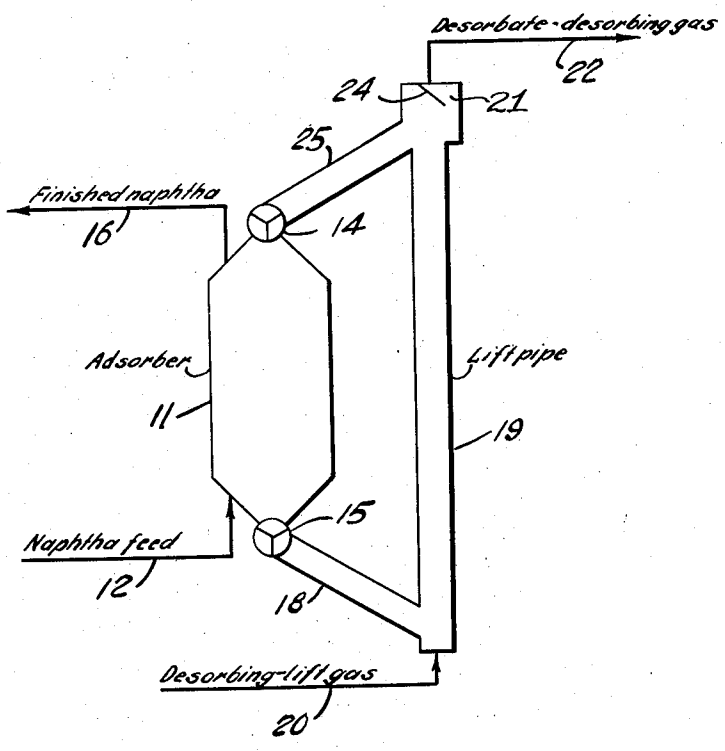
June 23, 1959 H. V. HESS ET AL 2,891,902

METHOD OF TREATING A PETROLEUM FRACTION USING SELECTIVE SOLID ADSORBENTS

Filed May 21, 1956 3 Sheets-Sheet 1

Fig. 1.



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METHOD OF TREATING A PETROLEUM FRACTION USING SELECTIVE SOLID ADSORBENTS

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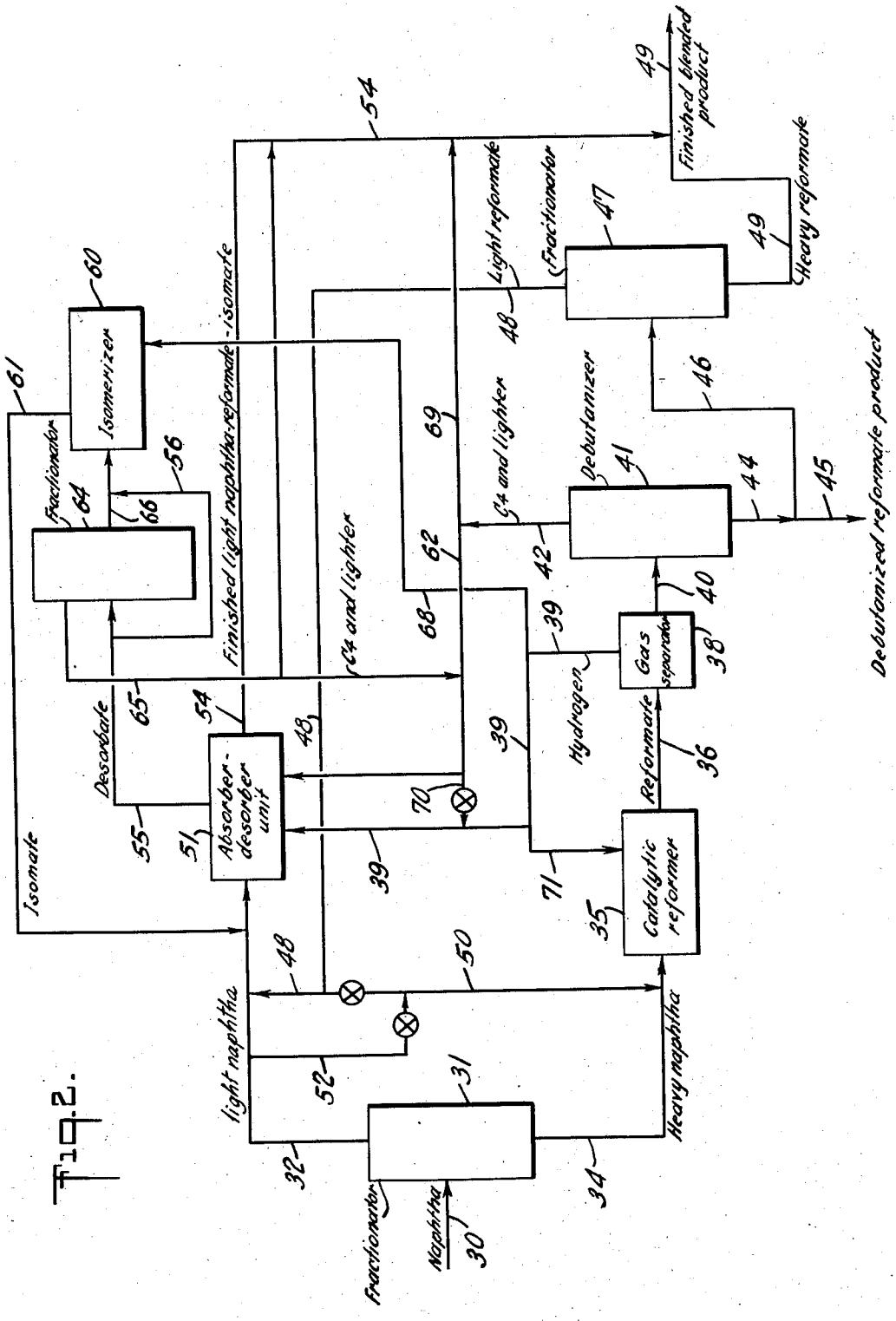


FIG. 2.

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METHOD OF TREATING A PETROLEUM FRACTION USING SELECTIVE SOLID ADSORBENTS

Filed May 21, 1956 3 Sheets-Sheet 3

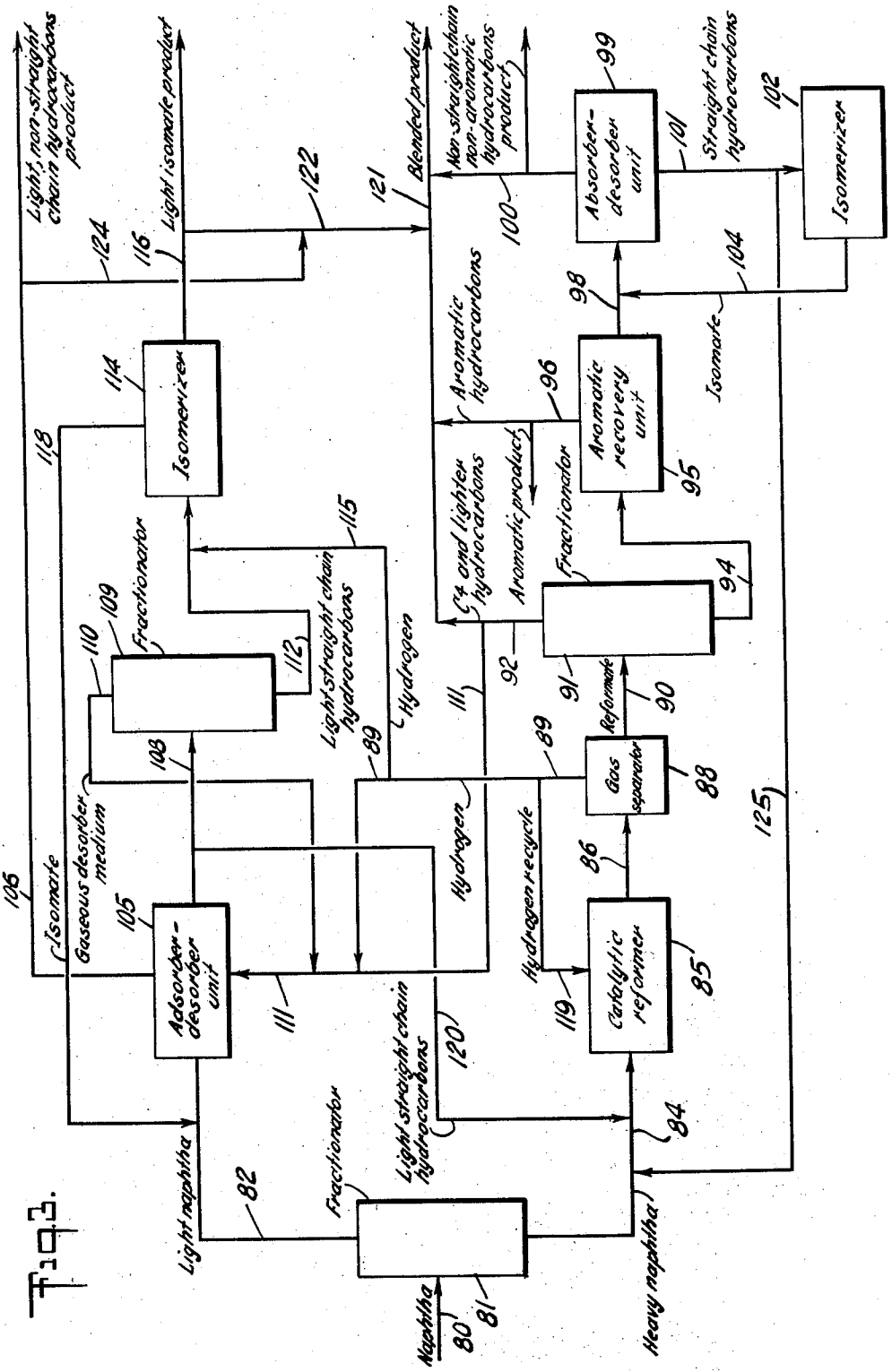


Fig. 1.

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2,891,902

METHOD OF TREATING A PETROLEUM FRACTION USING SELECTIVE SOLID ADSORBENTS

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Application May 21, 1956, Serial No. 586,218

11 Claims. (Cl. 208—65)

This invention relates to a method of treating hydrocarbon fractions, such as petroleum fractions and hydrocarbon synthesis (Fischer-Tropsch) fractions. In accordance with one embodiment, this invention relates to the treatment of hydrocarbon fractions in the naphtha or gasoline boiling range, said fractions containing straight chain hydrocarbons and non-straight chain hydrocarbons, in order to improve their quality as a motor fuel. In accordance with still another embodiment, this invention relates to an improved hydrocarbon conversion process. This invention is primarily directed to the upgrading of petroleum fractions containing straight chain hydrocarbons and non-straight chain hydrocarbons, especially naphtha stocks wherein the amount of straight chain hydrocarbons is substantial, e.g., in the range 2–30% by volume and higher.

Accordingly, it is an object of this invention to provide an improved process for treating hydrocarbon fractions containing straight chain hydrocarbons and non-straight chain hydrocarbons.

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

Still another object of this invention is to provide a combination hydrocarbon treating process for treating hydrocarbon fractions containing straight chain hydrocarbons and non-straight chain hydrocarbons wherein the straight chain hydrocarbons are selectively adsorbed by means of a solid selective adsorbent, followed by desorption of the straight chain hydrocarbons in a special manner in accordance with this invention.

Still another object of this invention is to provide a combination hydrocarbon treating process wherein a hydrocarbon fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons can eventually be converted substantially entirely to non-straight chain hydrocarbons.

Yet another object of this invention is to provide a combination hydrocarbon treating process wherein a hydrocarbon fraction containing aromatic hydrocarbons, branched chain aliphatic hydrocarbons and straight chain hydrocarbons is separated into each of these components.

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 drawing wherein:

Fig. 1 schematically illustrates one embodiment of the practice of this invention employing a special desorption zone wherein regeneration and transfer of the special selective adsorbent are simultaneously effected, and

Fig. 2 schematically illustrates an embodiment of the practice of this invention employing in combination a prefractionation operation, catalytic reforming, a subsequent distillation fractionation operation, an adsorption operation, a desorption operation and isomerization of

the resulting desorbate, all the aforementioned operations being carried out in combination to produce a blended hydrocarbon fuel especially suitable for use in spark ignition internal combustion engines, and

Fig. 3 schematically illustrates another embodiment of the practice of this invention employing in combination catalytic reforming, solvent extraction, selective adsorption, all cooperating to produce separate hydrocarbon streams containing substantially only aromatic hydrocarbons, non-straight chain non-aromatic hydrocarbons and straight chain hydrocarbons.

In accordance with our invention we have provided an improved process for treating or converting a hydrocarbon fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises subjecting a hydrocarbon fraction to be treated to contact with a selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said fraction, separating from the aforesaid adsorption operation a resulting treated effluent having a reduced straight chain hydrocarbon content and said solid selective adsorbent containing straight chain hydrocarbons therein, and regenerating the resulting separated adsorbent within a desorption zone by contact with a gaseous desorbing medium wherein the adsorbed straight chain hydrocarbons are desorbed from the selective adsorbent and wherein simultaneously the selective adsorbent undergoing regeneration is swept along and entrained by the gaseous desorbing medium to one other end of the desorption zone where the resulting regenerated adsorbent is separated from the gaseous desorbing medium and the resulting gaseous desorbed straight chain hydrocarbons. Following the above-mentioned regeneration-desorption operation the resulting regenerated selective adsorbent is returned to contact additional hydrocarbon feed containing straight chain hydrocarbons and non-straight chain hydrocarbons for the separation of straighe chain hydrocarbons therefrom.

By straight chain hydrocarbon is meant 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 poly-olefins, 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. Straight chain hydrocarbon-containing mixtures which are suitably treated in accordance with this invention include the various petroleum fractions, such as a naphtha fraction, a gasoline fraction and the like. Particularly suitable for treatment in accordance with this invention are straight chain hydrocarbon-containing fractions having a boiling point or a boiling range in the range of 40–600° F. and higher and containing a substantial amount of straight chain hydrocarbons, e.g., 2–35% by volume and higher. More particularly, a petroleum fraction suitable for use in the practice of this invention might have an initial boiling point in the range 40–300° F. and an end point in the range 150–600° F. 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 the following composition:

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

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

Any solid selective 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 selective adsorbent certain natural or synthetic zeolites or alumino-silicates, such as a calcium alumino-silicate, or a sodium calcium alumino-silicate, which exhibit the property of a molecular sieve, that is, matter made up of porous crystals wherein the pores of the crystals are of molecular dimension and are of substantially uniform size.

A particularly suitable solid adsorbent for straight chain hydrocarbons is a calcium alumino-silicate, apparently actually a sodium calcium alumino-silicate manufactured by Linde Air Products Company and designated Linde Type 5A Molecular Sieve. The crystals of this particular calcium alumino-silicate have a pore size or diameter of about 5 Angstrom units, a pore size sufficiently large to admit straight chain hydrocarbons, such as the normal paraffins and normal olefins, to the substantial exclusion of the non-straight chain naphthenic, aromatic, isoparaffinic and isoolefinic hydrocarbons. This particular selective adsorbent is available in various sizes such as $\frac{1}{8}$" or $\frac{1}{16}$" cylindrical pellets, microspheroids or as a finely divided powder having a particle size in the range 0.5–5.0 microns, exhibiting a bulk density in lbs. per cubic foot of 33, and a particle density in grams per cc. of 1.6.

Other suitable solid selective adsorbents 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 possessing larger molecular dimensions. The naturally occurring zeolite, chabazite, exhibits such desirable properties. Another suitable naturally occurring zeolite is analcite $NaAlSi_2O_6.H_2O$, which, when dehydrated, and when all or part of the sodium is replaced by an alkaline earth metal, such as calcium, by base exchange yields a material which may be represented by the formula (Ca, Na_2) $Al_2Si_4O_{12}.2H_2O$ 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 base exchange modifications of these zeolites are also suitable.

Other solid inorganic or mineral selective adsorbents are known and may be employed in the practice of this invention. It is contemplated that selective adsorbents having the property of selectively adsorbing straight chain hydrocarbons to the substantial exclusion of 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.

Encapsulated solid selective adsorbents are particularly useful in the practice of this invention. Encapsulated adsorbents wherein the selective adsorbent, such as a sodium calcium alumino-silicate (Linde 5A Molecular Sieve), which normally are friable and fragile materials, is encapsulated within a porous envelope, such as wire mesh or a porous ceramic envelope or coating, are particularly useful in the practice of this invention. Suitable encapsulated adsorbents are disclosed in our copending patent application Serial No. 511,952, filed May 31, 1955, and in copending patent application Serial No. 511,949, filed May 31, 1955, in the name of Howard V. Hess, one

of the coinventors of this invention. The disclosures of the above-identified patent applications are herein incorporated and made part of this disclosure.

The adsorptive separation of the straight chain hydrocarbons from the hydrocarbon fraction undergoing treatment is preferably carried out in the gaseous phase and at any suitable temperature and pressure effective during the adsorptive separation operation to maintain the hydrocarbon fraction undergoing treatment in the vapor phase. For example, the adsorptive separation of the straight chain hydrocarbons by the solid selective adsorbent can be carried out at a temperature in the range 150–900° F. and at any suitable pressure, such as a pressure in the range 0–2000 p.s.i.g. and higher, the temperature and pressure being adjusted with respect to the hydrocarbon fraction undergoing treatment to maintain the hydrocarbon fraction in the vapor phase.

The regeneration of the selective adsorbent or the desorption of the straight chain hydrocarbons contained adsorbed in the solid selective adsorbent can be made at any suitable temperature and pressure, preferably at a temperature and pressure such that the resulting desorbed straight chain hydrocarbons are in the vapor phase.

For example, the regeneration-desorption operation may be carried out at a pressure in the range 0–2000 p.s.i.g. or less. Generally a desorption pressure in the range 10–750 p.s.i.g. is suitable. It is sometimes desirable to carry out the desorption operation at a pressure substantially lower than the adsorption pressure. The pressure employed during the adsorptive separation operation is not determinative of the desorption pressure and any suitable desorption pressure may be employed. Substantially the same comment may be made with respect to the desorption temperature in the practice of this invention. It is sometimes desirable, however, to carry out substantially isothermal adsorption-desorption operations. Any suitable desorption temperature in the range 300–1100° F., higher or lower, may be employed. It is preferred, however, to carry out the regeneration-desorption operation at an elevated temperature, such as a temperature in the range 400–900° F., or at a temperature at least about 100 degrees Fahrenheit higher than the adsorption temperature, especially in an isobaric adsorption-desorption operation. It is realized, of course, that the desorption temperature should not be excessively high, for example, not greater than about 1100–1300° F. in the case of Linde Type 5A Molecular Sieve, since such high temperatures would lead to the destruction of the adsorbent material, presumably by collapse of the crystal structure, with resultant loss of its selective adsorption properties.

Although it is possible to effect desorption of the adsorbed straight chain hydrocarbons from the solid adsorbent by the application of heat alone, for example, by radiant heating, it is a feature of this invention that the desorption operation is carried out within a desorption zone in the presence of a gaseous desorbing medium whereby the selective adsorbent undergoing desorption or regeneration is simultaneously selectively desorbed or relieved of the adsorbed straight chain hydrocarbons and carried along or entrained by the gaseous desorbing medium.

As a general rule any suitable gaseous desorbing medium may be employed in the practice of this invention. A suitable gaseous desorbing medium is methane, ethane, propane, natural gas, hydrogen, flue gas, carbon dioxide, carbon monoxide, nitrogen, high temperature superheated steam, or mixtures thereof. In general, any gaseous or vaporized material chemically inert with respect to the adsorbent and readily separable by fractionation, liquefaction, solvent extraction or adsorption and the like from the desorbed straight chain hydrocarbons is suitable as the desorbing medium in the practice of this invention. It is preferred, however, to employ as the gaseous desorbing medium a hydrogen-

containing stream, such as the gaseous hydrogen-containing effluent recovered from a catalytic reforming operation, e.g., the hydrogen-containing effluent from a Platformer. Also preferred as the gaseous desorbing medium is a C_4 hydrocarbon fraction, e.g., n-butane and/or isobutane and similar hydrocarbons, including their higher molecular weight homologs, C_5 and higher hydrocarbons, which are readily separable as by distillation from the resulting desorbed straight chain hydrocarbons.

Referring now to the drawing and in greater detail to Fig. 1 a vaporized petroleum fraction or naphtha feed, such as a dependentanized light catalytically reformed naphtha or a light straight run naphtha, having a boiling range in the range 75–250° F., is introduced into adsorber **11** via line **12** wherein it countercurrently contacts a downwardly moving mass of solid selective adsorbent or freely falling solid selective adsorbent which selectively absorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons. The selective adsorbent enters adsorber **11** via star valve **14**, the amount and/or rate of introduction of selective adsorbent into adsorber **11** and the amount or rate of removal of selective adsorbent from adsorber **11** via star valve **15** being controlled to maintain a downwardly moving bed or mass of adsorbent or freely falling adsorbent as desired. Adsorber **11** is operated under suitable conditions of temperature and pressure to effect adsorption of straight chain hydrocarbons from naphtha feed introduced thereinto with the result that there issues from the upper portion of adsorber **11** via line **16** a finished naphtha substantially free of straight chain hydrocarbons or having a substantially reduced straight chain hydrocarbon content.

The adsorbent removed from adsorber **11** via star valve **15** enters conduit or transfer means **18** wherein it travels downwardly to the lower end of lift pipe **19**. The adsorbent entering the lower end of lift pipe **19** is substantially saturated with straight chain hydrocarbons. At the lower end of lift pipe **19** the adsorbent is contacted with hot desorbing-lift gas introduced into the lower end of lift pipe **19** via line **20**. The temperature of the desorbing-lift gas thus introduced into lift pipe **19** is such as to effect rapid desorption of the adsorbed straight chain hydrocarbons from the adsorbent, thereby regenerating the adsorbent. Further, the quantity and rate of introduction of the desorbing-lift gas introduced into lift pipe **19** is such that the adsorbent is entrained in the upward flowing desorbing-lift gas within lift pipe **19** and transported to the upper end thereof. C_3, C_4, C_5 and higher molecular weight hydrocarbons, e.g., normal butane and/or isobutane, are particularly suitable as a desorbing-lift gas.

When the adsorbent is transported by the desorbing-lift gas into the upper end of lift pipe **19** into enlarged section **21** thereof the velocity of the desorbing-lift gas therein is reduced with the result that the entrained adsorbent tends to drop out of the desorbing-lift gas. It is mentioned at this time that the entrainment or lifting of the adsorbent within lift pipe **19** is aided by the release of the desorbed straight chain hydrocarbons within lift pipe **19**, thereby introducing a greater quantity of gaseous materials within lift pipe **19** and leading to a higher gas velocity which aids in entraining the adsorbent. The desorbing-lift gas as well as the resulting desorbed straight chain hydrocarbons are removed from enlarged section **21** at the upper end of lift pipe **19** via line **22**. A baffle is provided within enlarged section **21** of lift pipe **19** in order to promote and facilitate the separation of the entrained adsorbent from the entraining streams of desorbing-lift gas and gaseous desorbed straight chain hydrocarbons. The resulting regenerated adsorbent now having a substantially reduced straight chain hydrocarbon content or substantially free of straight chain hydrocarbons is removed from the enlarged section **21** and passed via conduit **25** to star valve **14** through which it is controlledly introduced into adsorber **11** to contact additional naphtha feed for the separation and removal of straight chain hydrocarbons therefrom.

Referring now to Fig. 2 of the drawing which schematically illustrates another embodiment of the practice of this invention, a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons, such as a relatively wide boiling naphtha fraction, e.g., a straight run naphtha having a boiling range in the range 60–450° F., is introduced via line **30** into fractionator **31** from which there is removed overhead via line **32** a dependentanized light naphtha stream having a boiling range in the range 75–275° F. and from the lower portion of fractionator **31** via line **34** a heavy naphtha stream, such as a naphtha stream having a boiling range in the range 200–450° F.

The heavy naphtha stream in line **34** is introduced into catalytic reformer **35** wherein it undergoes catalytic reforming, involving isomerization, dehydrogenation, aromatization or dehydrocyclization, disproportionation, all taking place more or less simultaneously. Catalytic reforming is a well known operation as evidenced by the many commercially available catalytic reforming processes, e.g., Platforming, Ultraforming, Powerforming, Houdriforming, Sovaforming, Catforming and the like. Usually catalytic reforming processes employ an active dehydrogenating platinum-containing catalyst, which catalyst is also effective as an isomerization and dehydrocyclization catalyst. Catalytic reforming is usually carried out at a relatively elevated temperature in the range 700–1000° F., more or less, and at a relatively elevated pressure in the range 50–900 p.s.i.g. in the presence of recycle hydrogen recovered from the resulting catalytic reformer effluent.

There issues from catalytic reformer **35** a catalytic reformate via line **36** which is introduced into gas separator **38** from which there is separated overhead via line **39** a gaseous stream containing a large proportion of or substantially only hydrogen. The remaining reformate stream removed from separator **38** via line **40** is introduced into debutanizer **41** from which there is removed overhead via line **42** a normally gaseous hydrocarbon stream containing C_4 and lighter hydrocarbons. The remaining catalytic reformate is removed from the lower end of debutanizer **41** via line **44**. If desired, a debutanized reformate may be removed as product from line **44** via line **45**.

In the preferred manner of operation in accordance with this invention the debutanized reformate from line **44** is introduced via line **46** into fractionator **47** where there is removed overhead via line **48** a light reformate fraction, such as a dependentanized light reformate fraction. The remaining heavy reformate fraction is recovered from the lower end of fractionator **47** via line **49**.

The light reformate fraction in line **48** may be recycled in part, if desired, via lines **50** and **34** to catalytic reformer **35**. The light catalytic reformate in line **48**, however, is advantageously introduced via line **32** into adsorber-desorber unit **51** in admixture with the light naphtha issuing from fractionator **31** via line **32**. As indicated in Fig. 2, if desired, a part of the light naphtha issuing from fractionator **31** via line **32** may be introduced via lines **52**, **50** and **34** to catalytic reformer **35** along with the light catalytic reformate removed from fractionator **47** via line **48**.

Within adsorber-desorber unit **51** the light naphtha and light catalytic reformate streams introduced thereinto are contacted with a suitable solid selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons so as to effect removal of the straight chain hydrocarbons therefrom. Adsorber-desorber unit **51** may be operated in any suitable manner, such as in the manner illustrated in Fig. 1 of the drawing, effective to separate straight chain hydrocarbons. There issues from adsorber-de-

sorber unit 51 via line 54 a finished light naphtha-reformate stream substantially free of straight chain hydrocarbons or having a reduced straight chain hydrocarbon content. The desorbed straight chain hydrocarbons recovered from adsorber-desorber unit 51 via line 55 are subjected to isomerization within isomerizer 60. Desirably the hydrogen-containing effluent recovered from gas separator 38 via line 39 is employed as the desorbing medium to desorb the adsorbed straight chain hydrocarbons from the adsorbent within adsorber-desorber unit 51. When such a hydrogen-containing gaseous desorbing medium is employed the resulting desorbed straight chain hydrocarbons together with the gaseous hydrogen-containing desorbing medium is introduced directly into isomerizer 60 via lines 55 and 56. The isomerization reaction carried out within isomerizer 60, preferably in the presence of a platinum-containing catalyst so as to effect isomerization of the desorbed straight chain hydrocarbons from adsorber-desorber unit 51, converts a substantial amount of the desorbed straight chain hydrocarbons into non-straight chain hydrocarbons which are removed from isomerizer 60 as isomate via line 61. Advantageously the isomate is returned to adsorber-desorber unit 51 to effect removal of the remaining unconverted straight chain hydrocarbons therefrom. As a result there is recovered from adsorber-desorber unit 51, as indicated in Fig. 2, a finished light naphtha-reformate-isomate stream via line 54 having a substantially reduced straight chain hydrocarbon content or a stream substantially free of straight chain hydrocarbons. The resulting finished light naphtha-reformate-isomate stream from line 54 is blended with the heavy reformate stream in line 49 from fractionator 47 to produce a finished blended product particularly suitable as a motor fuel in a spark ignition internal combustion type engine.

When the C_4 gaseous effluent recovered from debutanizer 41 via line 42 introduced into adsorber-desorber unit 51 via line 62 is employed as the desorbing medium the resulting desorbate which issues from adsorber-desorber unit 51 via line 55 is desirably fractionated in fractionator 64 for the separation and recovery of the C_4 hydrocarbon gaseous desorbing medium which is recovered from fractionator 64 via line 65 for recycle via line 62 to adsorber-desorber unit 51 as gaseous desorbing medium. After separation of the C_4 and lighter hydrocarbons the remaining desorbate from fractionator 64 is introduced via line 66 into isomerizer 60 to undergo isomerization, preferably in the presence of gaseous hydrogen which advantageously is supplied from gas separator 38 via lines 39 and 68. As indicated in Fig. 2, at least a portion of the C_4 and lighter hydrocarbons separated from debutanizer 41 may be added or otherwise blended via lines 42, 69 and 54 into the finished blended product recovered via line 49. Further, as indicated in Fig. 2, a portion of the C_4 and lighter hydrocarbons recovered from debutanizer 41 via line 42 may be added via lines 62 and 70 to the gaseous hydrogen stream in line 39 in order to aid or better effect the desorption of the adsorbed straight chain hydrocarbons from the adsorbent within adsorber-desorber unit 51. As already mentioned, the gaseous hydrogen effluent from gas separator 38 is recycled at least in part to catalytic reforming unit 35 via lines 39 and 71.

If desired, although not specifically illustrated in Fig. 2, the heavy naphtha stream removed from fractionator 31 via line 34 may be contacted with a selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to effect the removal of straight chain hydrocarbons therefrom in the manner described hereinabove prior to catalytic reforming, with the thus-separated straight chain hydrocarbons being recovered and isomerized in the manner indicated with respect to the straight chain hydrocarbon desorbate issuing via line 55 from adsorber-desorber unit 51. An operation wherein a hydrocarbon stream is specially treated to effect the removal of straight chain hydrocarbons therefrom prior to catalytic reforming is described in our copending patent application Serial No. 478,426 filed December 29, 1954, the disclosures of which are herein incorporated and made part of this disclosure.

Referring now to Fig. 3 of the drawing which schematically illustrates another embodiment of the practice of this invention, a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons, such as a relatively wide boiling naphtha, e.g., a straight run naphtha having a boiling range in the range 60–450° F., is introduced via line 80 into fractionator 81 from which there is removed overhead via line 82 a depentanized light naphtha stream having a boiling range in the range 75–275° F. From the lower end of fractionator 81 there is removed via line 84 a heavy naphtha stream, such as a naphtha stream having a boiling range in the range 200–450° F.

The heavy naphtha stream in line 84 is introduced into catalytic reformer 85 wherein it undergoes catalytic reforming, involving isomerization, dehydrogenation and aromatization or dehydrocyclization, all taking place more or less simultaneously.

There issues from catalytic reformer 85 via line 86 a catalytic reformate which is introduced into gas separator 88 from which there is separated overhead via line 89 a gaseous stream containing a large proportion of or substantially only hydrogen. The remaining reformate stream from separator 88 is introduced via line 90 into debutanizer or fractionator 91 from which there is removed overhead via line 92 a normally gaseous hydrocarbon stream containing C_4 and lighter hydrocarbons. The remaining catalytic reformate is removed from the lower end of debutanizer 91 via line 94.

The catalytic reformate in line 94 is introduced into aromatic hydrocarbon recover unit 95 wherein aromatic hydrocarbons are separated therefrom leaving recovery unit 95 via line 96. Aromatic recovery unit 95 may comprise any suitable system involving solvent extraction, extractive distillation, adsorption, and the like, separately or in combination, for the separation of aromatic hydrocarbons from non-aromatic hydrocarbons. Suitable methods for the removal of aromatic hydrocarbons from non-aromatic hydrocarbons include silica gel adsorption, as exemplified by the Arosorb Process, solvent extraction with a glycol such as diethylene glycol as exemplified by the Udex Process, extractive distillation by contact with a liquid phenol stream or solvent extraction employing liquid furfural, liquid sulfur dioxide, liquid dimethylformamide, Chlorex (β,β' dichloroethyl ether) and the like. A suitable process for the recovery of aromatic hydrocarbons from a catalytic reformate is known as Rexforming which involves the solvent extraction of a catalytic reformate with a glycol solution for the recovery of high octane aromatic hydrocarbons as extract.

The resulting catalytic reformate now substantially free of aromatic hydrocarbons or having a reduced aromatic hydrocarbon content is recovered from aromatic recovery unit 95 via line 98 and introduced into adsorber-desorber unit 99 wherein it contacts a selective adsorbent for the adsorptive separation of straight chain hydrocarbons. There is removed from adsorber-desorber unit 99 via line 100 a finished effluent stream comprised predominantly of non-straight chain non-aromatic hydrocarbons. From adsorber-desorber unit 99 there is also recovered as a separate stream via line 101 an effluent stream comprised predominantly of straight chain hydrocarbons. The effluent stream of straight chain hydrocarbons in line 101 is introduced into isomerizer 102 where the straight chain hydrocarbons are aromatized or isomerized, preferably by means of a platinum-containing catalyst, to an isomate comprising straight chain hydrocarbons and non-straight chain hydrocarbons which are recovered from isomerizer 102 via line 104 and returned

via line **98** to adsorber-desorber unit **99** for the separation of the converted, non-straight chain hydrocarbons.

The light naphtha stream recovered overhead from fractionator **81** is introduced via line **82** into adsorber-desorber unit **105** wherein it contacts a solid selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons. There is recovered from adsorber-desorber unit **105** via line **106** a finished effluent stream comprised predominantly of light non-straight chain hydrocarbons. There is also recovered from adsorber-desorber unit **105** as desorbate via line **108** a stream comprised predominantly of straight chain hydrocarbons which are introduced into fractionator **109** for the separation therefrom via line **110** of the gaseous desorbing medium which may be a gaseous desorbing medium comprised predominantly of hydrogen and introduced into adsorber-desorber unit **105** from gas separator **88** via lines **89** and **111**. The separated straight chain hydrocarbon desorbate is recovered from fractionator **109** via line **112** and introduced into isomerizer **114** where it is aromatized or isomerized, preferably in the presence of a platinum-containing catalyst and hydrogen gas supplied from gas separator **88** via lines **89**, **115** and **112**, to an isomate comprising straight chain hydrocarbons and non-straight chain hydrocarbons. The resulting light isomate may be recovered from isomerizer **114** as product via line **116**. The light isomate, however, is also advantageously recovered from isomerizer **114** and recycled via lines **118** and **82** to adsorber-desorber unit **105** for the separation of the converted, non-straight chain hydrocarbons.

As indicated in Fig. 3 of the drawing, hydrogen is recycled from gas separator **88** via lines **89** and **119** to catalytic reformer **85**. Further, as indicated in Fig. 3, the C_4 hydrocarbons stream recovered overhead from fractionator **91** via line **92** are advantageously employed as the gaseous desorbing medium within adsorber-desorber unit **105** being supplied thereto via line **111**. Further, as indicated in Fig. 3 of the drawing, the straight chain hydrocarbon desorbate may, if desired, be supplied from adsorber-desorber unit **105** directly to catlytic reformer **85** via lines **108**, **120** and **84**. As is apparent from the foregoing operations, there is produced a final blended product via line **120** containing C_4 hydrocarbons recovered overhead from fractionator **91** via line **92**, aromatic hydrocarbons recovered from aromatic recovery unit **95** via line **96** and a non-straight chain non-aromatic hydrocarbon stream recovered from adsorber-desorber unit **99** via line **100**. If desired, the blended product stream recovered via line **121** might also include the light isomate recovered from isomerizer **114** via lines **116** and **122**. Also, as indicated in Fig. 3, the blended product in line **121** might also include the light non-straight chain hydrocarbon fraction recovered from adsorber-desorber unit **105** via lines **106** and **124**. Further, as illustrated in Fig. 3, the straight chain hydrocarbon desorbate recovered from adsorber-desorber **99** via line **101** may advantageously be returned to catalytic reformer **85** via lines **125** and **84**, thereby avoiding or bypassing the use of isomerizer **102**.

Illustrative of the practice of this invention a mixture of straight chain hydrocarbons comparable to the mixture of straight chain hydrocarbons recovered as desorbate from adsorber-desorber unit **51** of Fig. 2 and adsorber-desorber units **99** and **105** of Fig. 3 and comprising 23% by vol. n-pentane, 56% by vol. n-hexane and 21% by vol. n-heptane was contacted with a particle-form dehydrogenation-aromatization catalyst comprising Cr_2O_3—MgO—Al_2O_3 at various temperatures and at a space velocity of about 0.4 v./hr./v. at a pressure of about 40 p.s.i.g. and at a H_2 recycle rate of 1200 cu. ft./bbl. of feed. The properties of the resulting upgraded product are set forth in Table No. I.

Table No. I

Reaction Temp., ° F	920	943
Wt. percent recovery	93.8	81.3
Bromine No	20	22
Vol. percent aromatics	15	13
ASTM Res. Clear Oct. Proc	60.6	57.6
+3 cc. TEL/gal	80.4	80.2

Likewise, the same mixture of straight chain hydrocarbons was contacted with a number of platinum-containing reforming or predominantly isomerizing catalysts at a pressure of about 500 p.s.i.g., a H_2 recycle rate of about 4000 cu. ft./bbl. charge. The results are set forth in Table No. II.

Table No. II

Reaction Temp., ° F	800			850			900		
Catalyst	A	B	C	A	B	C	A	B	C
P.D. Gas Make	0.209	0.173	0.150	0.414	0.338	0.299	2.567	2.609	0.715
Liq. Rec., Wt. Percent	95.9	99.3	90.1	95.0	99.0	88.2	67.6	70.1	72.7
Isomate ASTM Res., Clear	60.0	51.0	54.0	75.4	74.0	77.1	89.6	70.0	78.9
Finished (straight chain hydrocarbons removed) ASTM Res., Clear	78.0	61.0	72.0	84.0	82.0	82.6		80.3	
Finished+3 cc. TEL/gal		86.0							

A—Platforming catalyst.
B—Sinclair-Baker Rd 150 catalyst.
C—Ultraforming catalyst.

For purposes of simplicity and clarity, conventional control equipment, valves, pumps, compressors, heaters, coolers and supplementary gas-liquid, gas-solids and liquid-solids separators, fractionators, etc. have for the most part not been illustrated in the drawings. The location and employment of these auxiliary pieces of equipment such as may be necessary in the practice of of this invention are 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.

We claim:

1. A method of treating a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises fractionating said fraction to produce a light naphtha having an end boiling point in the range 150–250° F. and a heavy naphtha having an end boiling point in the range 350–450° F., subjecting said heavy naphtha to catalytic reforming with the resulting production of hydrogen, C_5, C_4 and lighter hydrocarbons and a relatively wide boiling reformate, separating said hydrogen and said C_4 hydrocarbons from said reformate, fractionating the remaining reformate into a light reformate having an end boiling point in the range 150–250° F. and a heavy reformate having an end point in the range 350–450° F., introducing said light naphtha and said light reformate into contact with a selective solid adsorbent which selectively adsorbs

straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to remove straight chain hydrocarbons therefrom to yield a resulting treated light naphtha-reformate effluent, having a reduced straight chain hydrocarbon content, desorbing the adsorbed straight chain hydrocarbons from said adsorbent by contacting said adsorbent at an elevated temperature with said separated C_4 hydrocarbons, separating from the resulting desorption effluent the C_4 hydrocarbons and the resulting desorbed straight chain hydrocarbons, introducing the resulting desorbed straight chain hydrocarbons into contact with an isomerization catalyst to isomerize said straight chain hydrocarbons, recovering from the isomerization reaction an isomate, introducing said isomate into contact with a selective solid adsorbent material which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to selectively remove straight chain hydrocarbons from said isomate thereby yielding a resulting treated isomate having a reduced amount of straight chain hydrocarbons and blending the resulting treated isomate, said treated light naphtha-reformate effluent and said heavy reformate to produce a petroleum product suitable as a motor fuel.

2. A method in accordance with claim 1 wherein said isomerization reaction is carried out in the presence of said separated hydrogen.

3. A method in accordance with claim 1 wherein said light naphtha and said light reformate are introduced into contact with said selective solid adsorbent in an adsorption zone wherein said solid adsorbent material moves downwardly and wherein the adsorbed straight chain hydrocarbons are desorbed from said adsorbent by contacting said adsorbent within a vertically extending desorption zone under conditions such that straight chain hydrocarbons are desorbed from said adsorbent and simultaneously the solid adsorbent material is entrained and carried along upwardly within said desorption zone by said separated C_4 hydrocarbon employed as the gaseous desorbing medium.

4. A method of treating a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises fractionating said fraction to produce a light naphtha having an end boiling point in the range 150–250° F. and a heavy naphtha having an end boiling point in the range 350–450° F., subjecting said heavy naphtha to catalytic reforming with the resulting production of hydrogen, C_4 and lighter hydrocarbons and a relatively wide boiling reformate, separately separating said hydrogen and said C_4 and lighter hydrocarbons from said reformate, fractionating the remaining reformate into a light reformate having an end boiling point in the range 150–250° F. and a heavy reformate having an end point in the range 350–450° F., introducing said light naphtha and said light reformate and isomate, produced as set forth hereinbelow, into contact with a selective solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to remove the straight chain hydrocarbons therefrom to yield a resulting treated light naphtha-reformate-isomate effluent, desorbing the adsorbed straight chain hydrocarbons from said adsorbent by contacting said adsorbent at an elevated temperature with said separated hydrogen, introducing the resulting desorbed straight chain hydrocarbons together with said hydrogen into contact with an isomerization catalyst to isomerize said straight chain hydrocarbons, recovering from the isomerization reaction said isomate and blending the resulting treated light naphtha-reformate-isomate effluent with said heavy reformate to produce a petroleum product suitable as a motor fuel.

5. A method of treating a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises fractionating said naphtha to produce a light naphtha having an end boiling point in the range 150–250° F. and a heavy naphtha having an end point in the range 350–450° F., subjecting said heavy naphtha to catalytic reforming with the resulting production of hydrogen, C_4 and lighter hydrocarbons and a relatively wide boiling reformate, separately separating said hydrogen, said C_4 and lighter hydrocarbons and said reformate, fractionating said reformate into a light reformate having an end boiling point in the range 150–250° F. and a heavy reformate having an end point in the range 350–450° F., introducing said light naphtha, said light reformate and an isomate, produced as described hereinbelow, into contact with a selective solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to remove straight chain hydrocarbons therefrom to yield a resulting treated light naphtha-reformate-isomate effluent, desorbing the adsorbed straight chain hydrocarbons from said adsorbent by contacting said adsorbent with said separated C_4 hydrocarbon stream, separating from the resulting desorption effluent C_4 hydrocarbons and the resulting desorbed straight chain hydrocarbons, introducing the resulting desorbed straight chain hydrocarbons into contact with an isomerization catalyst in the presence of said separated hydrogen to isomerize said straight chain hydrocarbons, recovering from the isomerization reaction said isomate, and blending the resulting treated light naphtha-reformate-isomate effluent with said heavy reformate to produce a petroleum product suitable as a motor fuel.

6. A method in accordance with claim 5 wherein a portion of said separately separated C_4 hydrocarbon is blended with said petroleum product.

7. A method of treating a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises fractionating said fraction to produce a light naphtha having an end point in the range 150–250° F. and a heavy naphtha having an end point in the range 350–450° F., subjecting said heavy naphtha to catalytic reforming with the resulting production of hydrogen, C_4 hydrocarbons and a reformate containing aromatic hydrocarbons, separating said hydrogen and said C_4 hydrocarbons from said reformate, treating the remaining reformate to separate therefrom a separate stream comprising said aromatic hydrocarbons, introducing the resulting reformate stream now having a reduced aromatic hydrocarbon content into contact with a selective solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-staright chain hydrocarbons therefrom to yield a treated reformate having a reduced straight chain hydrocarbon content and comprised predominantly of non-straight chain, non-aromatic hydrocarbons, desorbing the adsorbed straight chain hydrocarbons from said adsorbent, isomerizing the desorbed straight chain hydrocarbons to produce an isomate containing straight chain hydrocarbons and non-straight chain hydrocarbons, contacting said isomate with said solid adsorbent to separate straight chain hydrocarbons therefrom to yield a treated isomate having a reduced amount of straight chain hydrocarbons, isomerizing the aforesaid separated light naphtha, and blending said separated C_4 hydrocarbons, said aromatic hydrocarbons, said treated isomate, the resulting isomerized light naphtha and said non-straight chain, non-aromatic hydrocarbons to produce a blended product having an improved quality as a motor fuel for spark ignition internal combustion engines.

8. A method of treating a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises fractionating said fraction to produce a light naphtha having an end point in the range 150–250° F. and a heavy naphtha having an end point in the range 350–450° F., subjecting said heavy naphtha to catalytic reforming with the resulting production of hydrogen, C_4 hydrocarbons and a reformate

containing aromatic hydrocarbons, separating said hydrogen and said C_4 hydrocarbons from said reformate, treating the remaining reformate to separate therefrom a separate stream comprising aromatic hydrocarbons, introducing the resulting reformate stream now having a reduced aromatic hydrocarbon content into contact with a selective solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to remove straight chain hydrocarbons therefrom to yield a treated reformate having a reduced straight chain hydrocarbon content and comprised predominantly of non-straight chain, non-aromatic hydrocarbons, desorbing the adsorbed straight chain hydrocarbons from said adsorbent, isomerizing the desorbed straight chain hydrocarbons to produce an isomate containing straight chain hydrocarbons and non-straight chain hydrocarbons, contacting said isomate with said solid adsorbent to separate straight chain hydrocarbons therefrom and to yield a treated isomate having a reduced amount of straight chain hydrocarbons, blending said separated C_4 hydrocarbons, said aromatic hydrocarbons, said treated isomate and said non-straight chain, non-aromatic hydrocarbons to produce a blended product having an improved quality as a motor fuel for spark ignition internal combustion engines, contacting the aforesaid light naphtha with a solid selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to remove straight chain hydrocarbons therefrom to yield a treated light naphtha having a reduced straight chain hydrocarbon content, separating said treated light naphtha, adding said treated light naphtha to said blended product, desorbing the adsorbed straight chain hydrocarbons derived from said light naphtha from said adsorbent, isomerizing the resulting desorbed straight chain hydrocarbons to produce a corresponding isomate containing straight chain hydrocarbons and non-straight chain hydrocarbons and adding said corresponding isomate to the aforesaid blended product.

9. A method of treating a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises fractionating said fraction to produce a light naphtha having an end point in the range 150–250° F. and a heavy naphtha having an end point in the range 350–450° F., subjecting said heavy naphtha to catalytic reforming with the resulting production of hydrogen, C_4 hydrocarbons and a reformate containing aromatic hydrocarbons, separating said hydrogen and said C_4 hydrocarbons from said reformate, treating the remaining reformate to separate therefrom a separate stream comprising said aromatic hydrocarbons, introducing the resulting reformate stream now having a reduced aromatic hydrocarbon content into contact with a selective solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to remove straight chain hydrocarbons therefrom to yield a treated reformate having a reduced straight chain hydrocarbon content and comprised predominantly of non-straight chain, non-aromatic hydrocarbons, desorbing the adsorbed straight chain hydrocarbons from said adsorbent, isomerizing the desorbed straight chain hydrocarbons to produce an isomate containing straight chain hydrocarbons and non-straight chain hydrocarbons, contacting said isomate with said solid adsorbent to separate straight chain hydrocarbons therefrom, blending said separated C_4 hydrocarbons, said aromatic hydrocarbons and said non-straight chain, non-aromatic hydrocarbons to produce a blended product having an improved quality as a motor fuel for spark ignition internal combustion engines, contacting the aforesaid light naphtha with a solid selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to remove straight chain hydrocarbons therefrom to yield a treated light naphtha having a reduced straight chain hydrocarbon content, separating said treated light naphtha, adding said treated light naphtha to said blended product, desorbing the adsorbed straight chain hydrocarbons derived from said light naphtha from said adsorbent, isomerizing the resulting desorbed straight chain hydrocarbons to produce a corresponding isomate containing straight chain hydrocarbons and non-straight chain hydrocarbons, contacting said corresponding isomate with said solid adsorbent to separate straight chain hydrocarbons therefrom to produce a treated corresponding isomate having a reduced straight chain hydrocarbon content and adding said treated corresponding isomate to said blended product.

10. A method of treating a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons in accordance with claim 7 wherein said separated hydrogen is present during the operation wherein said desorbed straight chain hydrocarbons are isomerized to produce an isomate containing straight chain hydrocarbons and non-straight chain hydrocarbons.

11. A method of treating a petroleum fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons in accordance with claim 7 wherein said separated hydrogen is employed to desorb the adsorbed straight chain hydrocarbons from said adsorbent and wherein said separated hydrogen is present during the isomerizing operation wherein the resulting desorbed straight chain hydrocarbons are isomerized to produce an isomate containing straight chain hydrocarbons and non-straight chain hydrocarbons.

References Cited in the file of this patent

UNITED STATES PATENTS

2,425,535	Hibshman	Aug. 12, 1947
2,495,842	Gilliland	Jan. 31, 1950
2,522,426	Black	Sept. 12, 1950
2,552,436	Bennett et al.	May 8, 1951
2,651,597	Corner et al.	Sept. 8, 2953
2,697,684	Hemminger et al.	Dec. 21, 1954
2,801,966	Mertes et al.	Aug. 6, 1957
2,818,449	Christensen et al.	Dec. 31, 1957