catalyst, particularly a platinum-containing catalyst, is also 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 or unit 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 and/or treating process which is capable of handling a wide variety of petroleum fractions containing straight chain hydrocarbons and non-straight chain hydrocarbons, especially petroleum fractions in the gasoline boiling range, either a wide boiling or a narrow boiling cut.

Still another object of this invention is to provide a treating process wherein the useful onstream life of a treating catalyst, especially a platinum-containing catalyst, is substantially increased, particularly when compared with the same catalyst employed in a catalytic conversion or treating operation in the conventional manner at the same degree of severity.

Still another object of this invention is to provide a combination treating operation wherein the amount of improved high quality, high octane motor fuels is increased.

Yet another object of this invention is to provide a method employed in combination with a petroleum converting or treating operation for increasing throughput when operated at a given degree of severity or conversion.

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

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

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

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

Fig. 2 is a schematic flow diagram illustrating and setting forth various embodiments 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 contacting said fraction 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 and subjecting the resulting petroleum fraction now having a reduced proportion of straight chain hydrocarbons to a treating or converting operation, such as catalytic reforming, to produce a petroleum fraction of improved quality. The practice of this invention is particularly applicable to any petroleum fraction suitable for use in a reforming operation for the production of aromatics or improved naphthas or motor fuels in the gasoline boiling range, said petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons. By straight chain hydrocarbons is meant any aliphatic, acyclic or open chain hydrocarbon which does not possess side chain branching. 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, of course, the aromatic and naphthenic hydrocarbons as well as the iso-olefinic and iso-paraffinic 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 the range 200°-475° F. more or less. Furthermore, 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 a composition in the range:

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

The straight chain hydrocarbon or n-paraffin content of petroleum fraction suitable for use in the practice of this invention is frequently in the range 5-50% by volume more or less. Typical refinery stocks or fractions such as a wide boiling straight run naphtha, a light straight run naphtha, a heavy straight run naphtha, a catalytic cracked naphtha, a thermally cracked or a thermally reformed naphtha may be employed in the practice of this invention.

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 alumino-silicates such as a calcium alumino-silicate which exhibit the property of a molecular sieve, that is, inorganic materials made up of porous crystals wherein the pores of the crystal are of molecular dimension and are of uniform size. A particularly suitable solid adsorbent for straight chain hydrocarbons is a calcium alumino-silicate manufactured by Linde Air Products Company and designated Type 5A molecular sieve. The crystals of this particular calcium alumino-silicate, apparently actually a sodium calcium alumino-silicate, 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 up to at least C₁₄ in chain length to the substantial exclusion of the naphthenic and aromatic hydrocarbons, and the isoparaffins, isobutane and higher. This particular selective adsorbent is available in various sizes such as 1/16" and 1/8" diameter pellets as well as finely divided powder form.

Other solid selective adsorbents may be employed in the practice of this invention. For example, it is contemplated that selective solid adsorbents having the property of selectively adsorbing straight chain hydrocarbons over 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 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 dimensions sufficiently large to adsorb straight chain hydrocarbons but sufficiently small to exclude non-straight chain hydrocarbons. The naturally occurring zeolite chabazite exhibits such desirable properties. Another suitable naturally occurring zeolite is analcite NaAlSi₃O₆·H₂O 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



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, gruelinite, harmotome 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 n-olefins to the substantial exclusion of the non-straight chain hydrocarbons, including the aromatic and naphthenic hydrocarbons, are also 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 hydrocarbons) is optionally supplied to a suitable feed preparation and/or fractionation unit. Should the fresh feed contain substantial amounts of undesirable polar or polarizable compounds such as sulfur-containing compounds, oxygenated hydrocarbons, nitrogen-containing compounds and the like, it is sometimes desirable, although not necessary, to remove these materials from the fresh feed prior to the special subsequent feed treatment in accordance with this invention. The removal of these polar or polarizable materials may be accomplished by solvent extraction, extractive distillation, hydrogenation, dehydration, acid or caustic washing and the like or by any suitable combination. Processes for removing or effectively neutralizing the above-indicated polar and polarizable materials in a petroleum fraction are well known in the art and form no part of this invention.

The above-mentioned feed preparation operation may be carried out in a vapor or liquid phase and, of course, might involve vapor-liquid, liquid-liquid, vapor-solid and liquid-solid contacting operations depending upon the operating conditions necessary to effect the desired feed preparation or purification. Following the above-indicated feed preparation or concomitantly therewith, if desired, the feed may be fractionated to produce the desired feed containing straight chain hydrocarbons and non-straight chain hydrocarbons to be treated in accordance with this invention. The fractionation operation may be operated to produce a narrow boiling or wide boiling fraction depending upon the qualities of the finished treated product desired.

Following the feed preparation and/or fractionation operations the feed is contacted with a solid selective adsorbent material, in powder, beaded, microspheroidal, granular or pelleted form, for the selective adsorption of the straight chain hydrocarbons from the feed. Although it is preferred to remove substantially all of the straight chain hydrocarbons, it is realized that it is not necessary in the practice of this invention to adsorb or separate substantially all of the straight chain hydrocarbons. The extent or degree of straight chain hydrocarbon removal is governed by various factors including capacity of the equipment involved, the quality desired in the finished treated product, yield considerations, the particular subsequent hydrocarbon treating or converting operation, and the like.

The feed petroleum fraction undergoing treatment may be present during the selective adsorption operation either in the liquid phase or in the 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 feed petroleum fraction in contact therewith provided, of course, sufficient time is allowed to substantially saturate the adsorbent.

The contact of the feed with the selective solid adsorbent may be effected by various means. For example, operating with the feed petroleum fraction in the liquid phase a simple and direct method of effecting contact with the solid particle form selective adsorbent is to form a slurry of the petroleum fraction and the solid adsorbent material. After sufficient time the slurry may be settled and the liquid phase decanted by suitable means. Advantageously the resulting solid adsorbent material is recovered and washed with a non-straight chain hydrocarbon such as a petroleum fraction having a boiling point such that the separation of this wash petroleum fraction from the surface occluded feed is readily accomplished by distillation. A suitable low boiling non-straight chain hydrocarbon wash liquid is isobutane. After washing to remove

the surface adsorbed material from the solid adsorbent the adsorbent is dried to remove as much as possible of the wash liquid therefrom. Following this drying operation the adsorbent is stripped of its straight chain hydrocarbon content by heat (elevated temperature). Heat may be applied to the adsorbent by forcing or by passing a high temperature gas or vapor therethrough, such as a flue gas, nitrogen, methane or natural gas, superheated steam and the like. The resulting stripped regenerated solid adsorbent material is then recycled to the aforementioned slurry operation.

Besides the above-indicated method of effecting contact between the feed petroleum fraction and the selective solid adsorbent material the following other methods may be employed. A suitable amount of the solid adsorbent may be introduced directly into a liquid or vapor stream of the feed, such as into a refinery transfer line, to effect contact. The resulting admixture may be separated by any suitable means such as by settling, filtration and by means of cyclone or gas-solids separators and the like. In accordance with yet another method of contacting, the feed petroleum fraction may be treated with the solid selective adsorbent by circulation pumping wherein a slurry of the liquid feed and solid adsorbent is continuously recycled within a suitable treatment vessel until the desired extent of straight chain hydrocarbon removal has been effected.

In still another method of effecting contact between the solid adsorbent and feed petroleum fraction, in the liquid or vapor phase, the feed is countercurrently contacted with a downwardly moving stream or bed of particle form selective adsorbent. The adsorbent upon issuing from the bottom of the contacting or adsorbing vessel is stripped of surface adsorbed material, especially when the feed is in the liquid phase, and passed to a regenerator or desorber wherein the adsorbent flows downwardly in countercurrent contact with a desorbing medium. The resulting desorbed or regenerated solid adsorbent is then recycled to the top of the aforementioned contacting or adsorbing vessel for further contact with the feed. In a modification of this particular operation, when the feed petroleum fraction being treated is in the vapor phase, the solid adsorbent issuing from the bottom of the contacting vessel may be subjected to a relative high temperature gas lift operation which would serve not only to desorb or regenerate the solid adsorbent material but also to lift and recycle the adsorbent back into the top of the contacting vessel.

In yet another method for effecting contact between the solid adsorbent material and the feed petroleum fraction for the removal of straight chain hydrocarbons therefrom, a fluidized bed of a solid adsorbent material may be maintained by passing upwardly therethrough the vaporized fresh feed to be treated. A stream of the adsorbent material is continuously removed from the fluid adsorber and passed through a fluid regenerator wherein the adsorbent material maintained in the fluidized condition is desorbed by passing upwardly therethrough at high temperature a suitable desorbing medium, such as flue gas, hydrogen, nitrogen, natural gas, superheated steam, etc. The desorbed and regenerated adsorbent is continuously removed from the fluid regenerator and recycled to the fluid adsorber to contact additional fresh feed.

In still another method for effecting the removal of straight chain hydrocarbons from a fresh feed petroleum fraction, liquid fresh feed is contacted with the solid particle selective adsorbent preferably in the form of a fixed bed. After the removal of straight chain hydrocarbons from the fresh feed has been carried out to the extent desired superheated water or superheated steam at an elevated temperature, preferably at temperature of 400° F. or higher, is passed into contact and through the fixed bed of adsorbent. The superheated water or steam after sufficient time displaces the adsorbed straight chain hydrocarbons within the pores of the solid ad-

sorbent material and the resulting desorbed hydrocarbons are separately recovered. It is contemplated that the desorption of the surface adsorbed hydrocarbons from the adsorbent material in the case of liquid superheated water will be materially aided by the presence of a surface active agent in the water. It is envisaged that by making the adsorbent more wettable with respect to the water, the displacement of desorption of the surface adsorbed hydrocarbons in this operation will be materially aided. After desorption of the straight chain hydrocarbons from within the pores of the selective adsorbent by liquid superheated water the desorbed adsorbent material is dried in order to remove substantially all the water therefrom by passing hot (a temperature in the range 500–1100° F., preferably 700–1000° F.) gas therethrough. A suitable drying or desorbing gas in a flue gas, nitrogen, methane, hydrogen, gaseous low boiling hydrocarbons or superheated steam.

It is mentioned that after each of the foregoing desorption of stripping operations it may be desirable to outgas the resulting desorbed or regenerated adsorbent material by subjecting the adsorbent to a reduced, sub-atmospheric pressure so as to substantially completely empty the pores of the adsorbent material preferably immediately prior to contact with the fresh feed petroleum fraction being treated.

Following the adsorption operation for removal of the straight chain hydrocarbons from the fresh feed petroleum fraction the resulting petroleum fraction now containing substantially only or exclusively non-straight chain hydrocarbons is passed to a subsequent treating or catalytic conversion operation. The practice of this invention is particularly applicable to an operation employing in combination a catalytic reforming step, such as a catalytic reforming operation wherein a mixture of non-straight chain hydrocarbons in vapor form contacts an active reforming catalyst. In this operation in combination with the prior feed treatment for the removal of straight chain hydrocarbons in accordance with this invention, throughput and catalyst life are increased because of the removal of the straight chain hydrocarbons. The high molecular weight C₇ and C₈ and higher straight chain hydrocarbons tend to crack and lay down carbon at an elevated temperature, such as a temperature in the range 900–1000° F., whereas the lower molecular weight C₆ and lower straight chain hydrocarbons are more refractory and less susceptible to reforming and tend to pass through the reforming operation relatively unchanged. Carbon deposition on a reforming catalyst, such as a platinum-containing catalyst tends to diminish its activity and shorten its useful catalyst life. The lower molecular weight straight chain hydrocarbons, since they are more refractory and less susceptible to reforming, pass through the reforming operation relatively unchanged and act somewhat as an inert diluent therein.

Various catalytic conversion and reforming operations and processes well known to those skilled in the art may be employed in combination with the practice of this invention. The reforming processes may be sufficiently identified and described to those skilled in the art by merely mentioning their descriptive name, and include such reforming processes as Platforming, Ultraforming, Houdriforming, Catalytic Reforming, Catforming, Cycloversion, fixed bed Hydroforming, Fluid Hydroforming, Hyperforming, Thermoform Catalytic Reforming or Sovaforming and the like. Generally these reforming processes 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 for producing high octane motor fuel components from naphthas or selected petroleum fractions, or for producing high yields of aromatics or petrochemicals or high quality motor fuel components. These 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 operated at a temperature in the range 825–1000° F. more or less, and a pressure in the range 150–900 p.s.i.g., more or less, depending upon the severity or extent of reforming desired or the quality or composition of the petroleum fraction undergoing reforming and/or product desired. Various catalysts suitable for converting or reforming hydrocarbons may be employed, e.g. platinum-containing catalysts, molybdena-alumina catalysts, chromia-alumina catalyst and cobalt molybdate catalysts, the reforming operation sometimes being defined merely by the particular catalyst employed therein.

As a result of the reforming operation there is recovered a reformat product of improved quality, in the case of motor fuel manufacture a reformed product comprising a high quality motor fuel having a research octane number clear of at least about 80 and higher. If desired, particularly when the fresh feed petroleum fraction comprises a heavy straight run naphtha, there may be blended with this reformat, if desired or in order to meet motor fuel volatility requirements or the like, a whole untreated light naphtha fraction, such as a light straight run naphtha, which might comprise straight chain and non-straight chain hydrocarbons possessing up to about a C₅ or C₆, inclusive, carbon atom content and which may be derived as a separate stream during the feed preparation and fractionation operation as indicated in Fig. 1.

The straight chain hydrocarbons adsorbed on the adsorbent material are desorbed or displaced therefrom by the application of heat (high temperature in the range 700–1000° F., more or less), preferably by means of superheated steam and are separately recovered, and the resulting desorbed or regenerated adsorbent material is contacted with additional fresh feed.

The recovered straight chain hydrocarbons are advantageously subsequently treated or converted, e.g. isomerized or reformed such as by catalytic reforming or by thermal reforming methods, catalytic or non-catalytic, to produce an isomertate or reformat having a substantial non-straight chain hydrocarbon content. This material now containing straight chain hydrocarbons together with a substantial amount of non-straight chain hydrocarbons is advantageously blended with the reformat product recovered from the first mentioned treatment or catalytic reforming of the non-straight chain hydrocarbons. If desired the straight chain hydrocarbon content of the isomertate or reformat resulting from the conversion or reforming of the desorbed straight chain hydrocarbons may be subjected to another adsorption operation for the substantially complete removal of straight chain hydrocarbons therefrom. The resulting material recovered from this last mentioned other adsorption operation is then blended with the first mentioned reformat to produce a finished product of improved quality. The straight chain hydrocarbons adsorbed during said other adsorption operation are recovered and subsequently recycled to the above-mentioned straight chain hydrocarbon isomerization or reforming operation to produce additional non-straight chain hydrocarbons. In the above-indicated manner it is seen that substantially all of the straight chain hydrocarbons in the original fresh feed petroleum fraction can, if desired, be converted to non-straight chain hydrocarbons. Moreover, if desired, a fraction of the desorbed straight chain hydrocarbons originally in the fresh feed, particularly the low molecular weight C₅ and lower boiling point hydrocarbons, may be blended in the finished converted or reformed product in order to meet volatility requirements as a motor fuel without at the same time unduly decreasing the octane number of the finished product since these low molecular weight straight chain hydrocarbons possess a rather high octane number. For example, n-butane has a research octane number of about 95 and n-pentane has a research octane number of about 62.

In Fig. 2 of the drawing there are schematically illus-

trated various embodiments of the practice of this invention. As indicated hereinabove the adsorption operation as applied to the separation of straight chain hydrocarbons from a hydrocarbon fraction containing the same together with non-straight chain hydrocarbons may be carried out in either the vapor or liquid phase, followed by the recovery of the non-straight chain hydrocarbons as a separate stream which is subsequently passed to a following conversion operation such as a catalytic reforming operation for the production of a high quality or improved motor fuel or gasoline. The adsorbed straight chain hydrocarbons are separately recovered from the selective adsorbent as a special product, e.g. for use as an industrial solvent, or separately treated or reformed for the production of additional non-straight chain hydrocarbons which advantageously are recovered as a separate product or blended with the reformat produced by the catalytic reforming of the non-straight chain hydrocarbons. Such an operation, as outlined above, is carried out in the practice of this invention as follows.

Referring now to Fig. 2 of the drawing a fresh feed petroleum fraction from tank 10 is passed via line 11 into feed preparation unit 12 for the removal of undesirable hydrocarbons or polar or polarizable components, e.g. sulfur-containing compounds. The resulting prepared feed is passed via line 13 to a fractionating column 14 wherein it is fractionated to produce overhead the relatively low molecular weight constituents thereof via line 15 and a side stream comprising a selected naphtha fraction, such as a heavy straight run naphtha fraction. A heavy straight run naphtha fraction might have the composition set forth in Table I.

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 No., 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

This selected naphtha fraction is passed from fractionator 14 via line 16 to heater 19 wherein its temperature is increased to a temperature in the range 300–600° F., usually in the range 400–500° F., but sufficient to insure complete vaporization of the naphtha fraction. This naphtha fraction leaves heater 19 via line 20 and is introduced by means of line 21 into the top of adsorber 22 which contains a fixed bed of solid particle form selective adsorbent for straight chain hydrocarbons. The adsorber 22 is operated at a temperature such that substantially all of the straight chain hydrocarbons, such as the normal paraffins in the vaporized naphtha fraction introduced into the adsorber 22, are adsorbed by the adsorbent material therein and there issues from the bottom of adsorber 22 via line 23 naphtha fraction now substantially free of straight chain hydrocarbons. Adsorption conditions within adsorber 22 are to some extent dependent upon the composition of the petroleum fraction undergoing treatment, e.g. the greater the amount of straight chain hydrocarbons therein the larger the adsorption or processing period required to effect substantially complete adsorption of the straight chain hydrocarbons therefrom or the desired composition of the effluent issuing from adsorber 22. Generally, processing periods in the range 2 to 5 minutes up to about 1½–2 hrs. at throughputs in the range ¼–½ v./hr./v. up to about 3–5 and higher v./hr./v. are satisfactory before the adsorbent material within adsorber 22 is substantially saturated with straight

chain hydrocarbons or to effect the removal of the straight chain hydrocarbons to the desired extent. Particularly satisfactory results have been obtained at an adsorption temperature in the range 400–600° F. and at a space velocity of about 1 v./hr./v. After the adsorbent material in this adsorber 22 is substantially saturated with straight chain hydrocarbon it is taken off stream and the straight chain hydrocarbons desorbed therefrom and the adsorbent material thereby regenerated in the manner described herein. After desorption-regeneration of the adsorbent it is again contacted with additional feed to effect the removal of the straight chain hydrocarbons therefrom.

The naphtha fraction issuing from adsorber 22 via line 23, now substantially free of straight chain hydrocarbons, is passed through heater 24 wherein its temperature is increased to a value in the range 800–1000° F. and by means of line 25 introduced into a reformer 26. Reformer 26 contains a solid particle 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 reformer 26 when employing a platinum-containing catalyst are as follows: inlet temperature of 875° F., a pressure of 250 p.s.i.g., a space velocity of 3 v./hr./v. with a recycle of 8,000 c.f./bbl. of charge naphtha of a gas containing about 97 mol percent hydrogen. Two or more of these catalytic reformers 26 may be employed in series or in parallel. The reformed naphtha fraction issues from a reformer 26 via line 29 and is then passed through a cooler 30 and by means of line 31 into a gas liquid separator 32 wherein the reformate separates into a gas phase and a liquid reformate phase. A portion of the gas phase recovered from separator 32 is recycled in the conventional manner via line 33 to reformer 26 to provide the desired hydrogen atmosphere therein. The liquid reformate is withdrawn from separator 32 via line 34 and a portion thereof may be withdrawn as product of improved quality via line 35. Another portion of the reformate withdrawn from separator 32 via line 34 may be recycled to adsorber 22 via line 36 and lines 39 to serve as an internal coolant and/or diluent therein so as to control better the adsorption temperature within adsorber 22, or to cool the hot desorbed regenerated adsorbent, following the desorption operation described hereinafter, the resulting hot vaporized recycled reformate then being passed in indirect heat exchange with the feed to reformer 26 to supply at least a portion of the heat necessary to bring the feed up to reforming temperature.

The heat of adsorption of straight chain hydrocarbons on certain selective adsorbent materials is considerable and if not controlled may lead to unduly high adsorption temperatures and adversely affect the operation of the adsorber 22. Since this recycled reformate is for the most part substantially free of straight chain hydrocarbons, its reintroduction into adsorber 22 during adsorption does not unduly affect the desorption operation. Liquid fresh feed or relatively cool vaporized feed introduced into adsorber 22 via lines 81 or 20, respectively, and line 21 may also be used to cool the hot desorbed adsorbent. Advantageously heat exchange means 40 is provided within adsorber 22 to serve as temperature control means during the adsorption operation and as a heating means during the desorption of the straight chain hydrocarbons from the adsorbent material contained within adsorber 22.

The desorption of the straight chain hydrocarbons from the adsorbent material within adsorber 22 is effected by supplying desorbing gas having a molecular diameter sufficiently small to penetrate the pores of the adsorbent, such as flue gas, methane, nitrogen, introduced via line 17, or superheated steam introduced via line 41 into line 16. Advantageously, when steam is employed as

the desorbing medium it is followed by a purge gas such as methane, nitrogen and the like to displace the steam from the pores of the adsorbent prior to contact with additional fresh feed. Within heater 19 the desorbing medium is, if necessary, brought up to the desired desorption temperature (which may be the same as the adsorption temperature) such as a temperature in the range 500–1100° F., usually 100–300° F. higher than the adsorption temperature and in the range 700–1000° F. 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 solid adsorbent or decomposition or cracking of the adsorbed hydrocarbons. The hot desorbing medium issues from heater 19 via line 20 and is introduced via line 21 into the top of adsorber 22 wherein upon passing through the adsorbent material therein it effectively strips and displaces the adsorbed straight chain hydrocarbons. The stripping medium together with desorbed straight chain hydrocarbons leaves adsorber 22, in the above-described operation, via line 42 and are passed via line 86 through a suitable cooler 43 and gas-liquid separator 44. The liquefied straight chain hydrocarbons are recovered from separator 44 via line 45 and introduced into heater 46 where they are heated to a suitable temperature for a subsequent converting or treating operation, such as a reforming or isomerization operation, e.g. a catalytic reforming or isomerization or thermal reforming or cracking operation.

The heated straight chain hydrocarbons issue from heater 46 via line 49 into a converter vessel 50. As schematically indicated in Fig. 2 the converter or reformer vessel is provided with a fluid bed of reforming catalyst such as a chromia-alumina reforming catalyst preferably containing ceria and potassia. The reforming catalyst is maintained in the fluidized condition by the upflowing stream of vaporized straight chain hydrocarbons introduced into converter 50 via line 49. The reforming operation carried out in vessel 50 is more severe than the reforming operation carried out within the reformer vessel 26 because the straight chain hydrocarbons supplied to reformer vessel 50 are more refractory and less susceptible to dehydrogenation and similar reforming reactions than the naphthenes which would usually comprise a substantial portion of the non-straight chain hydrocarbons supplied to reformer 26. Exemplary of suitable reforming conditions, reformer 50 may be operated at a temperature of 900–1000° F. more or less and at superatmospheric pressure with a space velocity of 0.4 v./hr./v. and a gas recycle rate of 1250 c.f./bbl. of feed. It is desirable to maintain in catalytic converter 50 a hydrogen atmosphere. Advantageously to provide such a hydrogen atmosphere hydrogen gas recovered from separator 32 is injected into a converter 50 via lines 51, 52 and 49 together with the feed to converter 50.

Because of the more severe reforming conditions employed in converter 50 and due to the fact that the straight chain hydrocarbons converted or reformed therein are prone to lay down or deposit carbon upon the catalyst surface, thereby adversely affecting the converting or reforming operation, a continuous stream of spent catalyst is removed from converter vessel 50 via line 53 and passed into catalyst regenerator 54 wherein the carbon content of the catalyst is burned by introducing air or other oxygen-containing gas in suitable quantities via lines 55 and 53. Hot regenerated catalyst is recycled to converter 50 via line 56. The flue gas issuing from regenerator 54 via line 59 may be employed, as indicated, via line 59 as a desorbing or stripping medium for the removal of the straight chain hydrocarbons from the adsorbent material within adsorber 22. Moreover, if desired, a portion of the hydrogen recovered from separator 32 may be recycled as a stripping or desorbing medium to adsorber 22 via lines 51 and 60. By employing gaseous hydrogen as a stripping medium for the

straight chain hydrocarbons there is advantageously produced a very suitable feed for converter 50 via lines 42, 57 and 45 and obviates the necessity for separately recovering the desorbed straight chain hydrocarbons from the desorbing medium such as would be the case if an inert gas or superheated steam or flue gas or natural gas and the like were employed as the stripping medium.

The reformed product issuing from converter 50 via line 61 is cooled by means of cooler 62 to liquefy the normally liquid hydrocarbons therein. The resulting cooled mixture is passed via line 63 through gas-liquid separator 64. A portion of the gas from gas-liquid separator 64 may be recycled to converter 50 via lines 65, 52 and 49 to the extent determined by the hydrogen content of this gas. If desired a portion of this gas recovered from separator 64 via line 65 may be removed via line 66 as a fuel gas for steam generation, power generation, flue gas generation and the like. The liquid reformat product recovered from separator 64 via line 69 may be separately withdrawn via line 70 as a liquid reformat product, such as a petroleum fraction in the gasoline boiling range having an improved octane number. If desired the liquid reformat product from separator 64 may be transferred via line 69 to the reformat blending tank 71 where it may be blended with the liquid reformat product recovered from separator 32 via line 34 to produce a blended product of improved quality.

After the adsorbent material in adsorber 22 has undergone a number of adsorption, desorption and regeneration cycles the effectiveness or adsorptive capacity of the adsorbent material sometimes becomes decreased apparently due to the accumulation of carbonaceous material on the surface of the adsorbent and/or within its pores deposited on the adsorbent during the desorption and regeneration of the adsorbent. This material can be readily removed by controlled burning. In accordance with one embodiment of this invention high temperature oxygen-containing gas or air is supplied to adsorber 22 via lines 17 and 16, heater 19 and lines 20 and 21 or controlled amount of air added via line 27 into flue gas line 59 and eventually into adsorber 22 as illustrated at a controlled temperature in the range 600-1100° F., such as a temperature in the range 700-900° F., to controlledly burn this undesirable carbonaceous material from the adsorbent without at the same time exposing the adsorbent to too high a temperature, such as 1500° F., which would adversely affect or destroy the adsorptive properties of the adsorbent. After regeneration in this manner it has been observed that the adsorptive capacity of the selective adsorbent, such as in the case of a calcium aluminosilicate adsorbent of the type exemplified by the Linde 5A molecular sieve, is restored to its original capacity. By regularly employing an oxygen-containing hot stripping gas (temperature of about 1,000° F., O₂ concentration in the neighborhood of about 3% by volume) the adsorbent material contained within adsorber 22 is maintained at its original high adsorptive capacity.

Example No. 1

The following is exemplary of a practice of this invention wherein a straight run naphtha is contacted in the vapor phase with a solid adsorbent, a sodium calcium aluminosilicate, as exemplified by Linde 5A molecular sieve, and wherein the recovered non-straight chain hydrocarbons are reformed catalytically, including the separate catalytic reforming of the desorbed recovered straight chain hydrocarbons such as may be contained and separated from the straight run naphtha feed in accordance with this invention. More particularly a straight run naphtha fraction containing about 28.5% by volume straight chain hydrocarbons, the remaining being non-straight chain hydrocarbons comprising naphthenic, aromatic and isoparaffinic hydrocarbons, said fraction having a research octane number of 44.1 clear, +3

cc. TEL 66.4, was contacted with the above-identified solid adsorbent to produce a platformer feed having an octane number research clear 62.8, and +3 cc. TEL 79.7. This feed was subjected to reforming by contact with a platforming catalyst at a temperature of about 900° F. and at a pressure of 500 p.s.i.g. employing a space velocity of 3 v./hr./v. There was produced a liquid reformat at a yield of 93.6% by volume based on the platformer feed substantially free of straight chain hydrocarbons and having a research octane number clear of 90, +3 cc. TEL 98.1.

A straight chain hydrocarbon fraction comparable to the desorbed straight chain hydrocarbons which are recovered from the above-mentioned adsorption operation and having a composition of about 24% by volume n-pentane, 56% by volume n-hexane and 20% by volume n-heptane and exhibiting an octane number of 28 was passed into contact with a platinum isomerization catalyst at a temperature of 800° F. and a space velocity of 1.0 v./hr./v. to produce an isomerate at a yield amounting to at least about 95% by volume, based on the charge to the isomerization reactor, and having an octane number of 58. This isomerate was subsequently contacted with a selective adsorbent material, Linde 5A molecular sieve, to produce a finished isomerate at a yield of 61.5% by volume based on the charge to the isomerizer having an octane number clear of 77.1, +3 cc. TEL 94. The straight chain hydrocarbons comprising substantially all n-paraffins and amounting to about 34% by volume of the original charge to the isomerizer are advantageously recycled to the isomerization unit together with additional fresh charge. By operating in the above-indicated manner substantially all of the straight chain hydrocarbon constituents of the initial naphtha fraction are changed to an improved high octane material.

Exemplary of the advantages to be obtained from the practice of this invention it was determined that when a reformer feed having a composition as set forth hereinabove, i.e. 28.5% normal paraffins, was passed directly through a reforming operation it was necessary to carry out the reforming operation at a higher temperature, namely 925° F., in order to achieve a liquid reformat product having the same (90 clear) octane number as was produced in the above-described combination operation employing a substantially n-paraffin free reformer feed and carrying out the platforming operation at a temperature of 900° F. Moreover because of the fact that it is necessary to operate the reforming operation in the instance of the untreated platformer feed at a higher temperature (925° F.) and because of the presence in the reformer feed of straight chain hydrocarbons, particularly the normal paraffins, the effectiveness or efficiency of the reforming catalyst is reduced because of the deposition of carbon upon the catalyst brought about by the degradation or cracking of the straight chain hydrocarbons or n-paraffin content of the reformer feed. Moreover it was observed that the total yield of liquid reformat in an operation in accordance with this invention for the production of a motor fuel of given octane number, was increased by about 1.5 volume percent, a significant improvement when it is realized that in a day's operation in a single reforming unit upwards of 20,000 and 30,000 barrels per day of a naphtha fraction are treated or reformed.

Moreover it is pointed out that should the catalytic reforming operation be carried out at the same temperature, 900° F., but without the benefit of treating the reformer feed in accordance with this invention for the removal of the straight chain hydrocarbons there was produced a liquid reformat product having a research octane number clear of 82, +3 cc. TEL 93.7, each, respectively, 8 and 4.4 octane numbers less than a liquid reformat produced by employing the combination treating operation of this invention. Moreover by operating in accordance

with this invention a yield advantage of 6% by volume is obtained in this instance.

In accordance with another embodiment of this invention employing in combination the removal of straight chain hydrocarbons from a naphtha fraction, especially a naphtha fraction containing 10% or more by volume straight chain hydrocarbons, and at least about 10% by volume naphthenes, followed by catalytic reforming of the remaining non-straight chain hydrocarbons together with the reforming of the straight chain hydrocarbons recovered from the adsorption step, the catalytic reforming of the non-straight chain hydrocarbons, containing aromatic, naphthenic and isoparaffinic hydrocarbons is carried out at such a level that substantially only the naphthenic hydrocarbons are dehydrogenated with the resulting production of additional aromatic hydrocarbons. The conditions of reforming are such that the isoparaffinic constituents are substantially unaffected or are not reformed to any significant degree. More particularly the reforming of the non-straight chain hydrocarbons under relatively mild conditions is conducted under pressures of about 200-700 or higher p.s.i.g. at a temperature in the range 750-975° F. in the presence of a reforming, predominantly dehydrogenating catalyst, preferably a platinum-containing catalyst, with a space velocity in the range 3-20 liquid volumes per hour per volume of catalyst. The operation is carried out in the presence of hydrogen by recycling gas containing 95% or higher of hydrogen, recovered from the reforming operation itself, at a rate of about 3,000-9,000 cu. ft. per barrel of liquid charge. This light reforming operation is preferably carried out in a fixed bed operation with the charge stock being preheated to approximately the reforming temperature and then contacted with the catalyst. In a specific typical operation the naphtha, after removal of substantially all of the straight chain hydrocarbons, is contacted with the catalyst at temperatures of 870-925° F. under 250 p.s.i.g. pressure with a space velocity of 3 v./hr./v. and with a recycle of 6,000 cu. ft. of hydrogen-containing gas per barrel of naphtha.

The straight chain hydrocarbons recovered from the selective adsorbent are separately subjected to a second, more severe reforming operation operated to promote isomerization, dehydrocyclization and the like of the straight chain hydrocarbons. The straight chain hydrocarbons are usually predominantly comprised of normal paraffins. The reforming conditions in this second stage operation are more severe than the relatively mild reforming or dehydrogenation conditions employed in the treatment of non-straight chain hydrocarbon fraction. Although the same catalyst may be employed in both operations it is preferred to employ in the second stage reforming operation a catalyst which can be readily regenerated. Desirably the catalyst in the second stage is a chromia-alumina catalyst preferably containing minor amounts of ceria and potassia. This catalyst is well known and readily available and usually contains about 10-20% chromia or alumina. It is desirable to exclude from the second stage reforming catalyst components which may promote cracking. The second stage reforming catalyst is preferably carried out in a hydrogenating atmosphere, preferably in the presence of a predominantly hydrogen atmosphere. Hydrogen gas for use in the second stage reforming operation may be obtained by the recovery of hydrogen gas from the first stage reforming operation.

The reforming conditions applicable in the above-described embodiment of this invention for the separate reforming of a non-straight chain hydrocarbon fraction and a straight chain hydrocarbon fraction, with respect to temperatures, pressures, catalyst employed, recycle ratios and the like are more completely described in co-pending, co-assigned patent application Serial No. 393,699, filed November 23, 1953, in the name of Norman D. Carter, Michael D. Riordan and Howard V. Hess, one

of the co-inventors of this invention, the disclosures and teachings of the above-identified co-pending, co-assigned patent application are herein incorporated and made a part of this disclosure.

By operating in the above-described manner, especially when the non-straight chain hydrocarbon fraction recovered from the adsorber is treated under relatively mild reforming conditions to effect substantially only dehydrogenation of the naphthenic hydrocarbons, the useful life of the catalyst can be greatly extended, almost to an indefinite length of time. This is especially beneficial when a platinum-containing catalyst is employed in the reforming of the non-straight chain hydrocarbon fraction.

Another method for increasing the useful life of a reforming catalyst employed in a reforming operation for upgrading a naphtha fraction or for obtaining a higher octane naphtha product than otherwise obtainable without adversely affecting the useful catalyst life is to treat the reformate, such as platformate, issuing from the reformer with a selective solid adsorbent to effect substantially complete removal of the straight chain hydrocarbons therefrom. The normal paraffins, particularly in the range C₇ and higher, have very poor anti-knock qualities, i.e. have a very low octane rating, and by removing the straight chain hydrocarbons from the reformate the octane rating of the reformate can be substantially increased. In conventional practice the higher the octane rating of a naphtha or motor fuel component produced as a reformate the more severe are the reforming or platforming conditions that must be employed. By removing the straight chain hydrocarbons from the reformate the resulting reformate will have a substantially increased octane number with the advantage that less severe reforming conditions may be initially employed and still at the same time, for a given feed, achieve the same octane number in the final product. This method of treating a petroleum fraction in combination with an antecedent conversion operation, e.g. increasing the octane number of a reformate such as a platformate by an operation involving the removal of straight chain hydrocarbons therefrom, is more particularly and thoroughly described in our co-pending patent application Serial No. 483,998, filed January 25, 1955.

As disclosed hereinbefore the treatment of a hydrocarbon fraction containing both straight chain hydrocarbons and non-straight chain hydrocarbons for the removal of straight chain hydrocarbons therefrom may be carried out in either the liquid or vapor phase. When operating in the liquid phase, and after suitable feed preparation, referring again to Fig. 2 of the drawing, a liquid naphtha fraction at a temperature below its initial boiling point or substantially above its boiling point provided sufficient pressure is employed to maintain it in the liquid phase is introduced via lines 13, 81, 20 and 21 into the top of adsorber 22 wherein it flows downwardly in contact with the selective adsorbent material for the straight chain hydrocarbons. A liquid fraction is recovered from the bottom of adsorber 22 via line 23 from which it passes into heater 24 and line 25 into reformer 26 and treated in the manner already described.

The desorption of the surface adsorbed hydrocarbons and the pore adsorbed straight chain hydrocarbons from adsorber 22 in this operation may be effected in the manner already described, that is employing a hot stripping or regenerating gas such as hydrogen or superheated steam or by displacement with liquid superheater water maintained at a suitable elevated temperature. When employing water as the desorbing medium, first the surface wetting and/or adsorbed, predominantly aromatic hydrocarbons are displaced followed by the desorption of the straight chain hydrocarbons from within the pores of the selective adsorbent. The displaced straight chain hydrocarbons are removed from the top of adsorber 22 via line 83. These displaced straight chain hydrocarbons can be recovered as a separate product by line 84 or subjected to a subsequent reforming operation, as already

described, by passing from line 83 and lines 85, 86, through cooler 43 and separator 44 if necessary, and line 45, heater 46 and line 19 to reformer 50 wherein they are upgraded by various reforming reactions, including isomerization, dehydrocyclization, and even cracking into a material more suitable for use as a motor fuel.

Instead of a liquid or vapor feed downflow within adsorber 22 the liquid or vapor fraction introduced into adsorber 22 for the removal of straight chain hydrocarbons therefrom may flow upwardly within adsorber 22 by introducing the liquid or vapor fraction into the bottom of adsorber 22 by means of line 91, after the feed has undergone suitable preparation or fractionation as already described. A fraction substantially free of straight chain hydrocarbons leaves adsorber 22 via line 83 for introduction into reformer 26 via lines 92, 23, heater 24 and line 25. The straight chain hydrocarbons are desorbed by introducing a stripping agent such as hydrogen, nitrogen, natural gas, flue gas and the like or water into the bottom of adsorber 22 via line 91 which is supplied with the stripping agent in the manner indicated in Fig. 2 of the drawing. The desorbed straight chain hydrocarbons are recovered from the top of adsorber 22 by means of line 83 and may be transferred in the manner already described to converter 50 to effect conversion or reforming of the desorbed straight chain hydrocarbons.

As indicated in Fig. 2 of the drawing an operation particularly suitable for the treatment of a wide boiling naphtha fraction such as a straight run naphtha fraction comprises fractionating a straight run naphtha feed introduced via line 11 into feed preparation unit 12 and line 13 into fractionator 14. A relatively heavy straight run fraction is separately recovered as a separate side stream via line 16 and treated in the manner described. The lighter components C_6 or C_5 and lighter are removed overhead from a fractionator 14 via line 15. All or a portion of the overhead fraction may be transferred via line 101 to line 25 to reformer 26 wherein, depending upon the severity of the reforming operations, they pass through relatively unchanged or are isomerized to some extent. The C_5 and lighter paraffinic hydrocarbons possess an octane number sufficiently high that their presence in the reformate issuing from reformer 26 is tolerable, if not desirable. Additionally the C_5 and lighter hydrocarbons impart desirable volatile characteristics to the reformate from reformer 26. Moreover all or part of the C_6 and lighter hydrocarbon fraction recovered from fractionator 14 via line 15 may be transferred to converter 50 via line 102, line 45, heater 46 and line 49 for subsequent conversion into more valuable material, e.g. reforming by isomerization and dehydrocyclization of the paraffinic constituents and dehydrogenation of the naphthenic constituents into a motor fuel component of improved quality. As indicated in the drawing all or a portion of the C_6 and lighter fraction may be admixed with the reformate product from reformer 26 by passage through cooler 103, if required, and line 104 into line 34. Moreover this same C_6 and lighter fraction may be admixed with the product or reformate from converter 50 and, if desired, transferred along line 34 into line 69 which serves as the inlet to the reformate blending tank 71. Line 47 is provided so that, if desired, the fresh feed in line 13 can be introduced directly into adsorber 22 via lines 81, 20 and 21 or via line 16, heater 19 and lines 20 and 21, by passing fractionator 14.

The above-described operations with respect to straight chain hydrocarbon adsorption, reforming of the initial straight chain hydrocarbon free material and isomerization or reforming of the desorbed straight chain hydrocarbon material can be carried out substantially continuously by employing a plurality of adsorbers 22, one or more adsorbers onstream and one or more adsorbers undergoing desorption and regeneration at the same time, likewise, if necessary, a plurality of converters 50. For purposes of simplicity and clarity only one adsorber 22

and one reformer 26 and one converter 50 have been shown. The employment of one or more adsorbers and reformers in the manner to effect substantially continuous operation is well known to those skilled in the art and the applicability to the practice of this invention is deemed obvious. The adsorption and desorption operations in accordance with this invention may be carried out at desired temperature or a pressure commensurate with the operating conditions desired, i.e. liquid or vapor phase adsorption and/or desorption. It is preferred to carry out adsorption and desorption in the vapor phase, at elevated temperature above 300° F. preferably in the range 400–600° F. and higher during desorption and to adsorb and desorb at substantially atmospheric pressure, employing a sufficient pressure to obtain a satisfactory throughput.

For purposes of simplicity and clarity the conventional control equipment, valves, pumps, heaters, coolers, gas-liquid separators, etc. have for the most part not been illustrated. The location and employment of these auxiliary pieces of equipment and the like in the practice of this invention are well known.

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.

We claim:

1. A method of reforming a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises contacting said fraction with a solid particle form molecular sieve aluminosilicate selective adsorbent made up of porous crystals wherein the pores of the crystals are of uniform size and have a pore size of about 5.0 Angstrom units, a pore size sufficient to admit straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons, and which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said fraction, subjecting the resulting petroleum fraction having a reduced proportion of straight chain hydrocarbons to catalytic reforming to produce a reformed petroleum fraction of improved quality.

2. A method of reforming a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises contacting said fraction with a solid particle molecular sieve aluminosilicate selective adsorbent made up of porous crystals wherein the pores of the crystals are of uniform size and have a pore size of about 5.0 Angstrom units, a pore size sufficient to admit straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons, and which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons from said fraction, subjecting the resulting petroleum fraction having a reduced proportion of straight chain hydrocarbons to catalytic reforming, including dehydrogenation, to produce a reformed petroleum fraction of improved quality and a resulting net production of hydrogen, recovering at least a portion of the resulting produced hydrogen and employing the recovered hydrogen as a stripping medium to desorb the adsorbed straight chain hydrocarbons from said adsorbent.

3. A method in accordance with claim 2 wherein the resulting desorbed straight chain hydrocarbons in admixture with hydrogen are subjected to a reforming operation to produce a separate reformate having improved motor fuel qualities with respect to said straight chain hydrocarbons charged to said reforming operation.

4. A method of reforming a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises contacting said fraction with a solid particle molecular sieve aluminosilicate selective adsorbent made up of porous crystals wherein

the pores of the crystals are of uniform size and have a pore size of about 5.0 Angstrom units, a pore size sufficient to admit straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons, and which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said fraction, subjecting the resulting petroleum fraction now consisting predominantly of non-straight chain hydrocarbons to catalytic reforming, including dehydrogenation, with a resulting net production of hydrogen, to produce a first reformat, recycling a portion of the produced hydrogen to said catalytic reforming operation, desorbing the adsorbed straight chain hydrocarbons from said solid adsorbent and subjecting the desorbed straight chain hydrocarbons in the presence of another portion of the hydrogen recovered from the aforesaid catalytic reforming operation to isomerization to produce an isomate, said reformat and said isomate having improved motor fuel qualities with respect to the material charged to their respective operations.

5. A method of reforming a petroleum fraction in the naphtha boiling range containing straight chain hydrocarbons and non-straight chain hydrocarbons, said non-straight chain hydrocarbons comprising isoparaffinic, naphthenic and aromatic hydrocarbons which comprises contacting said fraction with a solid particle molecular sieve alumino-silicate selective adsorbent made up of porous crystals wherein the pores of the crystals are of uniform size and have a pore size of about 5.0 Angstrom units, a pore size sufficient to admit straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons, and which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said fraction, subjecting the resulting petroleum fraction having a reduced proportion of straight chain hydrocarbons to catalytic reforming in the presence of a platinum-containing catalyst under mild reforming conditions to effect substantially only dehydrogenation of the naphthenic hydrocarbons to produce a first reformat having an increased proportion of aromatic hydrocarbons and improved motor fuel qualities, desorbing the straight chain hydrocarbons from said adsorbent and subjecting the desorbed straight chain hydrocarbons to a second catalytic reforming operation under more severe reforming conditions to effect a reforming of a substantial amount of the straight chain hydrocarbons to non-straight chain hydrocarbons.

6. A method in accordance with claim 5 wherein the catalyst employed in said second reforming operation is a chromia-alumina catalyst.

7. A method of reforming a wide boiling petroleum naphtha fraction in the naphtha boiling range containing a straight chain hydrocarbon in the range C₄-C₈ and higher and non-straight chain hydrocarbons which comprises fractionating said petroleum naphtha to produce overhead a low boiling fraction containing substantially only C₅ and lighter hydrocarbons, contacting the remaining fraction with a solid particle molecular sieve alumino-silicate selective adsorbent made up of porous crystals wherein the pores of the crystals are of uniform size and have a pore size of about 5.0 Angstrom units, a pore size sufficient to admit straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons, and which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons at an elevated temperature to adsorb the straight chain hydrocarbons in said remaining fraction, subjecting the resulting petroleum fraction having a reduced proportion of straight chain hydrocarbons to catalytic reforming to produce a reformat, admixing at least a portion of said overhead fraction with said reformat to produce a blended reformat, desorbing the adsorbed straight chain hydrocarbons from said solid

adsorbent and subjecting the resulting desorbed straight chain hydrocarbons to an isomerization operation to produce an isomate containing a substantial amount of non-straight chain hydrocarbons.

8. A method in accordance with claim 7 which includes contacting said isomate with additional said adsorbent material to separate straight chain hydrocarbons from said isomate, desorbing the resulting adsorbed straight chain hydrocarbons and recycling the desorbed straight chain hydrocarbons to the aforesaid straight chain hydrocarbon isomerizing operation to produce additional second reformat.

9. A method of reforming a petroleum fraction in the naphtha boiling range containing straight chain hydrocarbons and non-straight chain hydrocarbons said non-straight chain hydrocarbons being comprised of isoparaffinic, naphthenic and aromatic hydrocarbons which comprises contacting said fraction with a solid particle molecular sieve alumino-silicate selective adsorbent made up of porous crystals wherein the pores of the crystals are of uniform size and have a pore size of about 5.0 Angstrom units, a pore size sufficient to admit straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons, and which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said fraction, subjecting the resulting petroleum fraction having a reduced proportion of straight chain hydrocarbons to a first catalytic reforming, including dehydrogenation, to produce a first reformat and a resulting net production of hydrogen, recycling a portion of the produced hydrogen to said catalytic reforming operation, desorbing the straight chain hydrocarbons from said solid adsorbent, subjecting the resulting desorbed straight chain hydrocarbons to a second catalytic reforming operation by contact with a regenerable reforming catalyst to produce a second reformat with resulting deposition of carbon upon the catalyst employed in said second reforming operation, removing spent carbon-containing catalyst from said second reforming operation and regenerating said spent catalyst by contact with an oxygen-containing gas to oxidize the carbon deposited upon said catalyst and to regenerate said catalyst.

10. A process in accordance with claim 9 wherein said hydrogen recovered from said first catalytic reforming operation is employed as a desorbing medium for the desorption of adsorbed straight chain hydrocarbons from said adsorbent material.

11. A process in accordance with claim 9 wherein said first reforming catalyst is a platinum-containing catalyst.

12. A process in accordance with claim 9 wherein said second reforming catalyst is a chromia-alumina catalyst.

13. A process in accordance with claim 9 wherein said first reforming catalyst is a platinum-containing catalyst and wherein said second reforming catalyst is a chromia-alumina catalyst.

14. A method of reforming a petroleum fraction in the naphtha boiling range containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises contacting said fraction with a solid particle molecular sieve alumino-silicate selective adsorbent made up of porous crystals wherein the pores of the crystals are of uniform size and have a pore size of about 5.0 Angstrom units, a pore size sufficient to admit straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons, and which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said fraction, subjecting the resulting petroleum fraction having a reduced proportion of straight chain hydrocarbons to catalytic reforming including dehydrogenation, with the resulting net production of hydrogen to produce a reformed petroleum fraction, recycling a portion of the net hydrogen production to said catalytic reforming operation, desorbing the straight chain

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hydrocarbons from said solid adsorbent and subjecting the resulting desorbed straight chain hydrocarbons together with a portion of the hydrogen produced from said catalytic reforming operation to thermal reforming under conditions such that a substantial amount of the straight chain hydrocarbons are reformed into non-straight chain hydrocarbons.

15. A process in accordance with claim 14 wherein the reformate recovered from said thermal reforming operation is contacted with additional said adsorbent material for the separation of straight chain hydrocarbons which are subsequently desorbed and recycled to said thermal reforming operation for the production of additional non-straight chain hydrocarbons.

16. A method of reforming a petroleum fraction in the naphtha boiling range containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises contacting said fraction with a solid particle molecular sieve alumino-silicate selective adsorbent made up of porous crystals wherein the pores of the crystals are of uniform size and have a pore size of about 5.0 Angstrom units, a pore size sufficient to admit straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons, and which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said fraction, subjecting the resulting petroleum fraction having a reduced proportion of straight chain hydrocarbons to catalytic reforming, including dehydrogenation, in contact with a platinum-containing catalyst to produce a first reformate with a resulting net production of hydrogen, recycling a portion of said hydrogen to said first catalytic reforming operation, desorbing the

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adsorbed straight chain hydrocarbons from said solid adsorbent by employing as a desorbing medium a portion of the hydrogen produced during said first catalytic reforming operation, subjecting the resulting desorbed straight chain hydrocarbons together with the gaseous hydrogen desorbing medium to a second catalytic reforming operation in contact with a second reforming catalyst under reforming conditions such that a substantial amount of the straight chain hydrocarbons are reformed to non-straight chain hydrocarbons together with the resulting deposition of carbon under said second reforming catalyst, removing said second reforming catalyst from contact with straight chain hydrocarbons when the catalyst activity of said second reforming catalyst has become depleted due to carbon deposition thereon, regenerating spent second reforming catalyst by contact with an oxygen-containing stream to oxidize the carbon deposited thereon and recycling the resulting regenerated second reforming catalyst to said second reforming operation.

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