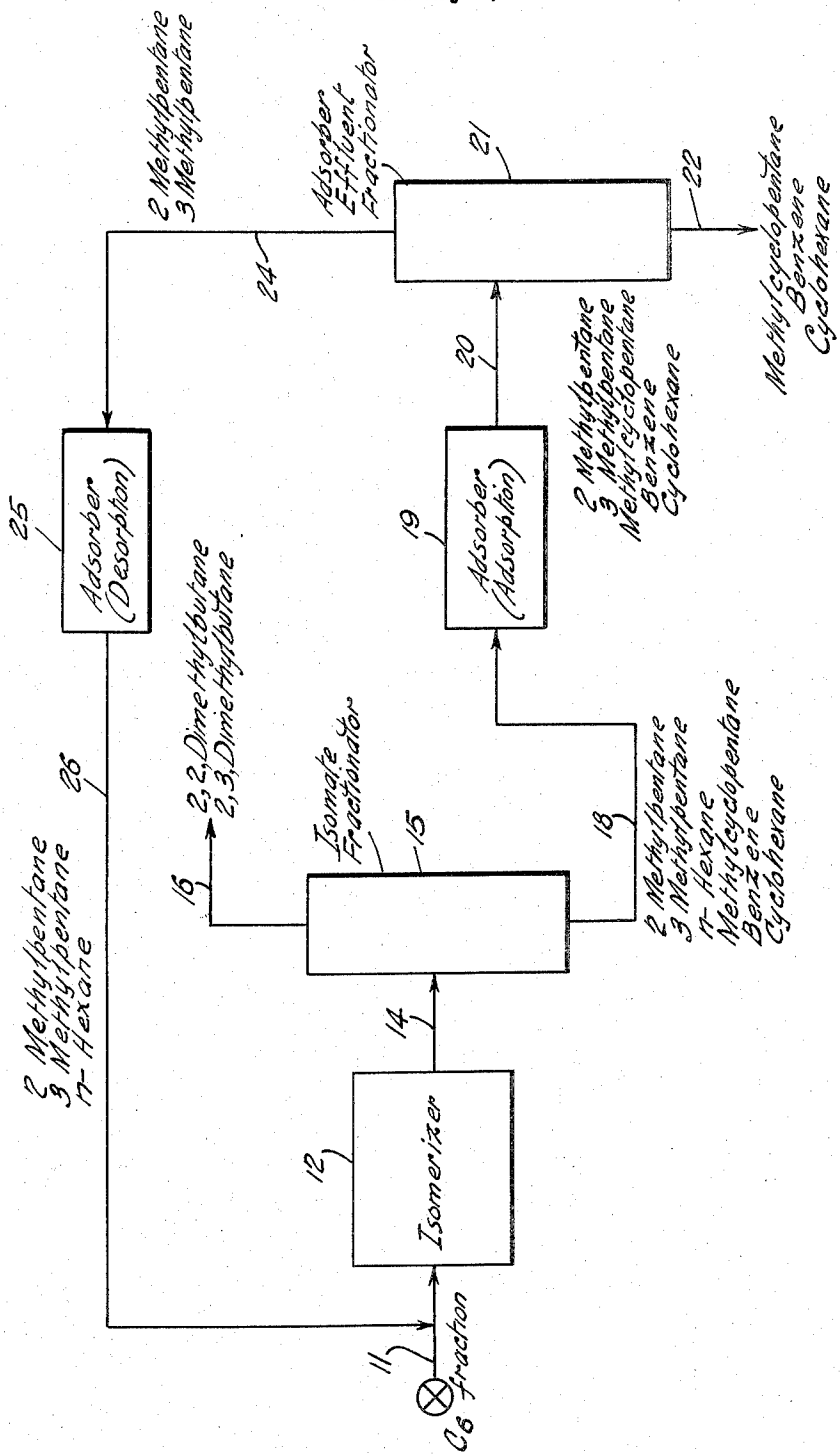
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ISOMERIZING A C_6 HYDROCARBON FRACTION

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ISOMERIZING A C_6 HYDROCARBON FRACTION

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This invention relates to a method of treating a C_6 hydrocarbon fraction. More particularly, this invention relates to a method of treating a C_6 petroleum fraction such as produced in the fractionation of petroleum naphthas, reformates, etc. Still more particularly, this invention relates to an improved method of treating a C_6 hydrocarbon fraction for the separation therefrom of a high octane material particularly useful as a blending agent for the manufacture of motor fuels.

In the manufacture of high octane gasoline or components therefor it has been suggested that a C_6 hydrocarbon fraction be subjected to isomerization for the production of a relatively high octane isomate. In the isomerization of a C_6 hydrocarbon fraction the hydrocarbons generally found in equilibrium in the resulting isomate are listed in accompanying Table No. I, along with their octane numbers and boiling points.

Table No. I

Hydrocarbon	Boiling Point, ° F.	Octane No.— ASTM — Research + 3 ccs. TEL
2,2-dimethylbutane	121.5	106.6
2,3-dimethylbutane	136.4	116.2
2-methylpentane	140.5	93.1
3-methylpentane	145.8	93.4
n-hexane	155.7	65.3
methylcyclopentane	161.3	105.3
benzene	176.2	106.0
cyclohexane	177.3	97.4

As indicated in accompanying Table No. I, a substantial number of the components found in the isomerization reaction products resulting from the isomerization of a C_6 hydrocarbon fraction have an octane number greater than 100. It is apparent, therefore, that if a C_6 isomerization treating process could be carried out such that substantially only those components having an octane number greater than 100 were produced the resulting treated isomerization reaction products would be very valuable as a high octane gasoline or blending agent for the preparation of high octane gasoline.

Accordingly, it is an object of this invention to provide an improved process for the manufacture of high octane gasoline or high octane gasoline blending components from a C_6 hydrocarbon fraction.

Another object of this invention is to carry out a C_6 isomerization process wherein substantially all of the isomerized products recovered therefrom have an octane number of at least 100.

Another object of this invention is to provide an improved process for isomerizing a C_6 hydrocarbon fraction such as a C_6 light petroleum naphtha as recovered from the distillation of crude oil, or from the reformate resulting from a catalytic reforming operation.

Yet another object of this invention is to provide a C_6 isomerization process wherein n-hexane and other

relatively low octane number hydrocarbons are recycled to extinction.

How these and other objects of this invention are achieved will become apparent in the light of the accompanying disclosure and drawing which schematically illustrates a process in accordance with the practice of this invention.

In accordance with this invention an improved C_6 isomerization reaction for the upgrading of a C_6 hydrocarbon or petroleum fraction for the production of high octane motor fuels is obtained by separately removing n-hexane and a mixture of 2-methylpentane and 3-methylpentane from the isomate and recycling these hydrocarbons to the isomerization reaction, the isomerization reaction being carried out and the resulting isomate being treated such that only the relatively high octane hydrocarbons such as 2,2-dimethylbutane, 2,3-dimethylbutane, methylcyclopentane, benzene and cyclohexane are directly removed as products from the isomerization reaction effluent.

More particularly, in the practice of this invention the isomerization reaction effluent resulting from the isomerization of a C_6 hydrocarbon fraction such as a light virgin or straight run naphtha or a light reformate is subjected to operations which include a fractional distillation step for the separation of 2,2-dimethylbutane and 2,3-dimethylbutane therefrom and which also includes the separation of normal hexane from the isomerization reaction effluent. In the practice of this invention n-hexane is removed from other components in the isomerization reaction effluent by contacting the isomerization reaction effluent with an alumino-silicate molecular sieve type selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons. Following the above-indicated selective adsorption operation for the removal of straight chain hydrocarbons, i.e., n-hexane from the isomerization reaction effluent, there is produced an isomerization reaction effluent substantially free of n-hexane.

In the practice of this invention any selective adsorption process effective for the removal of straight chain saturated hydrocarbons from branched chain hydrocarbons is satisfactorily employed in the practice of this invention. The invention, however, is particularly applicable to a selective adsorbent comprising certain natural or synthetic zeolites or alumino-silicates, such as a 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. In general, zeolites may be described as water-containing alumino-silicates having a general formula $(R,R'_2)O.Al_2O_3.nSiO_2.mH_2O$ wherein R may be an alkaline earth metal such as calcium, strontium or barium or magnesium and wherein R' is an alkali metal such as sodium or potassium or lithium. These materials when dehydrated retain their crystalline structure and are particularly useful as selective adsorbents for the selective adsorption of straight chain hydrocarbons.

A particularly suitable solid adsorbent for the adsorptive separation of 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 opening of about 5 Angstrom units, a pore size sufficiently large to admit straight chain hydrocarbons to the substantial exclusion of the non-straight chain hydrocarbons, i.e., naphthenic, aromatic, isoparaffinic and isoolefinic hydrocarbons. This particular selective adsorbent is available in various sizes, such as in the form of 1/8" or 1/16" diameter pellets,

or as a finely divided powder having a particle size in the range 0.5–5.0 microns. A selective adsorbent employed in the practice of this invention may be in any suitable form or shape, granular, spheroidal or microspheroidal.

Particularly suitable selective adsorbents which may be employed in the practice of this invention include the synthetic and natural zeolites which, when dehydrated, may be described as crystalline zeolites having a rigid three dimensional anionic network and having interstitial dimensions sufficiently large to adsorb straight chain hydrocarbons but sufficiently small to exclude the non-straight chain hydrocarbons 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 yields a material which may be represented by the formula $(Ca,Na_2)Al_2Si_4O_{12}.H_2O$ and which after suitable conditioning will adsorb straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons. Other naturally occurring or synthetically prepared zeolites such as phacolite, gmerlinite, harmotome and the like or suitable base exchange modifications of these zeolites may also be employed in the practice of this invention.

Other solid inorganic or mineral selective adsorbents are known. It is contemplated that selective adsorbents having the property of selectively adsorbing the 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 with various oxide gels of the polyvalent amphoteric metal oxides.

The selective adsorption of the n-hexane from the isomerization reaction effluent may be carried out in the liquid or gaseous phase and at any suitable temperature and pressure effective in the adsorptive separation operation. It is desirable, however, to coordinate the adsorption separation conditions, e.g., temperature and pressure, with the desorption separation conditions, more fully described hereinafter, so as to effect the most economical use of the materials employed and for ease of control.

The adsorptive separation or adsorption of the n-hexane from the isomerization reaction effluent by the selective adsorbent may be carried out at any suitable temperature, such as a temperature in the range 50–500° F., sufficient to effect the adsorptive separation of the n-hexane by the adsorbent, and at any suitable pressure, such as a pressure in the range 0–10,000 p.s.i.g. more or less, the temperature and pressure being adjusted with respect to the isomerization reaction admixture undergoing treatment depending upon whether or not it is desired to maintain the mixture undergoing separation in the liquid phase or in the vapor or gaseous phase. Liquid phase adsorption may be carried out by simply slurrying the solid selective adsorbent with the liquid isomerization reaction mixture being treated, followed by separation or decantation of the resulting treated isomate, now substantially free of or having a substantially reduced n-hexane content. Liquid phase adsorption may also be carried out by percolating the liquid hydrocarbon mixture to be treated through a bed of solid adsorbent material.

It is preferred, however, to carry out the adsorptive separation operation for the removal of n-hexane from the isomerization reaction effluent in the gaseous phase, that is, to maintain the isomate mixture undergoing treatment in the vapor phase during the adsorption operation. In such an operation any suitable method for effecting gas-solid contact may be employed, for example, a fixed bed, a moving bed, a fluidized bed or gas-entrained mass of selective adsorbent may be employed during the gas phase adsorptive separation operation. After sufficient time, the solid adsorbent is separated from the resulting treated isomate, now substantially free of n-hexane, and the resulting adsorbent, now substantially saturated with n-hexane, subsequently treated to desorb the adsorbed n-hexane therefrom.

The desorption of the n-hexane from the solid adsorbent material may be carried out at any suitable temperature and pressure. For example, the desorption operation may be carried out at a temperature in the range 0–10,000 p.s.i.g., more or less. It is preferred, however, that the desorption operation be carried out in the gaseous phase, that is, the desorption or desorbing fluid, in the practice of this invention a gaseous mixture containing 2-methylpentane and 3-methylpentane, being in the gaseous phase and the resulting desorbed n-hexane being present in the resulting desorption effluent in the gaseous or vapor phase. Accordingly, the desorption temperature and the desorption pressure are adjusted to maintain the desorbing fluid (2-methylpentane and 3-methylpentane) and the resulting desorbed n-hexane in the gaseous phase. Generally a desorption pressure in the range 10–2,000 p.s.i.g. is suitable. It is sometimes desirable, however, to carry out the desorption operation at a pressure substantially lower than the adsorption pressure. Isobaric adsorption-desorption operations are advantageous in some instances; however the pressure employed during the adsorptive separation operation is not determinative of the desorption pressure.

Any suitable desorption temperature sufficiently high to effect desorption of the adsorbed n-hexane may be employed in the practice of this invention. Usually a temperature in the range 200–800° F. is employed during the desorption operation, desirably a temperature above the critical temperature of n-hexane (455° F.). It is generally preferred to carry out the desorption operation at an elevated temperature in the range 300–600° F. The desorption temperature employed, however, should not be excessively high, for example not greater than 1100° F., particularly in the instance wherein a material such as Linde Type 5A Molecular Sieve, that is, calcium alumino-silicate is employed as the selective adsorbent, since these relatively high temperatures are excessive and lead to the destruction of the adsorbent material, presumably by collapse of the crystal structure with the resultant loss of the selective adsorption properties.

Although the desorption of n-hexane from the adsorbent containing the same may be accomplished by the mere application of heat, or by use of a gaseous desorbing medium such as hydrogen, which might be recovered from the isomerization reaction which is desirably carried out in the presence of hydrogen or by means of a gaseous desorbing fluid such as isobutane which is readily recoverable by distillation from the resulting desorbed n-hexane, it is preferred in the practice of this invention to employ a component or components separated from the isomerization reaction effluent itself, viz. 2-methylpentane and/or 3-methylpentane.

In the practice of this invention any suitable isomerization process effective for isomerizing n-hexane into its various corresponding C_6 isomate, might be suitably employed. Suitable processes are known for effecting the isomerization of a C_6 hydrocarbon such as n-hexane and generally employ a precious metal-containing catalyst such as a platinum-containing catalyst and are usually carried out in the gaseous or vapor phase. Suitable C_6 isomerization processes are well known in the art, for example see The Oil and Gas Journal, March 25, 1957, pages 153–165. The disclosures of the above-identified publication with respect to isomerization processes suitable for use in the practice of this invention are herein incorporated and made part of this disclosure. Other suitable isomerization processes for the isomerization of C_6 hydrocarbon fractions such as n-hexane are known and are suitably employed in the practice of this

invention. As indicated hereinabove, the desorption of n-hexane from the selective adsorbent, particularly when an alumino-silicate molecular sieve adsorbent is employed, is carried out substantially above the critical temperature of n-hexane (above about 454° F.). When the desorption operation is carried out at a temperature above the critical temperature of n-hexane substantially no hexane remains adsorbed in the adsorbent.

Referring now to the accompanying drawing which schematically illustrates a process in accordance with this invention and which is directed to the upgrading of a C_6 hydrocarbon fraction containing a substantial amount, e.g., at least about 5% by vol. of n-hexane, together with isomeric C_6 and other C_6 hydrocarbons, a C_6 hydrocarbon stream such as is derived from the distillation of crude oil, e.g., a light straight run naphtha in the C_6 boiling range, or a C_6 catalytic reformate fraction, is supplied via line **11** to isomerization reactor **12**. Within isomerization reactor **12** the C_6 hydrocarbon fraction undergoes isomerization, desirably in the presence of gaseous hydrogen, with the resulting production of an isomerization reaction effluent or isomate which is recovered therefrom via line **14** and passed to isomate fractionator **15**. The isomate leaving isomerization reactor **12** via line **14** will comprise the following components in admixture; 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, n-hexane, methylcyclopentane, benzene and cyclohexane.

Within isomate fractionator **15** the isomerization reaction effluent is fractionated and there is recovered overhead via line **16** an admixture comprising substantially all of the 2,2-dimethylbutane and 2,3-dimethylbutane present in the isomerization reaction effluent. At the same time there is recovered as a bottoms fraction from isomate fractionator **15** via line **18** an admixture comprising 2-methylpentane, 3-methylpentane, n-hexane, methylcyclopentane, benzene and cyclohexane. The bottoms fraction recovered from isomate fractionator **15** is supplied via line **18** to adsorber **19** wherein it contacts an alumino-silicate molecular sieve type selective adsorbent which selectively adsorbs the n-hexane therein to the exclusion of the other hydrocarbons.

There is recovered from adsorber **19** via line **20** a resulting treated effluent comprising 2-methylpentane, 3-methylpentane, methylcyclopentane, benzene and cyclohexane and substantially no n-hexane. The resulting treated effluent is then sent via line **20** to adsorber effluent fractionator **21** wherein there is recovered an overhead fraction comprising substantially all of the 2-methylpentane and 3-methylpentane in the adsorber effluent and a bottoms fraction recovered from adsorber effluent fractionator **21** via line **22** comprising methylcyclohexane, benzene and cyclohexane.

The fraction recovered overhead from fractionator **21** via line **24** and containing substantially all of the 2-methylpentane and 3-methylpentane in the isomerization reaction effluent is employed to effect desorption of the adsorbed n-hexane from the selective adsorbent employed.

As illustrated in the accompanying drawing while one adsorber, adsorber **19**, is employed in the adsorptive separation stage in the practice of this invention for the separation of n-hexane from the isomate, another adsorber, adsorber **25**, is undergoing the desorption stage for the desorption of the n-hexane from adsorbent previously employed in the adsorptive separation of n-hexane from the isomate. As a result of the desorption operation carried out in adsorber **25** there issues from adsorber **25** via line **26** a desorption effluent comprising 2-methylpentane, 3-methylpentane and the n-hexane originally present in the isomate. The resulting desorption effluent comprising substantially only these three components is then recycled via line **26** through line **11** to isomerization reactor **12**.

Although in the practice of this invention, as illustrated in the accompanying drawings, the selective adsorption of n-hexane from the isomate is shown as having been carried out subsequent to the fractional distillation of the isomate for the separation of 2,2-dimethylbutane and 2,3-dimethylbutane, if desired the separation of n-hexane from the isomate mixture may be carried out prior to the separation of 2,2-dimethylbutane and 2,3-dimethylbutane therefrom by fractional distillation. Also, if desired the C_6 hydrocarbon fraction undergoing treatment in accordance with this invention prior to being supplied to the isomerization reaction may, if desired, be subjected to a selective adsorption operation for the separation of n-hexane therefrom and to a fractional distillation step for the removal of 2,2-dimethylbutane and 2,3-dimethylbutane therefrom and for the recovery of 2-methylpentane and 3-methylpentane therefrom. The thus-separated 2,2-dimethylbutane and 2,3-dimethylbutane then separately recovered as product and the separated n-hexane desorbed from the adsorbent by contact with 2-methylpentane and 3-methylpentane and the resulting desorption effluent supplied as substantially the only feed to the isomerization reactor.

In the accompanying disclosure and drawing no reference has been made to conventional operating accessory equipment such as heat exchangers, pumps, instruments, flow regulating devices, liquid level regulating devices and the like for reasons of clarity and so as not to clutter up the specification and drawing. The employment of such devices, equipment and instruments in an operation in accordance with this invention is readily apparent to those skilled in the art in the light of this disclosure. Further, it is evident from the foregoing disclosure that many modifications, substitutions and alterations are possible in the practice of this invention without departing from the spirit or scope thereof.

We claim:

1. A method of treating a hydrocarbon fraction containing a major amount of C_6 hydrocarbons which comprises subjecting said fraction to isomerization to yield an isomate, subjecting said isomate to fractionation to separate therefrom substantially all of the 2,2-dimethylbutane and 2,3-dimethylbutane in said isomate, subjecting the remaining isomate to contact with an alumino-silicate molecular sieve adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to separate n-hexane therefrom and to yield a treated effluent substantially free of n-hexane, subjecting said treated effluent to fractionation to separate therefrom a fraction consisting essentially of 2-methylpentane and 3-methylpentane, employing the thus-separated 2-methylpentane and 3-methylpentane to desorb the adsorbed n-hexane from said adsorbent and returning the desorption effluent resulting from the desorption of n-hexane from the adsorbent by contact with 2-methylpentane and 3-methylpentane to the isomerization reaction in admixture with the C_6 hydrocarbon fraction undergoing treatment.

2. A method in accordance with claim 1 wherein said isomerization reaction is carried out in the presence of a platinum-containing catalyst.

3. A method in accordance with claim 1 wherein said C_6 hydrocarbon fraction prior to isomerization is subjected to fractionation for the removal of 2,2-dimethylbutane and 2,3-dimethylbutane therefrom prior to subjecting the C_6 hydrocarbon fraction to isomerization.

4. A method in accordance with claim 1 wherein said C_6 hydrocarbon fraction is subjected to contact with said selective adsorbent for the removal of n-hexane therefrom and the resulting treated C_6 hydrocarbon fraction, now substantially free of n-hexane, fractionated for the removal of 2,2-dimethylbutane and 2,3-dimethylbutane therefrom and the remaining C_6 fraction fractionated for the separation of the 2-methylpentane and 3-methylpentane components therefrom, which components are then employed to desorb n-hexane from said adsorbent

and the resulting desorption effluent passed to the isomerization reaction.

5. A method of treating a C_6 hydrocarbon fraction which comprises subjecting said fraction to isomerization to yield an isomate mixture comprising 2,2-dimethylbutane, 2,3-dimethylbutane, n-hexane, 2-methylpentane, 3-methylpentane, methylcyclopentane, benzene and cyclohexane, subjecting said isomate mixture to fractional distillation to separate overhead a fraction consisting essentially of 2,2-dimethylbutane and 2,3-dimethylbutane, recovering from the aforesaid fractionation operation a bottoms fraction consisting essentially of 2-methylpentane, 3-methylpentane, n-hexane, methylcyclopentane, benzene and cyclohexane, subjecting said bottoms fraction to contact with an alumino-silicate molecular sieve selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb n-hexane therefrom, recovering from the aforesaid selective adsorption operation an effluent consisting essentially of 2-methylpentane, 3-methylpentane, methylcyclopentane, benzene and cyclohexane, subjecting said effluent to fractionation to recover overhead a fraction containing substantially only 2-methylpentane and 3-methylpentane and to yield a bottoms fraction containing substantially only methylcyclopentane, pentane and cyclohexane, employing said overhead fraction containing 2-methylpentane and 3-methylpentane to desorb the adsorbed n-hexane from said adsorbent and returning the resulting desorption effluent consisting essentially of 2-methylpentane, 3-methylpentane and n-hexane to the aforesaid isomerization reaction.

6. A method of treating a C_6 hydrocarbon fraction which comprises subjecting said fraction to isomerization to yield an isomate mixture consisting essentially of 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, n-hexane, methylcyclopentane, benzene and cyclohexane, subjecting said isomate to contact with an alumino-silicate molecular sieve adsorbent for the removal of n-hexane therefrom, fractionating the resulting treated effluent to separate therefrom a relatively low boiling fraction consisting essentially of 2,2-dimethylbutane and 2,3-dimethylbutane, an intermediate boiling fraction consisting essentially of 2-methylpentane and 3-methylpentane and a relatively high boiling fraction consisting essentially of methylcyclopentane, benzene and cyclohexane, employing said intermediate fraction to desorb the adsorbed n-hexane from said adsorbent and returning the resulting desorption effluent consisting essentially of 2-methylpentane, 3-methylpentane and n-hexane to the aforesaid isomerization reaction.

7. A method in accordance with claim 6 wherein the fractions containing 2,2-dimethylbutane, 2,3-dimethylbutane, methylcyclopentane, benzene and cyclohexane are recovered and blended to yield a high octane motor fuel component.

References Cited in the file of this patent

UNITED STATES PATENTS

2,395,022	Sutton et al.	Feb. 19, 1946
2,396,331	Marschner	Mar. 12, 1946
2,766,302	Elkins	Oct. 9, 1956
2,818,455	Ballard et al.	Dec. 31, 1957