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DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Process for producing Gasoline of improved quality

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organised under the Laws of the State of Delaware, United States of America, of No. 30, Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for improving the antiknock properties of gasoline boiling range fractions of petroleum or its conversion products as well as other quality characteristics of such gasoline products by means of a combination of individual refining stages integrated into a process in which the components of lower quality present in the gasoline feed stock are converted into products of higher quality for motor fuel use, particularly products of higher octane number and improved burning characteristics.

Because of the ever-increasing demand by the motoring public for more powerful motor vehicles and the response of the automobile industry to such demand by supplying engines of higher compression ratios, the petroleum refining industry is constantly in search for processes to convert gasoline boiling range fractions of petroleum to products of higher quality, particularly with respect to their antiknock or octane ratings. This insatiable demand for higher quality gasoline has been partially met by the catalytic reforming process whereby the lower grade components of the gasoline fraction are converted to aromatic hydrocarbons. However, to increase the octane number of the gasoline by means of reforming is costly insofar as loss in yield is concerned, and the highly aromatic product, although of higher octane number, possesses certain undesirable burning characteristics when used as fuel in high compression engines because of the high carbon-to-hydrogen ratio in the aromatic components present in the resultant gasoline. The ideal route to octane improve-

ment of gasoline boiling range motor fuels is by converting the normal paraffin components (of low octane number) into isoparaffins which have a substantially higher octane rating and yet do not possess the undesirable burning characteristics of aromatic hydrocarbons of the same carbon atom content. Motor fuels of optimum burning characteristics for use in internal combustion engines contain certain maximum and minimum proportions of aromatic to isoparaffinic hydrocarbons depending upon the identity of the particular aromatic component, and generally, the maximum limitation is more critical than the minimum. The present invention provides a novel combination process of mutually related and interdependent steps whereby gasoline boiling range fractions are upgraded to products of high octane number and in which ideal proportions of aromatic and isoparaffinic components are present for motor fuel use.

In accordance with the present invention a paraffinic gasoline charge is subjected to fractional distillation and therein a light charge fraction consisting of C_5 and C_6 components is separated from a heavy charge fraction containing the C_7 and heavier components of said gasoline charge, the heavy charge fraction is subjected to catalytic reforming, C_5 and C_6 reformat hydrocarbons are separated from a higher boiling reformed gasoline fraction by fractional distillation of the reformed product, these C_5 and C_6 reformat hydrocarbons are subjected in a sorption separation zone to contact with a solid molecular sieve sorbent and therein normal paraffins are retained while branched-chain and cyclic hydrocarbons are rejected, the sorbed normal paraffin component of the C_5 and C_6 reformat hydrocarbons is recovered from the molecular sieve sorbent and is then subjected together with at least the normal paraffin portion of said light charge fraction to catalytic isomerization, the hydrocarbon product of the catalytic isomerization is subjected to separation in said sorption separation zone, and the non-sorbed

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effluent of the sorption separation zone comprising branched-chain paraffins is separately recovered and then commingled with the higher boiling reformed gasoline fraction to form the gasoline of improved quality.

5 In a more specific embodiment of this process the hydrocarbon product of the catalytic isomerization is commingled with the C_5 and C_6 reformat hydrocarbons directly
10 upon their separation from the higher boiling reformed gasoline fraction, the hydrocarbon mixture thus obtained is introduced into the sorption separation zone for the separation of the normal paraffin component from the
15 branched-chain and cyclic hydrocarbons of said mixture, and the entire light charge fraction is supplied to the catalytic isomerization directly upon its separation from the heavy charge fraction. In another specific embodi-
20 ment of the present process the light charge fraction upon separation of the latter from the heavy charge fraction is commingled with the hydrocarbon product of the catalytic isomerization and with the C_5 and C_6 reformat
25 hydrocarbons separated from the higher boiling reformed gasoline fraction, and the hydrocarbon mixture thus obtained is introduced into the sorption separation zone for the separation of the normal paraffin component
30 from the branched-chain and cyclic hydrocarbons of said mixture.

Further embodiments of the present process and various modifications thereof will be explained in the following, more detailed
35 description of the invention.

Catalytic reforming of gasoline fractions considerably improves the octane rating of gasoline, primarily by converting C_5 and C_6 naphthenic compounds into their corresponding aromatic derivatives. However, the
40 pentanes present in the gasoline fraction undergo only minor conversion when subjected to reforming in admixture with the higher boiling gasoline components. Consequently, it is generally preferred to separate the pentanes
45 from the gasoline feed stock and to blend the separated pentanes with the reformed gasoline product. It is evident, however, that the pentane fraction (as well as the hexane fraction) contains normal paraffin components
50 which have low octane numbers and which substantially lower the octane number of the branched chain and cyclic hydrocarbons with which they may be mixed. In the process of
55 the present invention, the pentanes and hexanes are removed from the gasoline feed stock prior to the reforming conversion and are subjected to a particular type of separation process, hereinafter more specifically characterized,
60 which removes the normal paraffin components from the C_5 and C_6 fractions, the thus-recovered normal C_5 and C_6 hydrocarbons being individually or collectively converted by catalytic isomerization into their
65 more desirable branched chain analogs. If

desired, although not generally preferred, the C_5 — C_6 fraction separated from the reformed product, as well as the C_5 — C_6 fraction separated from the initial gasoline feed stock, may be subjected to isomerization treatment
70 followed by separation of the unreacted normal paraffins of these C_5 and C_6 fractions and further isomerization treatment of the separated normal paraffins. The isomerization
75 process, however, is an equilibrium reaction in which the proportion of branched chain components in the isomate product is in equilibrium with the unconverted normal components also present therein. By subjecting the C_5 — C_6 fractions to a separation
80 procedure in which the normal components are segregated from the branched chain hydrocarbons prior to the isomerization treatment, a relatively greater conversion per pass through the isomerization catalyst is realized,
85 since in such mode of operation branched chain hydrocarbons are absent from the feed stock entering the isomerization reactor; that is, the removal of the branched chain (and cyclic) components prior to isomerization increases the amount of the normal compound which can be converted to establish the equilibrium ratio of iso to normal compounds. As
90 an illustration of the effect of normal hydrocarbons on the octane number of their corresponding analogs, isopentane, when leaded with 0.75 cc. of tetraethyl lead per liter, has a Research octane number of 107.0. Normal
95 pentane on the other hand, has a leaded octane number of only 85. It is evident that the presence of normal pentane in a gasoline blend in admixture with other hydrocarbons would substantially reduce the octane number of the blended gasoline product. Similarly,
100 normal hexane has a leaded octane number of only 65.3 whereas its isomers (isohexanes) have leaded octane numbers above 93. The object of the present invention is to provide a process for removing the low octane number normal paraffin components from the gasoline
105 fraction and converting them into their higher octane rated isomeric analogs, to produce a final gasoline blend of substantially higher octane number than the gasoline starting material.

Although the boiling point of the normal isomer for each of the C_5 and C_6 paraffins is somewhat higher than the boiling point of any other isomer in admixture therewith, the normal isomer forms a mixture having a constant boiling point with other C_5 and C_6 isomeric paraffins and it is accordingly impossible to prepare a pure mixture of C_5 and C_6 isoparaffins by distillation means only.
120 Thus, even with extensive distillation and high reflux ratios, a C_5 or C_6 distillate obtained from the top of a column during the fractionation of a mixture of normal and other isomers of C_5 and C_6 hydrocarbons will contain a minimum of from 6 to about 10%
130

of the normal isomer and the presence of even such relatively low proportions of the normal component substantially reduces the octane number of the branched chain C_5 and C_6 paraffins. In the process of the present invention, however, a method of separation and a particular separating agent is employed which is capable of removing 100% of the normal component and the iso-product from the separation unit is prepared in purities of from 98 to 100% of the branched chain isomers; the octane number of the resulting iso-product from the sorption stage of the present process is thus the octane number of substantially pure isopentane or of the mixed isohexanes, uncontaminated with the octane number-depreciating normal isomers.

It will be noted from the above description that the present invention provides an integrated combination of molecular sieve sorption-separation and of isomerization and catalytic reforming reaction stages for producing a high octane gasoline of exceptionally high quality. The latter gasoline product cannot be achieved by catalytic reforming alone, except by operating the reforming process at extremely severe conditions which, in turn, result in excessive loss of yield, as well as low catalyst life. Even at such extreme reforming conditions, the octane number of the product is largely the result of its aromatic content. When ignited in an internal combustion engine the resulting reformed gasoline produces a smoky flame and causes the undesirable "rumble" characteristic of high compression engines. These considerations limit the practical or commercial use of the catalytic reforming process for the production of high octane motor fuels. Although various processes combining a catalytic reforming treatment of gasoline hydrocarbons with the catalytic isomerization of relatively low boiling charge or product fractions have been suggested in the prior art the improvements obtainable thereby have not been sufficient for present day requirements and the operating conditions, particularly in regard to fractionation requirements have been such that these known processes have attained only limited industrial utilization.

It will be noted that by virtue of the present process, the low octane number normal paraffin components are selectively separated from the C_5 and C_6 fractions and independently converted into their high octane branched chain isomers. In thus separating the components which have low octane numbers and subjecting them to conversion under conditions particularly selected for the conversion of normal paraffins into isoparaffins, improved results are obtained, including: (1) high overall yields of the high octane gasoline components, (2) the ability to operate the catalytic reforming stage at substantially less severe conditions with attending higher yields

and longer catalyst life in the reforming stage and, (3) greater flexibility of operation which permits the utilization of a variety of gasoline charge stocks. As hereinbefore noted, by selective separation of the low octane normal components from their higher octane branched chain isomers, followed by isomerization of the separated material, the normal components are converted to their branched chain isomers without conversion of the branched chain isomers originally present in the feed stock mixture to normal paraffin isomers having lower octane numbers.

The present invention is further described by reference to the accompanying diagrammatic drawing which illustrates several embodiments of the invention. The diagram is presented for illustrative purposes only, and in the interest of simplicity this diagram illustrates a preferred embodiment of the invention, although other alternative embodiments which will not necessarily give exactly the same results will also be described in the following description.

The gasoline boiling range fraction utilized as feed stock may be derived from any of a large number of sources, such as for example straight-run gasolines, natural gasolines, and hydrogenated mixtures of olefin polymers. This charge is introduced into the process flow through line 1 which conveys the charge into a fractionating column, such as distillation zone 2, from which an overhead cut comprising C_4 and lighter hydrocarbons is removed through line 3 and discharged from the process. An intermediate cut consisting of the pentane and hexane components of the feed stock is withdrawn as a side-cut from column 2, through line 4, being thereafter diverted to process equipment hereinafter described. The preferred gasoline boiling range feed stocks have an end boiling point of about 204°C . although, this may be as high as 232°C . A bottoms fractions substantially dehexanized is removed from column 2 through line 5, being referred to as a C_7 and heavier fraction or by the symbol C_7+ . In accordance with the present process the C_7+ fraction from column 2 is subjected to catalytic reforming, preferably in the presence of hydrogen in sufficient molar proportion to the hydrocarbons present in the reforming zone to prevent the formation of olefins.

While the catalytic reforming step is illustrated as a single reaction zone 6, it is understood that this conversion is generally effected with a system of apparatus comprising heaters, heat exchangers, a series of reaction zones, (generally 3 or 4) containing a suitable reforming catalyst, coolers, pumps and receivers, not illustrated on the accompanying diagram, in order to simplify description thereof. The reforming conversion is effected at a temperature of from about 427° to about 566°C ., at a pressure of from about 6.8 to

about 68 atmospheres at a liquid hourly space velocity through the catalyst of from about 0.5 to about 10 volumes of feed stock per volume of catalyst per hour and in the presence of sufficient hydrogen to provide a molar ratio of hydrogen to hydrocarbons of from about 0.5 to 1 to about 20 to 1.

Any suitable reforming catalyst may be utilized in the reforming zone, the preferred catalyst comprising a composite of alumina and platinum, the platinum being present in the composite in amounts of from about 0.01 to about 5% by weight of the catalyst composite. A particularly preferred reforming catalyst is a composite of alumina, platinum, and a combined halogen, the platinum being present in an amount from about 0.1 to about 1% by weight and the halogen in an amount of from about 0.2 to about 3% by weight of the catalyst composite. The halogen is preferably fluorine or a mixture of chlorine and fluorine. Other supports may be utilized in the catalyst composite, such as silica. Other suitable catalytic composites comprising platinum are selected from platinum-silica, platinum-silica-alumina, platinum-silica-zirconia, platinum-silica-alumina-thoria, and composites comprising magnesia with one or more of the foregoing oxides and with platinum.

The products of the reforming stage of the process are withdrawn from zone 6 through line 7 into stabilizer 8 which may be in the form of a simple receiving vessel from which a hydrogen-containing light gas is withdrawn through line 9. While all or a portion of the light gas may be removed from the process flow through valve 10 in line 11 at least a portion of the hydrogen in said gas is recycled to the reforming zone through line 11 connecting with line 5 which returns the hydrogen to reforming zone 6.

The reformed gasoline product is withdrawn from stabilizer 8 through line 12 into distillation zone 13 from which the C_4 and lighter components in the reformate are withdrawn as a vapor overhead through line 14 and discharged from the process flow. Distillation zone 13 is operated in a manner which will provide for the separation of C_5 and C_6 reformate hydrocarbons as a side-cut intermediate withdrawn from distillation zone 13 through line 15 being thereafter discharged into line 4 for further conversion in the manner hereinafter set forth. A relatively large proportion of the C_5 and C_6 components in the reformate product consists of normal or low octane number paraffins which is desirably subjected to isomerization in the isomerization stage of the present process, as hereinafter described. The C_7 and heavier reformed gasoline product comprising the bottoms fraction of distillation zone 13 is withdrawn therefrom through line 16, being thereafter directed into gasoline blending tank 17 wherein the final gasoline product, blend of

the present invention is produced.

The C_5 and C_6 hydrocarbons separated in distillation zone 2 as the side-cut fraction removed through line 4 are thereafter treated in accordance with one of several alternative procedures comprising the process flow of the present invention. Since the C_5 and C_6 hydrocarbons separated from certain gasolines, such as a straight-run gasoline, generally contain a high proportion of normal paraffins, one of the process flows of this invention provides for isomerization of this C_5 — C_6 fraction directly in a suitable isomerization zone. In the event that the latter procedure is employed in the process, valve 18 in line 4 is closed, thereby directing the flow of the C_5 — C_6 fraction into line 19 which connects with line 4, the fraction thus being discharged directly into isomerization zone 20. In the commercial operation of an isomerization system the latter comprises suitable heaters, heat exchangers, reactor vessels, and coolers; these items of equipment, however, are not illustrated on the accompanying diagram for the sake of simplicity, since such equipment is well known in the art and the present invention is not predicated on a detailed exposition of such conventional components of the isomerization equipment. Any suitable isomerization catalyst may be utilized in zone 20. One of the preferred catalysts for this purpose is a platinum-containing composite, and still more particularly preferred are alumina-platinum-combined halogen catalytic composites containing from 0.1 to about 3% by weight of platinum and from 0.1 to about 10% and more preferably from about 0.5 to about 5% by weight of combined halogen selected from the group consisting of fluorine and chlorine. In the presence of the isomerization catalyst, the mixture of C_5 and C_6 paraffins is readily isomerized at temperatures of from about 93° to about 482° C., and more preferably, at temperatures of from about 149° to about 454° C. (depending upon the composition of the particular catalyst utilized in the process) and at pressures of from about 3.4 to about 68 atmospheres, at liquid hourly space velocities of from about 0.5 to 5 and hydrogen to hydrocarbon ratios of from about 0.5 to 5. The isomerization reaction is preferably effected in the presence of hydrogen which may be supplied from an external source or recycled in the system from the hydrogen produced in the reforming zone. Although, substantially no net consumption or production of hydrogen takes place during the isomerization reaction, the presence of hydrogen reduces the tendency of the hydrocarbons to deposit carbon on the catalyst during the process.

The mixture of isomerized paraffins, at or near the equilibrium concentration of branched chain C_5 and C_6 paraffins to normal components, is withdrawn from isomerization zone

20 through line 21 and discharged therefrom into line 22 which conveys the isomate product into line 4 on the downstream side of valve 18, feeding into sorption zone 23. This unit contains a solid sorbent, preferably as a fixed-bed thereof, capable of segregating normal paraffins from branched chain and/or cyclic hydrocarbons. A number of solid sorbents are known in the art for effecting separation of normal paraffins from branched chain or cyclic hydrocarbons, one of the preferred classes of sorbent materials for this purpose being alkali metal- or alkaline-earth metal-aluminosilicates which upon dehydration contain pores of from 4 to about 5 Ångstrom units in cross-sectional diameter, pores which selectively admit straight chain compounds, such as normal paraffins, but reject branched chain and cyclic hydrocarbons such as methylpentane and cyclohexane. Upon passage of the mixture of normal and iso or cyclic hydrocarbons, in either gaseous or liquid phase, into sorption separation zone 23, the sorbent selectively retains the normal components of the mixture, permitting the branched chain and/or cyclic components, also present in the isomate mixture, to continue their flow through the sorption zone, the latter "raffinate" mixture of C_5 and C_6 iso and/or cyclic hydrocarbons being removed from zone 23 through line 24 to product blending tank 17 wherein the higher octane C_5 and C_6 iso paraffins and cyclics are mixed with the higher boiling reformat product recovered from distillation zone 13 to form the present gasoline product blend, as herein-after more fully described.

The sorbent utilized in separation zone 23 has a limited capacity to retain normal paraffins; in other words, the sorbent becomes "spent" and is thereafter incapable of further sorbing additional normal paraffins. At the latter stage of sorbent saturation, the sorbent is regenerated by the removal of sorbed normal C_5 and C_6 paraffins therefrom, leaving the sorbent in its porous, regenerated condition for further treatment of additional isomate product. Several procedures which effect regeneration of the present sorbent are known in the art for reviving the activity of solid sorbents. Thus for example, the "spent" sorbent may be reactivated by vapor phase desorption utilizing a gas at a high temperature, sufficient to not only vaporize the paraffin residue from the surface of the sorbent, but also to drive out the sorbed normal paraffin from the pores of the sorbent. Typical vapor phase desorbents of this type are such gases as nitrogen, super-heated steam, and propane, at temperatures above about 100° C., up to about 900° C., depending upon the type of sorbent utilized in the process.

One of the preferred desorption procedures applicable in the present process to recover

the n-paraffin sorbate from the molecular sieve sorbent comprises desorption in the liquid phase at temperatures approximately equal to the sorption temperature, utilizing a lower molecular weight normal paraffin capable of displacing the sorbed normal paraffin from the pores of the spent sorbent by operation of the Mass Action effect. Thus, in the present process, the sorbed normal C_5 and C_6 paraffins are preferably displaced from the molecular sieve sorbent with normal butane, supplied in sufficient molar excess to provide a Mass Action effect of sufficient intensity to displace the sorbed normal paraffin with the liquid normal butane surrounding the spent sieves. The principal advantage of liquid phase desorption is that the sorption-desorption cycle may be effected isothermally and isobarically, thereby minimizing consumption of utilities to complete the process. The resulting mixture of n-butane desorbent and normal C_5 and C_6 sorbate is withdrawn from sorption separation zone 23 through line 25 and thereafter discharged into distillation zone 26 through valve 27 in line 25, or diverted as a mixture into line 28 by closing valve 27 which thereby directs the mixture of normal paraffins into line 19 leading into isomerization zone 20. In the latter alternative flow herein, the entire mixture of normal paraffins recovered from sorption separation zone 23 is charged into isomerization zone 20, the C_5 and C_6 normal paraffins present in this stream being thereby simultaneously converted in the same isomerization zone to form an equilibrium mixture of iso and normal C_5 and C_6 paraffins by virtue of the isomerization which occurs in zone 20.

Since the optimum conversion of normal pentane occurs at a somewhat different set of reaction conditions (temperature, pressure, and space velocity) than the optimum conversion of normal hexane, it is generally preferred to subject the mixture of normal pentane and normal hexane recovered from sorption separation zone 23 to distillation, whereby normal pentane is separately recovered from normal hexane, and each paraffin is thereafter separately isomerized in individual isomerization zones. The principal advantage of such separate C_5 and C_6 isomerization reactions is that each isomerization zone may be selectively and separately controlled to realize optimum conversion of both the C_5 and C_6 components. Thus, isomerization of n-hexane reaches equilibrium at a much faster rate than isomerization of n-pentane. If the mixture of C_5 and C_6 paraffins is subjected to isomerization at conditions which are tailored to effect maximum conversion of the most refractory C_5 component, then the conditions at which the reaction zone is maintained are no longer optimum for the C_6 paraffin, and a greater proportion of the component will tend to undergo cracking to

form products of less economic value. In order to provide selective isomerization of both the C_5 and the C_6 paraffins the mixture of normal C_5 and C_6 hydrocarbons recovered from sorption separation zone 23 through line 25 is directed through open valve 27 into distillation zone 26 wherein a normal pentane overhead is distilled from zone 26 through line 29 and a normal hexane bottoms is recovered from zone 26 through line 30.

It is evident that if liquid phase desorption is utilized in zone 23, for example, with liquid n-butane, the desorbed effluent from zone 23 will contain n-butane as well as the desorbed normal C_5 and C_6 paraffins and in such an operation, the effluent is prefractonated (not illustrated) to distill the n-butane from the desorbed C_5 and C_6 hydrocarbons prior to further treatment of the latter.

The normal pentane overhead from zone 26 is directed in liquid phase into isomerization zone 31 containing an isomerization catalyst which effects isomerization of the normal pentane to an equilibrium mixture of isomeric pentanes comprising predominantly branched chain pentanes which are removed from isomerization zone 31 through line 32 and discharged into line 22.

The normal hexane recovered as bottoms from zone 26 through line 30 is conveyed via line 19 into isomerization zone 20 for conversion into an equilibrium mixture of branched and normal hexane isomers, and this mixture is removed therefrom through line 21 for discharge into line 22, which recycles the resulting mixture of C_5 and C_6 isomers to sorption separation zone 23 for recovery of the normal components therefrom. It is evident that through such a combination of normal paraffin recovery and selective isomerization of the continuously recovered normal components, accompanied by the separate, selective removal of the iso and cyclic isomers from the process flow, the normal components are eventually recycled to extinction, being wholly converted to their higher octane branched chain and cyclic isomers. Both isomerization zones 20 and 31 may contain the same or different isomerization catalysts, preferably of the type hereinabove described as a platinum-containing catalyst. Composites of platinum, alumina, and combined halogen selected from fluorine and chlorine (preferably fluorine) when utilized for isomerization catalysts in zones 20 or 31 preferably contain a relatively high percentage of combined halogen, up to about 10% of the weight of the catalyst composite (and more preferably, up to about 5% by weight) to thereby enhance the conversion of the normal paraffins in the isomerization zones 20 and 31 to equilibrium mixtures of paraffin isomers.

The reaction conditions maintained in zone 31 for isomerization of n-pentane to an equilibrium mixture of isomeric pentanes are

preferably somewhat different than the reaction conditions maintained in zone 20 for the conversion of n-hexane to its equilibrium mixture of hexane isomers. Thus, in the presence of the preferred platinum-alumina-combined halogen composites containing up to about 10% halogen, preferably fluorine, isomerization zone 20 is operated at temperatures of from about 93° to about 371°C. and more preferably at from about 149° to about 316° C. and at space velocities of from about 0.5 to 1 to about 10.0 to 1 volumes of liquid hydrocarbon per volume of catalyst per hour. The n-hexane feed stock charged to zone 20 is converted to an equilibrium mixture of hexane isomers generally, and more preferably, at somewhat milder temperatures than that provided for conversion of the n-pentane in the zone 31, which is maintained at from about 149° to about 399° C. and more preferably from about 204° to about 371° C. and at space velocities of from about 0.2 to 1 to about 5.0 to 1.

Although the aforementioned platinum-containing composites are preferred catalysts for isomerization in zone 20, or in zones 20 and 31, respectively, other suitable isomerization catalysts may also be employed, such as anhydrous aluminum chloride, aluminum bromide, zinc chloride, a ferric halide, such as ferric chloride, generally together with the corresponding hydrogen halide. When the latter metal halides are utilized as the isomerization catalyst in zone 20 or 31 in a fixed-bed arrangement, the metal halide is preferably composited with a suitable support such as alumina or clay and the isomerization reaction is generally effected at somewhat lower temperatures (generally from about 10° to about 149° C.). It is to be understood, however, that the various foregoing isomerization catalysts are not equally effective, the indicated platinum and combined halogen-containing catalysts being generally preferred.

Irrespective of the particular isomerization arrangement employed in the present process, the reaction conditions of the isomerization zones 20 and 31 are selected on the basis of effecting a minimum degree of side reactions, such as cracking, and other types of degradation reactions. By separately subjecting the normal pentane fraction recovered from the sorption separation zone to isomerization in an independent reaction zone at optimum reaction conditions and with the recycle operation illustrated herein the isomate product is again subjected to sorption separation in zone 23, the normal isomer being thereby separated from the isomate product and continuously recycled, substantially complete isomerization of the normal pentane to isopentane may be realized in the present process. Through such means, the amount of normal pentane in the final gasoline blended product is nil, provid-

ing a blended product of maximum octane number. On the other hand, the inclusion of pentanes in the gasoline feed stock to the reforming zone effects substantially no isomerization of the normal pentane to isopentane and the normal compound therefore remains in the product to substantially reduce the net octane number of the product.

As in the case of separate isomerization of the normal pentane recovered from sorption separation zone 23, the separate isomerization of normal hexane in isomerization zone 20, coupled with recirculation of the isomate product to the sorption separation zone, results in substantially complete conversion of the normal hexane present in the system to its branched chain hexane isomers having substantially higher octane numbers than the normal hexane component. While the isomerization conditions maintained in zone 20 are within the same general ranges of temperature and pressure as the isomerization reaction in zone 31 and while similar catalysts may also be utilized in both zones 20 and 31, the conditions maintained in zone 20 and zone 31 are preferably selected and independently controlled to effect maximum conversion of the different normal paraffins to their isomate mixtures.

Because of the relatively large proportion of branched chain and cyclic hydrocarbons in the C_5-C_6 fraction of the reformate product distilled therefrom in distillation zone 13, the branched chain and cyclic pentanes and hexanes are preferably separated therefrom prior to subjecting these mixtures to isomerization; hence the C_5-C_6 fraction of the reformate product withdrawn as a side-cut from distillation zone 13 through line 15 is charged into the inlet side of sorption separation zone 23, the branched chain and cyclic C_5 and C_6 present in this fraction being recovered as the raffinate effluent from zone 23 and removed through line 24. Any normal C_5 and C_6 present in the reformate fraction thus leaves sorption separation zone 23 in admixture with the normal C_5 and C_6 paraffins distilled from the feed stock and supplied to zone 23 through line 4. The branched chain and cyclic pentanes and hexanes are separated from the normal isomers and the latter make up the feed stock to isomerization zones 20 and 31 in the absence of any isomeric or cyclic component, thereby enhancing the total conversion of the normal components to their branched chain and cyclic isomers. Although separation of the normal components from the C_5-C_6 reformate fraction by sorption thereof in zone 23 is generally preferred, this fraction may also be supplied directly to isomerization by connecting line 15 with line 19, for example, through line 33.

In the interest of simplicity, auxiliary items of equipment such as heaters, heat exchangers, coolers, condensers, pumps, receivers and

similar items of equipment which generally are essential in the actual operation of the process but are of conventional design have been omitted from the drawing. The introduction of side streams in the process, such as for example of desorbent in the sorption separation zone, has also been omitted in the interest of simplicity. These details are specific process design problems and their inclusion in the accompanying diagram are not essential to an understanding of the basic process flow of the present invention. Similarly, detailed aspects of the fractionating zones, such as side-cut condensers, receivers, fractionating trays and numerous other items which would ordinarily comprise an operable working system, are not essential to an understanding of the invention and have accordingly been omitted from the accompanying diagram.

As set forth above, the process of the present invention produces a high yield of a high octane gasoline product comprising a blend of C_7+ reformate and C_5-C_6 cyclic and branched chain paraffins produced by the present combination of a sorption separation stage and an isomerization stage, the gasoline blend being withdrawn from the process through line 34 from blending tank 17. The final gasoline product will have a leaded octane number substantially above 95, up to 104 or more. The production of the present high octane gasoline product, nevertheless, is effected without the loss of yield which accompanies severe reforming reaction conditions normally required to produce a high octane motor fuel product in the reforming stage alone, in the absence of the combined sorption separation and isomerization steps of the process. Utilizing the process flow provided in the present invention, including the isomerization step on the C_5-C_6 components of the present gasoline product, the yield of high octane gasoline product is from 6 to 10% over and above the yields previously obtained through reforming the feed stock alone. Such yields are obtained, even though the catalyst life of the reforming stage of the process is substantially increased by incorporating the present sorption separation zone and isomerization stages in the process flow.

The invention is further illustrated with respect to specific embodiments thereof in the following examples, which illustrate the novelty and utility of the process flow. The examples, however, are not necessarily intended to limit the scope of the invention in accordance therewith.

EXAMPLE I

A West-Texas crude oil was fractionated to separate a C_6+ straight-run gasoline fraction having an end boiling point of 171°C . Analysis of this fraction indicated the following composition:

C ₅ Cut	Vol. % of Feed	Composition of Cut. Vol. %	Octane No. of Cut	
			Clear	+0.795 ml. TEL/liter
	50		76.3	95.0
Isopentane		47.5		
N-pentane		52.5		
C ₆ Cut				
	23.8		60.8	86.0
Cyclopentane		2.5		
2,2-, and 2,3- dimethylbutanes		5.8		
Methylpentanes		44.8		
N-hexane		35.5		
Cyclohexanes		11.4		
C ₇ + Cut (90—171° C.)				
	21.2		55.2	75.0
Paraffins		56		
Naphthenes		38		
Aromatics		6		
C ₈ + Gasoline Fraction				
	100		67.0	88.0

Based on a total gasoline charging rate of 15,900 hectoliters per day (H/D), the gasoline fraction is split into a C₅ cut of 7,950 H/D, a C₆ cut of 3,784 H/D and a C₇+ cut of 4,166 H/D.

The C₇+ fraction (4,166 H/D) having an end boiling point of 171° C. was subjected to a catalytic reforming conversion in the presence of hydrogen, the catalyst being a composite of alumina, about 0.4% by weight of platinum and about 0.5% by weight of combined halogen, namely about 0.3% by weight combined fluorine and about 0.2% by weight combined chlorine. The above C₇+ fraction was charged at a temperature of about 477° C. and a space velocity of about 2.5 into a reforming reactor containing the aforementioned catalyst. The reactor was maintained at a pressure of about 34 atmospheres and hydrogen, largely derived as recycle from the reforming step of the process was charged with the hydrocarbon feed stock at a rate sufficient to maintain a hydrogen to a hydrocarbon molar ratio of about 8 to 1. The products of the reforming process were cooled at the above pressure to separate a C₄ and lighter fraction (102 H/D, liquid C₄) from a liquid bottoms portion of the product and the latter was charged into a distillation column to recover an overhead C₅—C₆ cut (890 H/D) from a liquid residue boiling within the gasoline boiling range. The latter liquid portion of the product was charged at

a rate of 2,830 H/D into a gasoline blending tank to produce the blended gasoline product, hereinafter described. The reformed gasoline product contains 23.4% aromatic hydrocarbons, 1.3% naphthenes and the balance aliphatic paraffins, the mixture having a clear Research octane number of 93.2 and a Research leaded octane number (+0.795 ml of tetraethyl lead) of 96.4.

The C₅—C₆ cut recovered from the catalytic reformat, in the amount corresponding to 890 H/D was mixed with the C₅ and C₆ fractions recovered from the straight-run gasoline feed stock and the combined C₅—C₆ mixture was charged at a rate of 12,625 H/D into a sorption separation column containing approximately 490 kg. of 0.29—0.42 mm particles of 5 Å molecular sieve sorbent composed of dehydrated calcium aluminosilicate, capable of sorbing straight-chain paraffins having at least 4 carbon atoms per molecule and leaving unsorbed the branched chain and cyclic components present in the combined C₅—C₆ charge stock. The latter feed stock was charged to the molecular sieve column at a temperature of 93° C. and at a pressure of 17 atmospheres, at which condition the C₅—C₆ mixture was substantially in liquid phase. A recycle fraction consisting of isomerized and normal pentanes and hexanes, produced as hereinafter indicated and as recovered from subsequent stages of the process, was charged at a rate of 8,068 H/D

into the sorption separation column containing the molecular sieves. This mixture of normal and branched chain C_5 and C_6 paraffins (produced by isomerization of the normal components separated from the streams charged into the sorption separation column) contained 12.1% normal pentane, 19.3% normal hexane, the remainder consisting of branched chain pentanes and hexanes, hereinafter more fully described.

A raffinate stream comprising the non-sorbed branched chain and cyclic components was obtained from the molecular sieve separation column at a rate of 11,868 H/D and was charged into the gasoline blending tank hereinabove described to be mixed with the reformed gasoline product for the production of the ultimate gasoline blend of the present process, a mixture of aromatic and branched chain and cyclic paraffins of high antiknock quality.

The normal paraffin components of the C_5 - C_6 mixture charged into the separation column were removed from the molecular sieve particles by desorption with a liquid stream of n-butane desorbent charged at the aforementioned temperature of 93° C. and pressure of 17 atmospheres at a rate sufficient to provide between 1.1 and 5.5 (preferably up to about 3.5) volumes of liquid normal butane per volume of normal paraffin sorbed on the molecular sieve sorbent particles. The effluent stream from the sorption separation column was a mixture of normal butane and desorbed normal pentane and normal hexane; this stream after debutanization, yielded a mixture of normal pentane and normal hexane containing less than 2.3% branched chain or cyclic hydrocarbons. The mixture of normal C_5 and C_6 paraffins was thereafter charged at a temperature of 379° C. and at a pressure of 21 atmospheres, in admixture with sufficient hydrogen to provide a hydrogen to hydrocarbon molar ratio of about 1:1 into an isomerization reactor containing the aforementioned platinum catalyst, (0.4% platinum and 4% combined fluorine supported on alumina) to effect the isomerization of the normal paraffins to an equilibrium mixture of iso and normal C_5 and C_6 paraffins, the mixture being charged at a rate corresponding to a liquid hourly space velocity of 3.5 at which rate equilibrium in the conversion of the most readily isomerized normal hexane component was obtained. It may be mentioned here that at a space velocity of 3.5 (volumes of liquid feed stock per volume of catalyst per hour) the conversion of the n-hexane component of the mixture to branched chain hexanes is approximately 62%, but the conversion of n-pentane to isopentane is only 41%. At lower throughput rates (for example at a space velocity of 1. to 1.5, or at longer contact times of the feed stock with the catalyst) a greater proportion of n-hexane is cracked

to lighter hydrocarbons and hydrogen, although the conversion of n-pentane to isopentane is increased to 65.3%. The mixture of C_5 and C_6 isomers produced by isomerization was withdrawn from the isomerization reactor and charged in liquid form into the inlet of the separation column containing the molecular sieve sorbent as described above.

In the foregoing operation wherein the normal pentane and normal hexane are combined and charged as a mixture into a single isomerization reactor, the net conversion of normal to isoparaffins (by analysis of the effluent isomate product) was 58.4%, the product containing 41.6% unconverted normal C_5 - C_6 paraffins. The mixtures of branched chain isomeric C_5 and C_6 paraffins recovered from the molecular sieve separation column utilizing the above method of isomerizing the combined C_5 - C_6 normal paraffins, represented a net isomate yield of 11,868 H/D. The octane number of the ultimate gasoline product blend (i.e., namely 2,830 H/D reformat and 11,868 selective isomate) was 94.3 clear and 101.2 by the Research method of octane number determination (i.e., plus 0.795 cc TEL per liter).

EXAMPLE II

In the following operation the procedure of Example I was modified by subjecting the normal paraffin sorbate product of the sorption separation stage (molecular sieve desorbate) to fractional distillation, separating thereby a normal pentane distillate from the normal hexane bottom fraction and separately recovering these two fractions. The normal pentane as an individual fraction (6,416 H/D) was thereafter charged into a separate isomerization reactor containing the aforementioned platinum-alumina-halogen catalyst composite (0.4% Pt and 4% combined fluorine) at a temperature of 321° C., at a space velocity of 1.5 and at a pressure of 21 atmospheres, utilizing a hydrogen to hydrocarbon molar ratio of 1:1. The normal hexane liquid residue of the distillation, as a separate stream (2,409 H/D) was charged at a temperature of 171° C., at a space velocity of 4.5 and at a pressure of 21 atmospheres into another isomerization reactor containing a fixed bed of the aforementioned isomerization catalyst consisting of 0.4% platinum and 4% fluorine supported on alumina, utilizing a molar ratio of hydrogen to hydrocarbon of 3:1. The effluent stream from the normal pentane isomerization unit indicated a conversion of n-pentane to isopentane of 68.9% (equilibrium concentration at the temperature of operation) and the effluent from the normal hexane isomerization unit indicated a conversion of normal hexane of 71.3%. The total isomate, product formed by separately isomerizing the n- C_5 and n- C_6 paraffin streams at isomerizing conditions optimum for each stream contained about



6.5%¹ less normal paraffin than the product of the isomerization operation of Example I in which both C_5 and C_6 normal paraffins were isomerized together at conditions which were optimum for the less rapidly isomerizable $n-C_5$ component of the mixture. The yield of total isomate product was substantially greater in the operation of Example II, since a lesser proportion of $n-C_5$ is lost to uneconomical gaseous by-products. The combined isomate products were similarly recycled to the sorption separation column containing the molecular sieve sorbent, as in Example I above. The yield of isoparaffins produced by way of the latter method of isomerizing, wherein the normal pentane and normal hexane streams were separately isomerized was 12,370 H/D, increasing the yield of net ultimate blended product by 3.4% over the method of conversion described in Example I above. The product of the present run was of even higher quality than the product of Example I, having a clear octane number of 95.1 (compared to 94.3) and a Research method octane number of 101.8 (compared to 101.2).

The above results may be compared with the results of reforming the entire C_5 + gasoline fraction by charging the same into a catalytic reforming unit operated at reaction conditions sufficiently severe to produce a product of 91.3 clear octane number. The proportion of aromatic components in the reformate was substantially higher, but the gasoline when tested in a high compression gasoline engine produced the undesirable "rumble" characteristic of higher aromatic content gasoline. The reforming conditions required to obtain an octane number of 91.3 clear included a temperature of 504°C . and a pressure of 38 atmospheres and the ultimate yield of gasoline product was reduced by 5.3%, relative to that obtained in Example I. The reforming operation applied to entire C_5 + gasoline fraction also required regeneration of the reforming catalyst at more frequent intervals as a result of carbon deposition on the catalyst during the reforming process. In order to maintain the quality of the product at the above level, the life of the reforming catalyst was approximately 70% of the onstream life of the catalysts utilized in the operations of Examples I and II.

WHAT WE CLAIM IS:—

1. A process for producing gasoline of improved quality from a paraffinic gasoline charge characterized by the combination of the steps of subjecting the gasoline charge to fractional distillation and therein separating a light charge fraction consisting of C_5 to C_6 components from a heavy charge fraction containing the C_7 and heavier components of said gasoline charge, subjecting said heavy charge fraction to catalytic reforming, separating C_5 and C_6 reformate hydrocarbons

from a higher boiling reformed gasoline fraction by fractional distillation of the reformed product, subjecting said C_5 and C_6 reformate hydrocarbons in a sorption separation zone to contact with a solid molecular sieve sorbent and therein retaining normal paraffins while rejecting branched-chain and cyclic hydrocarbons, recovering the sorbed normal paraffin component of said C_5 and C_6 reformate hydrocarbons from the molecular sieve sorbent and subjecting the same together with at least the normal paraffin portion of said light charge fraction to catalytic isomerization, subjecting the hydrocarbon product of the catalytic isomerization to separation in said sorption separation zone, separately recovering the non-sorbed effluent of said sorption separation zone comprising branched-chain paraffins and commingling the same with said higher boiling reformed gasoline fraction to form said gasoline of improved quality.

2. Process as claimed in claim 1, characterized in that the hydrocarbon product of the catalytic isomerization is commingled with the C_5 and C_6 reformate hydrocarbons directly upon separation of the latter from the higher boiling reformed gasoline fraction, the hydrocarbon mixture thus obtained is introduced into the sorption separation zone for the separation of the normal paraffin component from the branched-chain and cyclic hydrocarbons of said mixture, and the entire light charge fraction is supplied to the catalytic isomerization directly upon its separation from the heavy charge fraction.

3. Process as claimed in claim 1, characterized in that the light charge fraction upon separation of the latter from the heavy charge fraction is commingled with the hydrocarbon product of the catalytic isomerization and with the C_5 and C_6 reformate hydrocarbons separated from the higher boiling reformed gasoline fraction, and the hydrocarbon mixture thus obtained is introduced into the sorption separation zone for the separation of the normal paraffin component from the branched-chain and cyclic hydrocarbons of said mixture.

4. Modification of the process claimed in claim 1, characterized in that the C_5 and C_6 reformate hydrocarbons upon their separation from the higher boiling reformed gasoline fraction are commingled with the light charge fraction directly upon its separation from the heavy charge fraction, the resultant mixture is supplied to the catalytic isomerization together with the normal paraffin component recovered from the molecular sieve sorbent in the sorption separation zone, and the hydrocarbon product of the catalytic isomerization is introduced into said sorption separation zone for the separation of the normal paraffin component from the branched-chain and cyclic hydrocarbons of said product of isomerization.

70

75

80

85

90

95

100

105

110

115

120

125

130





6.5% less normal paraffin than the product of the isomerization operation of Example I in which both C_5 and C_6 normal paraffins were isomerized together at conditions which were optimum for the less rapidly isomerizable $n-C_5$ component of the mixture. The yield of total isomate product was substantially greater in the operation of Example II, since a lesser proportion of $n-C_5$ is lost to uneconomical gaseous by-products. The combined isomate products were similarly recycled to the sorption separation column containing the molecular sieve sorbent, as in Example I above. The yield of isoparaffins produced by way of the latter method of isomerizing, wherein the normal pentane and normal hexane streams were separately isomerized was 12,370 H/D, increasing the yield of net ultimate blended product by 3.4% over the method of conversion described in Example I above. The product of the present run was of even higher quality than the product of Example I, having a clear octane number of 95.1 (compared to 94.3) and a Research method octane number of 101.8 (compared to 101.2).

The above results may be compared with the results of reforming the entire C_5 +gasoline fraction by charging the same into a catalytic reforming unit operated at reaction conditions sufficiently severe to produce a product of 91.3 clear octane number. The proportion of aromatic components in the reformate was substantially higher, but the gasoline when tested in a high compression gasoline engine produced the undesirable "rumble" characteristic of higher aromatic content gasoline. The reforming conditions required to obtain an octane number of 91.3 clear included a temperature of 504° C. and a pressure of 38 atmospheres and the ultimate yield of gasoline product was reduced by 5.3%, relative to that obtained in Example I. The reforming operation applied to entire C_5 + gasoline fraction also required regeneration of the reforming catalyst at more frequent intervals as a result of carbon deposition on the catalyst during the reforming process. In order to maintain the quality of the product at the above level, the life of the reforming catalyst was approximately 70% of the onstream life of the catalysts utilized in the operations of Examples I and II.

WHAT WE CLAIM IS:—

1. A process for producing gasoline of improved quality from a paraffinic gasoline charge characterized by the combination of the steps of subjecting the gasoline charge to fractional distillation and therein separating a light charge fraction consisting of C_5 to C_6 components from a heavy charge fraction containing the C_7 and heavier components of said gasoline charge, subjecting said heavy charge fraction to catalytic reforming, separating C_5 and C_6 reformat hydrocarbons

from a higher boiling reformed gasoline fraction by fractional distillation of the reformed product, subjecting said C_5 and C_6 reformat hydrocarbons in a sorption separation zone to contact with a solid molecular sieve sorbent and therein retaining normal paraffins while rejecting branched-chain and cyclic hydrocarbons, recovering the sorbed normal paraffin component of said C_5 and C_6 reformat hydrocarbons from the molecular sieve sorbent and subjecting the same together with at least the normal paraffin portion of said light charge fraction to catalytic isomerization, subjecting the hydrocarbon product of the catalytic isomerization to separation in said sorption separation zone, separately recovering the non-sorbed effluent of said sorption separation zone comprising branched-chain paraffins and commingling the same with said higher boiling reformed gasoline fraction to form said gasoline of improved quality.

2. Process as claimed in claim 1, characterized in that the hydrocarbon product of the catalytic isomerization is commingled with the C_5 and C_6 reformat hydrocarbons directly upon separation of the latter from the higher boiling reformed gasoline fraction, the hydrocarbon mixture thus obtained is introduced into the sorption separation zone for the separation of the normal paraffin component from the branched-chain and cyclic hydrocarbons of said mixture, and the entire light charge fraction is supplied to the catalytic isomerization directly upon its separation from the heavy charge fraction.

3. Process as claimed in claim 1, characterized in that the light charge fraction upon separation of the latter from the heavy charge fraction is commingled with the hydrocarbon product of the catalytic isomerization and with the C_5 and C_6 reformat hydrocarbons separated from the higher boiling reformed gasoline fraction, and the hydrocarbon mixture thus obtained is introduced into the sorption separation zone for the separation of the normal paraffin component from the branched-chain and cyclic hydrocarbons of said mixture.

4. Modification of the process claimed in claim 1, characterized in that the C_5 and C_6 reformat hydrocarbons upon their separation from the higher boiling reformed gasoline fraction are commingled with the light charge fraction directly upon its separation from the heavy charge fraction, the resultant mixture is supplied to the catalytic isomerization together with the normal paraffin component recovered from the molecular sieve sorbent in the sorption separation zone, and the hydrocarbon product of the catalytic isomerization is introduced into said sorption separation zone for the separation of the normal paraffin component from the branched-chain and cyclic hydrocarbons of said product of isomerization.



component

5. Process as claimed in claim 1, characterized in that the normal paraffin component recovered from the solid molecular sieve sorbent in the sorption separation zone is fractionated into a first fraction consisting essentially of normal pentane and into a second fraction consisting essentially of normal hexane in a distillation zone which is separate from the zones wherein the gasoline charge and the reformed product are separately subjected to fractional distillation, said first fraction and said second fraction are separately converted by catalytic isomerization into an equilibrium mixture of pentane isomers and an equilibrium mixture of hexane isomers, respectively, the resultant equilibrium mixtures are commingled and the isomerization product thus obtained is introduced into the sorption separation zone for the separation of the normal paraffin component from the branched-chain and cyclic hydrocarbons of said isomerization product.
6. Process as claimed in any of the claims 1 to 5, characterized in that the catalytic reforming of the heavy charge fraction is effected in the presence of hydrogen and a reforming catalyst containing platinum, alumina and silica or platinum, alumina and combined halogen at a temperature in the range of from 427 to 566° C., the C₅ and C₆ hydrocarbons introduced into the sorption separation zone are maintained therein in liquid phase during the sorption of normal paraffin component therefrom by a solid molecular sieve sorbent having pores of about 5 Ångstrom units in cross-sectional diameter, the normal paraffin component is recovered from the molecular sieve sorbent by displacing the same in the liquid phase with liquid normal butane, and the catalytic isomerization is effected in the presence of hydrogen and a catalyst containing platinum, alumina and combined halogen at a temperature in the range of from 93 to 399° C.
7. Process as claimed in claims 5 and 6, characterized in that the isomerization of the pentane fraction is effected at a temperature of at least about 149° C. and the isomerization of the hexane fraction is effected at a temperature below 371° C. and below the pentane isomerization temperature.
8. The process for producing gasoline of improved quality substantially as described with reference to the drawing.
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