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CONVERSION OF HYDROCARBONS

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INVENTOR.

Robert M. Cornforth
Donald H. Dickey

BY

Attorney.

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CONVERSION OF HYDROCARBONS

Robert M. Cornforth, Gary, Ind., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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This invention relates to the production of high antiknock gasoline suitable for aviation fuels or as a blending stock therefor, and relates more particularly to the conversion of low octane number hydrocarbon mixtures to high octane number fuels of balanced distribution as regards boiling range and volatility, suitable for use as aviation gasoline or as a blending stock in the production of aviation fuels.

It has been discovered that the isomerization of high-boiling hydrocarbon mixtures is not practical or desirable, due to the fact that catalyst life is short and the yield is low, but that the isomerization of low-boiling hydrocarbons takes place readily with good yields. It has also been discovered that the catalytic reforming of such high-boiling stocks succeeds admirably in converting low anti-knock hydrocarbon mixtures to a blend of hydrocarbons having greatly increased octane number but that such a process, which is essentially an aromatization reaction, does not effect a similar beneficial conversion of the lower-boiling hydrocarbons.

It is an object of this invention to provide a process for the conversion of low octane number liquid hydrocarbons to high octane number liquid hydrocarbons suitable for use as premium fuels. Another object of my invention is to provide a process for the conversion of liquid hydrocarbons of gasoline boiling range containing a substantial amount of straight-chain hydrocarbons to hydrocarbons of similar boiling range rich in branched-chain and/or aromatic hydrocarbons. A further object of my invention is to provide a process for the catalytic conversion under hydrogen pressure of low octane number hydrocarbons to gasoline of increased octane number. An additional object of my invention is to provide a process whereby high octane number hydrocarbon mixtures suitable for blending with other hydrocarbon mixtures of varying octane number properties can be obtained from low octane number stocks unsuitable for blending. Further objects and advantages of my process will become apparent as the description thereof proceeds.

Briefly described, my process contemplates the conversion of low octane number naphtha to high octane number motor fuels by the catalytic isomerization of the lower boiling hydrocarbons to branched-chain paraffinic hydrocarbons and the catalytic reforming of the higher boiling hydrocarbons to aromatic hydrocarbons, both reactions being carried out in an atmosphere of hydrogen, the hydrogen formed during the aromatization

being sufficient to supply the isomerization reaction, as well as the aromatization reaction, with the necessary hydrogen pressure.

The single drawing which forms a part of this specification illustrates in the form of a simplified flow diagram apparatus suitable for carrying out my process.

Referring now to the drawing: Feed stock enters through line 10 and is directed to fractionator 11 by pump 12. As feed stock I can use, for example, a petroleum fraction containing virgin gasoline which is substantially propane-free and which has an end point of about 300 to 400° F. This can be a light virgin naphtha or straight-run gasoline or may be "distillate" gasoline or similar hydrocarbon mixtures recovered from "distillate" wells or natural gas wells. Such light virgin naphtha or straight-run gasoline or "distillate" gasoline or similar hydrocarbon mixtures, all of which are substantially saturated, are called "paraffinic naphtha" as distinguished from olefin and aromatic-containing cracked naphtha obtained by catalytic or thermal conversion processes but such paraffinic naphthas may, of course, contain naphthenes as well as paraffins. Such gasolines and naphthas are, generally speaking, of low octane number, being characterized by the presence of considerable amounts of straight-chain hydrocarbons and comparatively free of highly branched-chain hydrocarbons and aromatics which impart high octane number characteristics to a motor fuel and whose presence is desirable in gasolines used for aviation engines or premium motor fuels.

Fractionator 11 is so operated that a fraction having an end point of about 150 to 175° F. is taken overhead while the remainder is withdrawn as bottom stock. The significance of the 150 to 175° F. range will be apparent from hydrocarbon boiling point tables which show that heptanes boil above about 175° F. while methyl pentanes boil below about 150° F.; the particular cut point of about 150 to 175° F. thus means that the heptanes are excluded from the low boiling fraction and that methyl pentanes are excluded from the high boiling fraction. Top-cooling means 13 and bottom-heating means 14 can be used to aid in effectuating the separation. I can maintain fractionator 11, for example, at a gage pressure of from about 0 pounds per square inch to 25 pounds per square inch, preferably 5 pounds per square inch, with a top temperature of from 130° F. to 190° F., preferably 150° F., and a bottom temperature of from 160° F. to 310° F., preferably 200° F. The lighter hy-

drocarbons, having an end point of about 150 to 175° F. pass overhead through line 15 and, if desired, can be directed through line 16 by opening valve 17 therein to debutanizer 18 equipped with top-cooling means 19 and bottom-heating means 20 wherein hydrocarbons having four carbon atoms per molecule are taken overhead through line 21. The "butane" can be discarded from the system by opening valve 22 in line 23 or can be used for blending with the finished product to provide additional volatility if necessary by opening valve 24 in line 25. It can also be converted by means of such processes as dehydrogenation, polymerization, alkylation, etc., to high octane number gasoline-like products; can be used for blending with butane-deficient motor fuels; or can be similarly utilized in various processes known to those skilled in the art.

The debutanized light naphtha is withdrawn through line 26 and can be directed as such to an isomerization process by opening valve 27 in line 28 or can be depentanized by opening valve 29 in line 30 which leads to depentanizer 31. Under suitable conditions of temperature and pressure a fractionation can be carried out in depentanizer 31 whereby the major portion of the hydrocarbons having five carbon atoms per molecule pass overhead through line 32 while the higher boiling hydrocarbons are withdrawn through line 33. Depentanizer 31 can be suitably maintained with a top temperature of from about 140° to about 220° F., preferably about 190° F., and a bottom temperature of from about 220 to about 300° F., preferably about 270° F. at a gage pressure of from about 25 to 75 pounds per square inch, preferably 50 pounds per square inch. Top-cooling means 34 and bottom-heating means 35 aid in this fractionation. The "pentane" in line 32, which will contain both isopentane and normal pentane can be further fractionated in fractionator 36 to separate the isopentane from the normal pentane. Fractionator 36 can be maintained with a top temperature of about 140° F. to about 200° F., preferably about 175° F., and a bottom temperature of about 155° F. to about 215° F., preferably about 190° F., at a gage pressure of from about 25 pounds per square inch to about 75 pounds per square inch, preferably about 50 pounds per square inch.

Isopentane is a particularly valuable product for use in aviation motor fuel, due both to its high octane number and its volatility. Many aviation fuels, particularly those prepared by the catalytic production of "isooctane" from butane and butylenes are deficient in low-boiling high octane number hydrocarbons and require the addition of more volatile stocks in order to obtain a balanced fuel. Normal pentane on the other hand, while of sufficient volatility, does not possess the desirable high octane number characteristics so that we prefer to convert it by isomerization to the corresponding isomeric hydrocarbon. Accordingly, normal pentane is withdrawn from fractionator 36 by line 37 and can be discharged from the system by opening valve 47 in line 48 but preferably is directed through line 50 by opening valve 49 therein to line 42 which leads to an isomerization reactor. The isopentane passes overhead through line 43 and can be withdrawn through valved line 44 for use elsewhere, or by opening valve 45 in line 46 it can be directed for blending with the other products from our process as will be described later.

The heavier products from depentanizer 31 can be withdrawn by opening valve 38 in line 39 but preferably, since these too are of low octane number, they are directed to the isomerization reaction by opening valve 41 in line 40 which joins line 42. In the event that there was insufficient isopentane in the light naphtha cut in debutanizer 18 to warrant the separation thereof from the remaining hydrocarbons, the debutanized light naphtha from debutanizer 18 will be directed via line 28 to line 42 and thence to an isomerization reaction. Alternately, it is often undesirable or unnecessary to fractionate further the light naphtha from fractionator 11 and accordingly the entire fraction is directed to line 42 by opening valve 51 in line 52 which connects line 15 and line 42. By the proper manipulation of valves 17, 51, 29, 27, 41, 38, 49 and 47 it is possible to direct to the isomerization reaction a light naphtha which may be butane-free, pentane-free, isopentane-free, or may contain any or all of these constituents.

The light naphtha fraction from fractionator 11 as previously described passes from line 42 through coils 53 in heater 54 wherein the temperature of the naphtha is elevated to within the range of from about 100 to about 450° F. Hydrogen from any suitable source, and preferably from the aromatization reaction to be described later, enters through line 55 which joins the hydrocarbons in line 56 prior to reactor 57. The isomerization reaction is carried out under relatively high total pressures, for example, from about 250 to about 3000 pounds per square inch, preferably about 500 to about 1500 pounds per square inch. Of this total pressure, the partial pressure of hydrogen is from about 50 to about 2500 pounds per square inch, preferably about 400 to about 1000 pounds per square inch. The hydrogen need not be a pure product but may contain such impurities as methane, ethane, etc., in which case the total pressure can be somewhat higher than that specified above.

The heated hydrocarbons pass from coil 53 through line 56, together with hydrogen from line 55, to reactor 57. Catalyst from line 58 is added to the reactants and hydrogen halide from line 59 can be added to the reactor to promote the reaction. As catalysts I can employ an aluminum halide which can suitably be aluminum chloride or aluminum bromide in anhydrous form or can be the catalyst complex formed during the reaction or from a previous treatment of paraffinic, naphthenic or even olefinic hydrocarbons with aluminum chloride or aluminum bromide in the presence of a hydrogen halide. The aluminum chloride or bromide is preferably introduced into the reaction zone in the form of a slurry or in suspension in, for example, a portion of the feed stock to the reactor. The concentration of the catalyst can vary within rather wide limits depending primarily upon the temperature, reaction time and the catalyst activity. As hydrogen halides I can suitably use hydrogen chloride or hydrogen bromide, or I can employ organic chlorides such as ethyl chloride, propyl chloride or the corresponding bromides, etc., which under the conditions present will break down to yield hydrogen halides.

Isomerization reactor 57 can be maintained at the proper temperature by a jacket 60 about reactor 57 through which flows a heating medium from line 61, discharging through line 62. A stirrer 63 within the reactor is employed to produce the necessary intimate contact between

the catalyst and the reactants—an essential for obtaining the proper yield and optimum operating efficiency. Other means for obtaining intimate contact can be substituted, of course, such as for example jet injectors, turbo mixers, towers, etc.

The catalyst and reactants from isomerization reactor 57 pass by line 64 through cooler 65 (if desired) to separator 66 wherein the catalyst settles and separates from the hydrocarbons, hydrogen and hydrogen halide, and can be withdrawn through line 67. If spent for isomerization the catalyst can be discharged through line 68 by opening valve 69 therein. If, however, it is still active for isomerization, the catalyst can be recycled to reactor 57 by opening valve 70 in line 71 which joins line 58. By the proper manipulation of valves 69 and 70, a part of the catalyst can be continuously withdrawn and the remainder recycled to supplement the fresh catalyst entering through line 58.

The hydrocarbons pass from separator 66 via line 72 to high pressure separator 73 wherein the hydrogen and hydrogen chloride are released and pass overhead through line 74 whence they can be recycled to reactor 57 by opening valve 77 in line 78 which joins line 55 prior to pump 79 which forces the hydrogen, together with any hydrogen halide, into line 56 at the pressures desired for carrying out the reaction. Generally speaking, some hydrogen will be consumed in maintaining the catalyst activity, so that all of the exit hydrogen can be recycled, supplemented by hydrogen from an extraneous source, preferably excess hydrogen from the aromatization process. High pressure separator 73 can be maintained at a gage pressure of about 200 pounds per square inch and a temperature of from 60° F. to 120° F., preferably 100° F.

The isomerized hydrocarbons are withdrawn from high pressure separator 73 by line 80 and may be discharged from the system by opening valve 81 in line 82, whereby they can be utilized for blending with high octane number stocks of insufficent volatility or with low octane number stocks to increase the octane number thereof. They can also (and preferably for our process) be directed to fractionator 83 by opening valve 84 in line 85 which joins line 86 leading to fractionator 83.

The bottom stock from fractionator 11 having an initial of about 150 to 175° F. and an end point of about 300 to 400° F., is withdrawn through line 87 and can be withdrawn from the system for blending or for use as motor fuels by opening valve 88 in line 89. However, since this fraction is deficient in high octane number constituents as well as "light ends" it is desirable to convert these hydrocarbons to hydrocarbons of gasoline boiling range having an increased octane number. Accordingly the fraction can be directed to a catalytic reforming process by opening valve 90 in line 91 which joins line 92 leading to coils 93 in heater 94, and thence by valve 95 in line 96 to catalytic chamber 97. Simultaneously with the introduction of the hydrocarbon fraction, hydrogen from any suitable source can be introduced by line 98 and valve 99, and by opening valve 100 in line 101 is directed through coil 102 in heater 94, whence it joins line 96 via line 103. Alternately, hydrogen can be mixed directly with the fraction from fractionator 11 prior to heating by closing valve 100 in line 101 and opening valve 104 in line 105 which joins line 92. Since my process involves a catalytic reforming

process with dehydrogenation and aromatization of straight-chain hydrocarbons, there is not only no hydrogen consumption, although the process is carried out in an atmosphere of hydrogen, but actually a net gain in hydrogen. Accordingly, hydrogen from an extraneous source is necessary only when starting up the process, the hydrogen produced during the reaction being sufficient to supply the necessary hydrogen atmosphere by recycling. In fact, since there is a continual increase in hydrogen as the reaction continues, sufficient excess hydrogen is obtained to satisfy the isomerization reaction hydrogen requirements.

Since the reaction is a dehydrogenation and aromatization reaction rather than a hydrogenation reaction, it is markedly endothermic. The charge and hydrogen are generally heated to a temperature above the desired average temperature in the reaction catalyst chamber to supply the endothermic heat of reaction and this is necessarily true if an unheated reactor is used, the temperature differential depending upon the proper conditions, the apparatus, its size and design. To maintain more uniform temperature and to minimize any purely thermal conversion, the hydrogen can be heated to a higher temperature than the charge and then can, if desired, be injected at multiple points in the catalyst bed.

The catalyst chamber 97 as shown has catalyst tubes 106 connected with headers 107 and 108, the space between the tubes being heated to compensate for the endothermicity of the reaction and maintain the required temperature. This can be accomplished by passing hot flue gas or other heating medium in through duct 109 and out through duct 110. As illustrated, a stationary catalyst bed is employed, but this can, with equal suitability, be a moving bed reaction chamber or can employ powdered catalyst. Various designs and modification will occur readily to those skilled in the art, and I do not intend to be limited to this specific design.

As catalysts, I prefer the oxides of the metals of the left-hand column of group VI of the periodic table, particularly chromium, molybdenum and tungsten, but I can also use other metallic oxides and/or metallic compounds particularly oxides of the metals of the lefthand column of groups IV and V of the periodic table, such as titanium, cerium, thorium and vanadium. These catalytic oxides can be used alone or on various supports including magnesia and particularly alumina, especially an activated alumina or an alumina gel. Mixed catalyst can also be used, for example, a mixture of chromium oxide and molybdenum oxide alone or on an alumina support. Another catalyst which can be used is magnesium chromite, either alone or on a support such as the above-mentioned alumina. My catalysts can include any which promote the dehydrogenation and cyclization of aliphatic hydrocarbons.

The aromatization process can be carried out at temperatures of from about 875° to 1075° F., preferably about 890° F., and at gage pressures of from 30 to 450 pounds per square inch, preferably from about 50 to 300 pounds per square inch. Another important operating variable is the "time factor" which may be defined as the amount of time in hours required to put through the catalyst a volume of feed (measured as liquid) equal to the volume of the catalyst chamber, the volume of the catalyst chamber being the over-all volume of that portion of the chamber

which is filled with the catalyst. In other words, time factor is the volume of catalyst space divided by the feed rate in volume per hour. I have found that the time factor should be between 0.1 and 25 and preferably between 0.2 and 20 hours. It is important to keep the hydrogen concentration within definite, rather than low limits, and it should preferably be between 0.5 and 8 mols of hydrogen per mol of hydrocarbon fraction charged. Since by this process, dehydrogenation and cyclization rather than hydrogenation is the ultimate object and will be accomplished under the conditions hereinabove set forth, there will be a net gain of hydrogen by the process, so that complete recycle of all of the hydrogen from the process is neither desirable nor permissible. The process effected under the conditions set forth in this paragraph with a catalyst as set forth in the previous paragraph is called "hydroforming" and the term "hydroforming" as employed in the appended claims is hereby defined to mean this process.

The charge and hydrogen from catalyst reactor 97 pass through line 111 and cooler 112 to high pressure separator 113 from which the hydrogen (usually containing some light hydrocarbon gases) passes out through line 114. As was previously remarked, there will be a production of hydrogen during the catalytic reforming so that not all of it can be recycled to the catalytic reforming process. Accordingly, a part of it can be discarded by opening valve 115 in line 116 while the remainder is recycled by opening valve 117 in line 118 and valve 119 in line 120 which joins line 98. Valve 119 should be so adjusted that the mol ratio of hydrogen to feed stock is maintained within the limits of from 0.5 to 8. Rather than discard the hydrogen through line 116 it is preferable for our process that the hydrogen be directed through valve 121 in line 122 to line 55 which leads to the isomerization reactor. If desired, the hydrogen in line 122 can be purified in hydrogen purifier 123 (shown generally) prior to its use in the isomerization reaction but this is not ordinarily essential, since the presence of minor amounts of light hydrocarbon gas is not detrimental to the proper functioning of the isomerization reaction. Any surplus of hydrogen not required by the isomerization reaction can of course be discarded through line 116.

The catalytically reformed heavy naphtha is discharged from high pressure separator 113 by line 124 and can be withdrawn for blending with other products or for use as such by opening valve 125 in line 126. However, since this product is more or less deficient in the more volatile gasoline-range hydrocarbons, I prefer to direct it via line 127 through valve 128 to line 86 which leads to fractionator 83. If the isomate from the isomerization reaction has also been directed via line 85 to fractionator 83, the products of the two processes will be simultaneously fractionated, the butanes discarded overhead through line 129 while the "polymers" heavier than aviation gasoline or motor fuel are withdrawn through line 130. Fractionator 83 can be maintained with a top temperature of about 120° to about 170° F., preferably about 150° F., and a bottom temperature of about 500° to about 600° F., preferably about 550° F., and at a gage pressure of about 60 pounds per square inch to about 120 pounds per square inch, preferably about 100 pounds per square in. Top-cooling means 131 and bottom-heating means 132 can be used to assist in the fractionation. A fraction comprising hydrocar-

bons of aviation and motor fuel gasoline boiling range is withdrawn from fractionator 83 by line 133 and can be rerun by opening valve 134 in line 135 which leads to rerun tower 136. In rerun tower 136 a separation is made between products of a boiling range suitable for aviation gasoline and the heavier products which can be incorporated in motor fuel and which, generally speaking, are too heavy to be used in aviation gasoline except aviation "safety fuels." The aviation fuel is withdrawn overhead via line 137 and the motor fuel withdrawn via line 138. On the other hand it may be possible to utilize the combined products as such, and these can be withdrawn by opening valve 139 in line 133. In the event that isopentane was previously separated from the light fraction this can also be blended with the product from fractionator 83 via lines 46 and 141 which join line 133 and the blended product withdrawn through line 142. Isopentane can also be blended with the aviation fuel in line 137 from rerun tower 136, by diverting it through line 143 and valve 144. By regulating valves 145 and 144 in lines 141 and 143, respectively, a part can be directed to the aviation fuel and a part to the heavier blended fuel. Also, butane from line 25 can be blended with the products of de-isopentanization, aromatization and isomerization to increase the volatility of the final product by opening valve 24 in line 25 which joins line 142.

As a specific example of my process, I may separate a debutanized light virgin naphtha into two fractions, one having an end point of about 158° F. and the other an end point of about 350° F. The lighter fraction is contacted with an aluminum chloride-hydrocarbon complex catalyst prepared by the reaction of aluminum chloride on an aromatic-free light naphtha in the presence of hydrogen chloride. Hydrogen chloride is added to the light hydrocarbon fraction and catalyst, and the whole thoroughly intermingled by stirring at a temperature of 330° F. for about one hour, at a gage pressure of about 1000 pounds per square inch, a part of said pressure being supplied by hydrogen. Simultaneously the heavy fraction is contacted with a catalyst comprising molybdenum oxide on alumina at a pressure of 200 pounds per square inch and at a temperature of 980° F. with a time factor of 1.0 hour. The pressure is supplied in part by hydrogen. The products from both reactions, after the release of fixed gases, are commingled and fractionated to yield a hydrocarbon mixture of gasoline boiling range of high antiknock characteristics.

Although I have described my process as regards certain apparatus, for the sake of clarity and simplicity certain details have been omitted; for example, top-cooling coils in any or all of the fractionating towers can be replaced by supplying reflux to the towers from an outside source or by cooling and condensing the top products from the fractionator towers and returning a portion of them to act as reflux. Similarly, in place of the bottom-heating means in the fractionators, I can withdraw a portion of the heavy product, heat it to increase the temperature sufficiently, and return the heated products to the fractionator whereby heat is supplied to the products to be fractionated. Also, I have omitted certain details as regards pumps, heat exchangers, cooling means, pressure release valves, etc., all of which will occur readily to one skilled in the art and which would naturally be used in any commercial plant employing my process. Moreover, although I have illustrated my process as having only one

isomerization reactor and one aromatization reactor, it is contemplated that more than one reactor can be employed, either in series or in parallel, in either reaction whereby separate regeneration of the catalyst as well as increased capacity can be attained without a "shutdown."

It will be apparent from the above description that I have provided an improved process for the production of aviation gasoline from low octane-number naphthas, wherein the lighter constituents are catalytically isomerized to yield branched-chain hydrocarbons, and the heavier constituents which are isomerized only with difficulty or with low yields are catalytically aromatized to yield maximum quantities of high octane-number gasoline-range fuels. Either of these products is suitable for blending with other stocks to increase the octane number and also to supply certain deficiencies in boiling range and/or volatility; together, the two products yield a high octane number balanced fuel of good lead response and of suitable boiling range and volatility. Moreover, by the combination of these processes, we can eliminate the necessity of an outside hydrogen supply after the system comes to equilibrium, since under the conditions set forth, the aromatization process not only supplies sufficient hydrogen for carrying out the dehydrogenation-cyclization reaction, but sufficient excess hydrogen is available to supply the isomerization reaction, making the entire process an integrated and self-sufficient one.

My process is also advantageous in that little or no "diluent" is charged to the isomerization process, particularly if the isopentane is eliminated from the light hydrocarbons. It has been found that an equilibrium between the converted isomeric hydrocarbons and unconverted straight-chain hydrocarbons is set up during catalytic isomerization, the conditions of operation and the catalyst determining this to a large extent. However, if isoparaffinic hydrocarbons are charged to the isomerization reactor, the amount of isomerization of straight-chain hydrocarbons is decreased in direct proportion to the amount of isoparaffinic hydrocarbons originally present. Consequently, if the isopentane is fractionated from the light naphtha cut, this valuable hydrocarbon can be used in the blending of aviation or motor fuels, while an equivalent amount of normal pentane can be converted to isopentane.

By my process, I can efficiently convert lower-boiling straight-chain hydrocarbons to the more desirable branched-chain hydrocarbons with optimum yield and long catalyst life, and convert higher boiling straight-chain hydrocarbons to high antiknock aromatics, which, when fractionated simultaneously, yield a high antiknock gasoline of suitable boiling range and volatility.

Although I have described my invention in relation to certain embodiments thereof, it should be understood that this is by way of illustration and not a limitation thereon, my invention being limited only as set forth in the appended claims.

I claim:

1. A process for the production of high octane number gasoline from a hydrocarbon fraction having a boiling range of from about 30° F. to 350° F. and containing a substantial amount of open-chain paraffinic hydrocarbons, which comprises separating said hydrocarbon fraction into a fraction rich in hydrocarbons having four carbon atoms per molecule, a fraction rich in isopentane, an isopentane-free fraction having an end point from about 150° to about 175° F. and a fraction having an initial boiling point from about 150° to 175° F. and an end point of about 350° F., contacting said isopentane-free fraction having an end point from about 150° to about 175° F. with an isomerization catalyst in the presence of hydrogen under conditions adapted to convert a substantial part of the paraffinic hydrocarbons contained therein to branched-chain paraffinic hydrocarbons with consumption of hydrogen, contacting said fraction having an initial boiling point from about 150° to about 175° F. with a catalyst adapted to promote the conversion of the open-chain hydrocarbons contained therein to aromatic hydrocarbons with the production of hydrogen, at a temperature of from about 875° to about 1075° F., a pressure of from about 30 to about 450 pounds per square inch and a time factor of from about 0.1 to about 25 hours in the presence of from about 0.5 to 8 mols of hydrogen per mol of said fraction having an initial boiling point of about 150° to about 175° F., separating said hydrogen from said aromatic hydrocarbons, directing at least a substantial portion of said hydrogen in amounts necessary to supply the hydrogen consumed therein to said contacting step for the conversion of straight-chain hydrocarbons to branched-chain hydrocarbons, blending said isopentane-rich fraction, said branched-chain paraffinic hydrocarbons and said aromatic hydrocarbons, and increasing the volatility of said blended hydrocarbons by adding at least a portion of said fraction rich in hydrocarbons having four carbon atoms per molecule.

2. A process according to claim 1 wherein said conversion of paraffinic hydrocarbons to branched-chain hydrocarbons is carried out in the presence of an aluminum halide catalyst selected from the group consisting of aluminum chloride, aluminum bromide, an aluminum chloride-hydrocarbon complex formed by the reaction of anhydrous aluminum chloride with a hydrocarbon in the presence of a hydrogen halide and an aluminum bromide-hydrocarbon complex formed by the reaction of anhydrous aluminum bromide with a hydrocarbon in the presence of a hydrogen halide.

3. A process for the production of high antiknock rating gasoline of balanced volatility from a hydrocarbon charging stock which contains a substantial amount of open chain paraffinic hydrocarbons which is substantially free from olefins and which boils within the naphtha boiling range, which process comprises obtaining from said charging stock a first fraction consisting essentially of butanes, a second fraction rich in isopentane, a third fraction higher boiling than isopentane and having an end point in the general vicinity of about 150° to 175° F. and a fourth fraction higher boiling than the third fraction and having an initial boiling point within the general vicinity of 150° to 175° F., contacting said third fraction with an isomerization catalyst under conditions for effecting substantial isomerization for the conversion of paraffinic hydrocarbons contained therein to paraffinic hydrocarbons of more highly branched-chain structure, contacting said fourth fraction with an aromatizing catalyst to produce aromatization products at a temperature within the approximate range of 875° to 1075° F., at a pressure within the approximate range of 30 to 450 pounds per square inch with a time factor of from about .1 to about 25 hours in the presence of about .5 to 8 mols of hydrogen per mol of hydrocarbons in said

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fourth fraction, separating hydrogen from the aromatization products and recycling at least a substantial portion of said hydrogen to said aromatizing catalyst contacting step, recovering a fraction rich in aromatics from the aromatization products, recovering a highly branched-chain paraffinic fraction from the products of the isomerization catalyst contacting step and blending at least a portion of each of said last-named two fractions with at least a portion of said fraction rich in isopentane and said fraction rich in isobutanes to produce a gasoline of balanced volatility and of high antiknock rating.

4. A process for the production of high antiknock rating gasoline of balanced volatility from a hydrocarbon charging stock which contains a substantial amount of open-chain paraffinic hydrocarbons, which is substantially free from olefins and which boils within the naphtha boiling range, which process comprises fractionating said charging stock to obtain a first low boiling fraction, a second intermediate boiling fraction having an end point in the general vicinity of about 150° to about 175° F. and a third high boiling fraction having an initial boiling point above 150° F., hydroforming said third fraction to produce higher octane number hydrocarbons along with a net production of hydrogen, isomerizing the second fraction with a halide isomerization catalyst under conditions for effecting substantial conversion of paraffinic hydrocarbons contained therein to paraffinic hydrocarbons of more highly branched-chain structure, effecting said isomerization in the presence of added hydrogen at superatmospheric pressure whereby isomerization catalyst activity is maintained with a net consumption of hydrogen, recovering a fraction rich in aromatics from the hydroforming step, recovering a lower boiling branched-chain paraffin

fraction from the products of the isomerization step and blending at least a portion of each of said last-named fractions with at least a portion of said low boiling fraction to produce a gasoline of balanced volatility and of high antiknock rating.

5. The process of claim 4 which includes the step of purifying at least a part of the hydrogen produced in the hydroforming step and employing hydrogen thus purified in said isomerization step.

6. In a process for the production of high antiknock rating gasoline of balanced volatility from a hydrocarbon charging stock which contains a substantial amount of open-chain paraffinic hydrocarbons, which is substantially free from olefins and which boils within the naphtha boiling range, which process comprises hydroforming a higher boiling fraction of said charging stock, isomerizing an intermediate boiling fraction of said charging stock and subsequently blending at least a portion of the products of the hydroforming and isomerization steps respectively with lower boiling hydrocarbons to produce a gasoline of balanced volatility and of high antiknock rating, the improved method of operation which comprises initially fractionating said charging stock to remove lower boiling hydrocarbons therefrom and to effect a cut point between an intermediate boiling fraction charged to isomerization and a higher boiling fraction charged to hydroforming in the general vicinity of about 150° to 175° F. whereby both heptanes and heavier hydrocarbons are substantially excluded from the isomerization step while methyl pentanes are excluded from the hydroforming step and converted into more highly branched-chain structure in the isomerization step.

ROBERT M. CORNFORTH.