July 26, 1960 D. L. MUFFAT ET AL 2,946,736

COMBINATION PROCESS FOR HIGH-OCTANE NAPHTHA PRODUCTION

Filed March 29, 1957 3 Sheets-Sheet 1

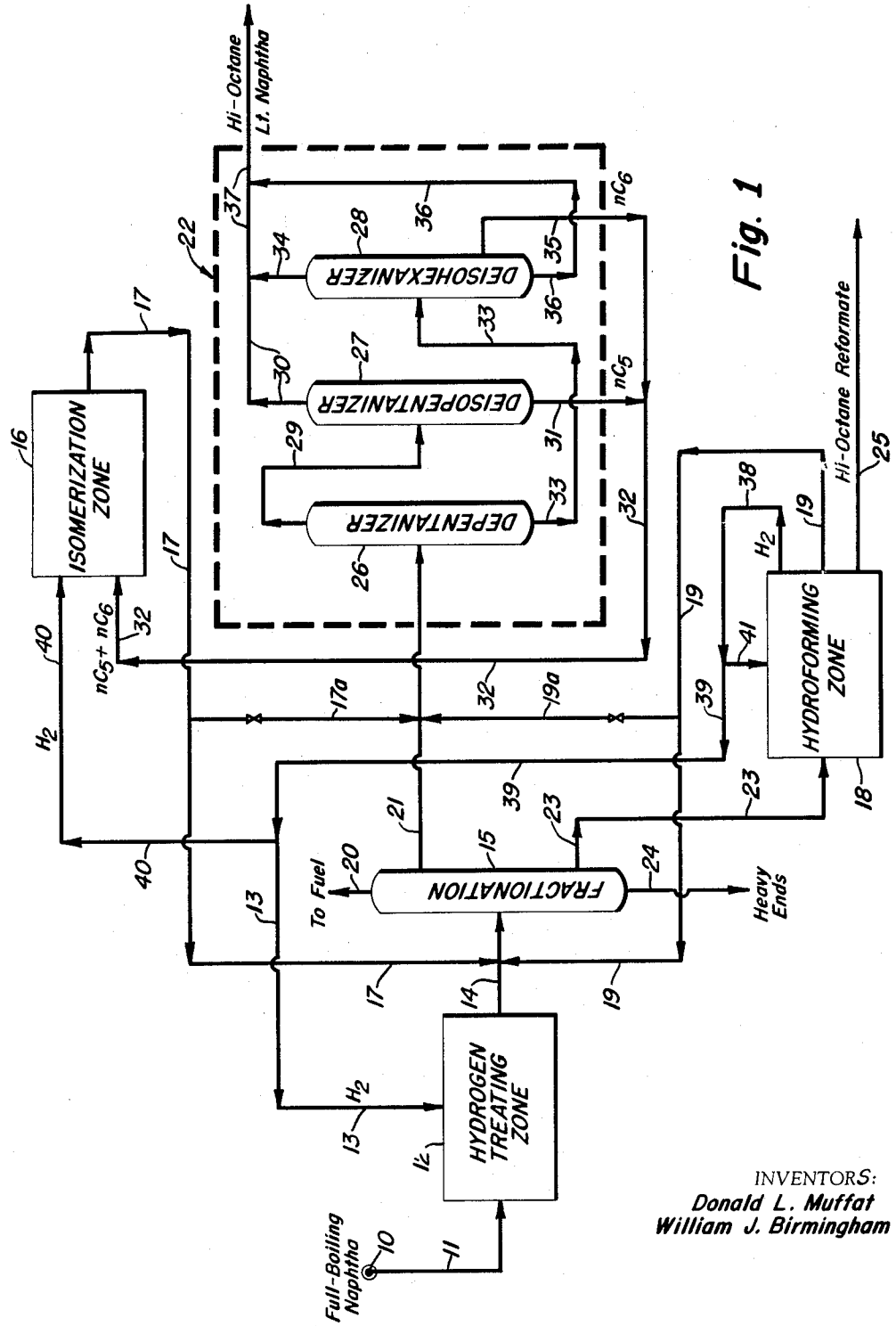


Fig. 1

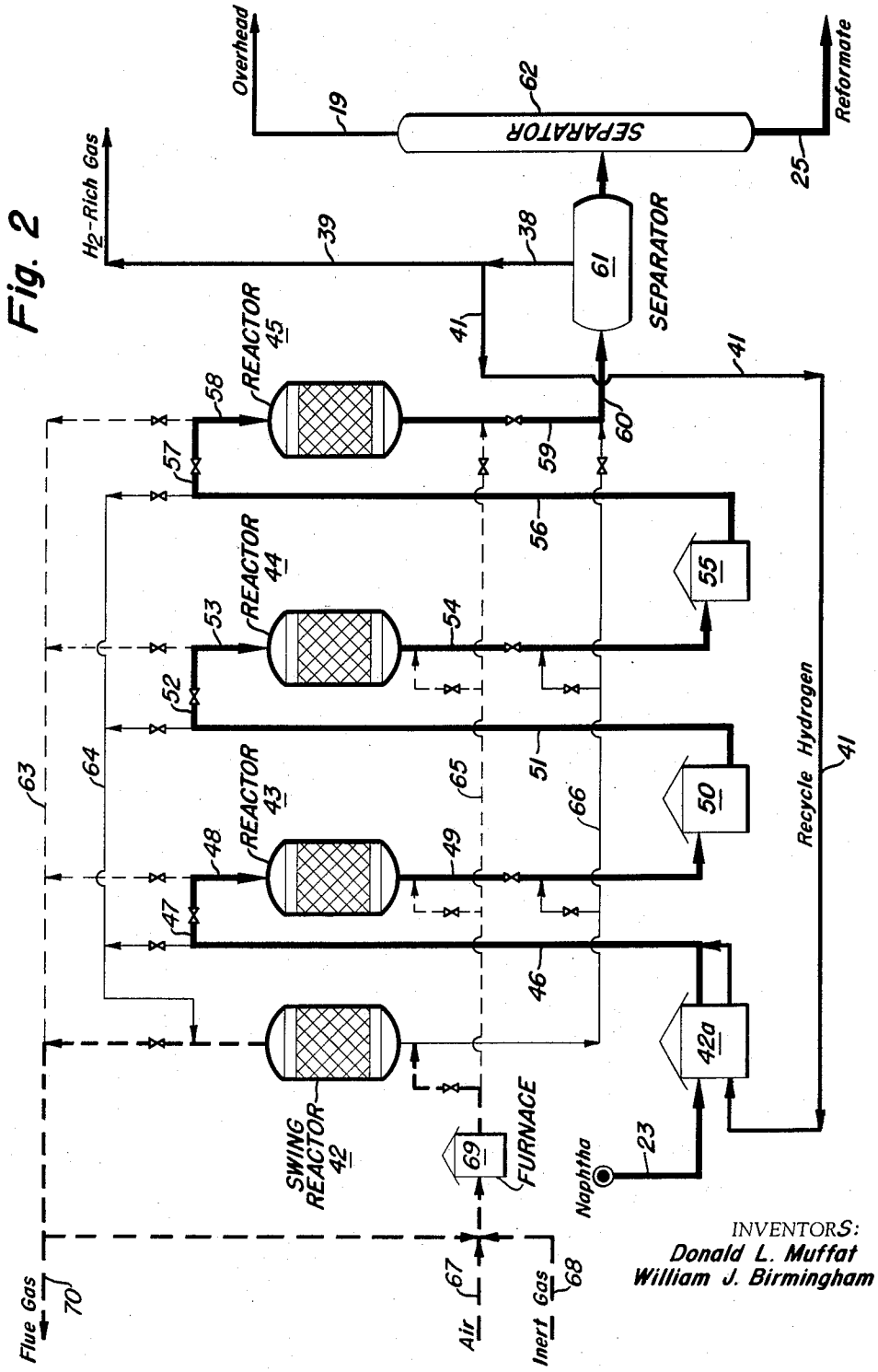
INVENTORS:
Donald L. Muffat
William J. Birmingham

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Filed March 29, 1957 3 Sheets-Sheet 2

Fig. 2



INVENTORS:
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William J. Birmingham

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Filed March 29, 1957 3 Sheets-Sheet 3

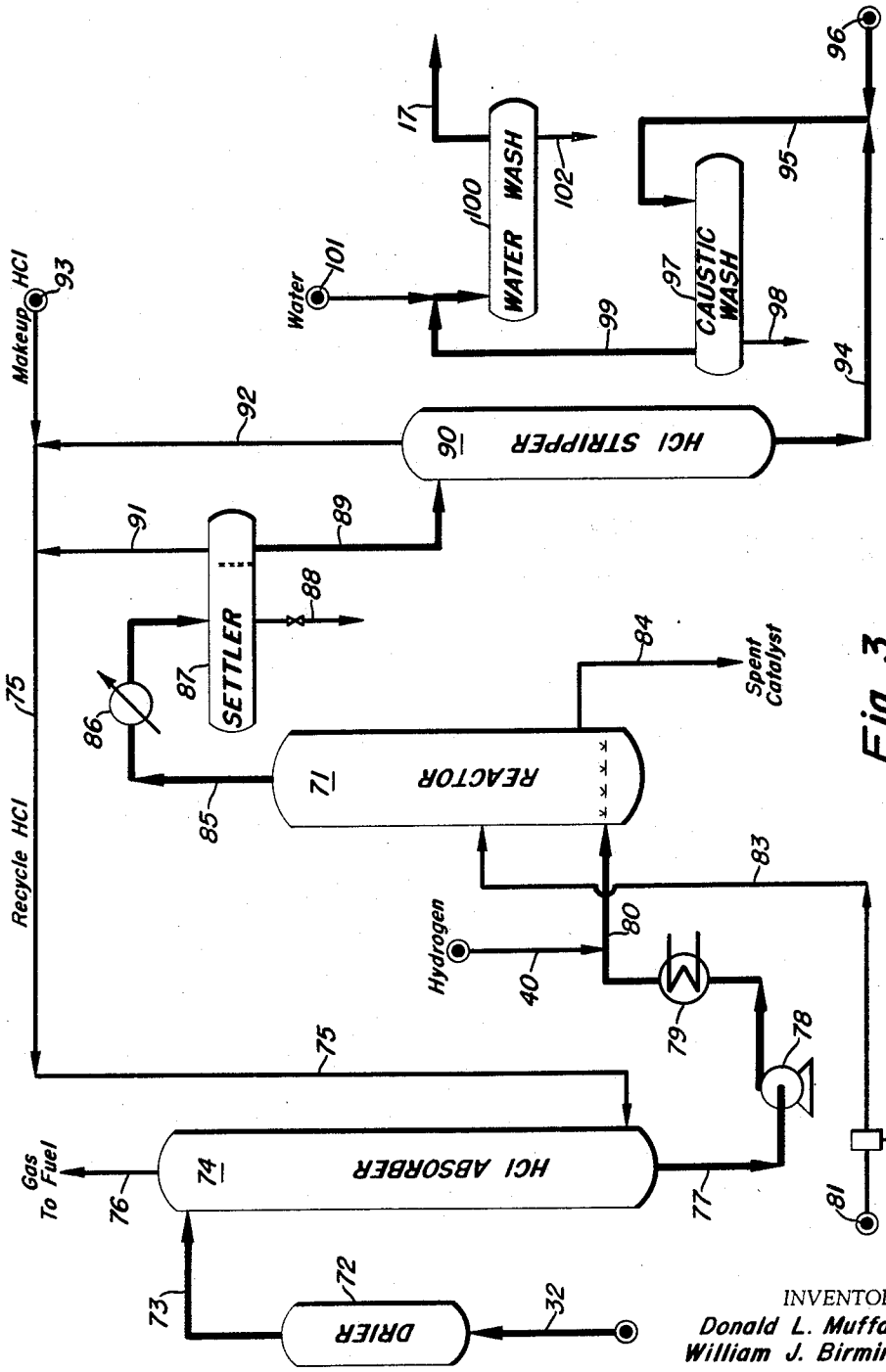


Fig. 3

INVENTORS:
Donald L. Muffat
William J. Birmingham

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COMBINATION PROCESS FOR HIGH-OCTANE NAPHTHA PRODUCTION

Donald L. Muffat, Lansing, and William J. Birmingham, Chicago, Ill., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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8 Claims. (Cl. 208—65)

This invention relates to a combination process for production of high-octane hydrocarbon fuels and more particularly to an integrated hydroforming-isomerization-separation process for preparing high-octane naphtha base stocks.

Since World War II octane number of motor fuel and aviation gasoline has risen at an accelerated rate along with the increase in compression ratios of piston-type internal combustion engines. To meet the continuing demand for higher octane gasoline, refiners have depended to a large measure on various catalytic reforming processes employing supported-platinum catalyst. To meet still further increases in octane number and to increase the proportion of premium grade fuels, measures in addition to hydroforming are becoming necessary. To obtain such improvement via the incremental hydroforming route would necessitate increased reforming intensities and charging a higher percentage of total available naphtha. Increased reforming intensities involve severe yield penalties. Charging a higher percentage of available naphtha requires use of marginal lighter stocks from which the octane improvement is limited and substantially more costly.

Isomerization of light naphtha, particularly C_5's and C_6's, instead of incremental hydroforming, is one particularly advantageous method of obtaining additional octane improvement. It is less costly than incremental hydroforming. It upgrades the available naphtha which is considered the poorest from a hydroforming standpoint. It provides a high-octane blending stock which has a lead susceptibility, i.e., octane response to tetraethyl lead, and octane blending characteristics which are far superior to those of hydroformate. Furthermore, isomers of C_5 and C_6 hydrocarbons have a desirable low Reid Vapor Pressure, and yet a desirable high percentage of low-boiling hydrocarbons, resulting in improved volatility characteristics.

It is an object of the present invention to provide an economic combination of hydroforming and isomerization which will produce high-octane base stocks of superior lead susceptibility, octane blending characteristics, and volatility. It is another object to provide a combination hydroforming-isomerization process which will maximize ceiling octane potential. A further object is to separate hydrocarbon naphtha fractions selectively to provide optimum hydroforming and isomerization charge stocks for octane improvement with maximum yields. A still further object is to integrate hydroforming and isomerization so as to optimize the yield-octane relationship with a minimum of process equipment and operating costs. These and other objects of our invention will become apparent as the detailed description thereof proceeds.

For maximum octane potential and optimum octane-yield relationship from a combination of hydroforming and isomerization we have discovered that there are a number of requirements. For example, when upgrading full-boiling range naphthas, heavy hydrocarbons i.e., hydrocarbons boiling above about 180° F., should be hydroformed, and normal pentane and hexane in lighter hydrocarbons, i.e., hydrocarbons boiling below about 180° F., should be separated and isomerized. Normal pentane and hexane produced in the hydroforming operation should be also separated and charged to isomerization. High octane isomers, e.g., isopentane, neohexane and diisopropyl, already present in the lighter fraction, should be removed before isomerization to maximize subsequent conversion of normal pentane and normal hexane. Naphthenes, e.g., cyclopentane, methylcyclopentane, and cyclohexane, already present in the lighter fraction, should also be removed from isomerization charge because these hydrocarbons already have high octane ratings and a substantial portion thereof would be cracked to gas during isomerization. Unconverted normal pentane and normal hexane in isomerization product should be separated and recycled so as to obtain substantially 100 percent conversion. Furthermore, heavier hydrocarbons boiling above about 180° F. in product from isomerization, which contain substantial naphthenic material, should be separated and further upgraded by hydroforming.

While we have found such selectivity in feed stock preparation to have very substantial advantages, the attendant separation problems are manifest. We have also discovered, however, an integrated hydroforming-isomerization-separation combination which achieves this selectivity and other objects of this invention with substantially no more separation equipment than would be associated with recycle isomerization alone. In accordance with one embodiment of our invention we economically produce high-octane naphtha base stocks from hydrocarbons boiling below about 400° F. by the method which comprises separating the hydrocarbons into at least a fraction rich in hydrocarbons boiling above about 180° F. and a fraction rich in hydrocarbon boiling below about 180° F., charging said fraction rich in hydrocarbons boiling above about 180° F. to a hydroforming zone in the presence of a hydroforming catalyst and under hydroforming conditions adapted to produce a reformate product of higher octane with a net production of hydrogen and additional hydrocarbons boiling below about 180° F., recycling a portion of said hydrogen to said hydroforming zone, charging hydrocarbons boiling below about 180° F., including the additional hydrocarbons produced in the hydroforming zone, to a separation zone wherein at least a substantial portion of normal pentane and normal hexane in the hydrocarbons boiling below about 180° F. are separated therefrom, charging the separated normal pentane and normal hexane to an isomerization zone in the presence of an isomerization catalyst and at least a portion of the remaining hydrogen produced in said hydroforming zone and under isomerizing conditions adapted to convert at least a substantial portion of said normal pentane and normal hexane to isomers thereof, and charging hydrocarbon effluent from said isomerization zone to said separation zone. The high octane products from this embodiment comprise said reformate product and isomers of C_5 and C_6 (e.g., isopentane, methylpentanes, neohexane, diisopropyl) and other high-octane components (e.g., cyclopentane, methylcyclopentane, cyclohexane, and heavier) from the separation zone.

In another embodiment of our invention we produce high-octane naphthas by the method which comprises charging substantially olefin-free naphtha to a fractionation zone wherein hydrocarbons are separated into at least a first fraction containing hydrocarbons boiling below about 400° F. and above about 180° F., and a second fraction containing hydrocarbons boiling below about 180° F. and above about 40° F., charging said

first fraction to a hydroforming zone in the presence of a hydroforming catalyst and under hydroforming conditions adapted to produce a reformate product of higher octane with a net production of hydrogen and additional hydrocarbons boiling below about 180° F., recycling a portion of said hydrogen to said hydroforming zone, charging said additional hydrocarbons boiling below about 180° F. produced in said hydroforming zone to said fractionation zone, charging said second fraction to a separation zone wherein at least a substantial portion of normal pentane and normal hexane in said second fraction are separated therefrom, charging the separated normal pentane and normal hexane to an isomerization zone in the presence of an isomerization catalyst and at least a portion of the remaining hydrogen produced in said hydroforming zone and under isomerizing conditions adapted to convert at least a substantial portion of said normal pentane and normal hexane to isomers thereof, and charging the hydrocarbon product from said isomerization zone to said fractionation zone. This embodiment permits separation in a single vessel of hydrocarbons boiling below about 40° F. from fresh charge stock and from the products of the hydroforming and isomerization zones. Principal products comprise said reformate product from the hydroforming zone and C_5—C_6 isomers and high octane light naphthenes (cyclopentane, and methylcyclopentane and cyclohexane) from the separation zone. These streams may be blended with each other to form a single high-octane base stock, or, preferably, used separately for selective blending.

Advantageous process equipment employed in our separation zone comprises fractionating facilities for separating normal pentane and isopentane from remaining hydrocarbons, fractionating facilities for separating normal pentane from isopentane, and fractionating facilities for separating normal hexane from said remaining hydrocarbons. Alternatively, the equipment may comprise fractionating facilities for separating normal hexane from remaining hydrocarbons, fractionating facilities for separating normal pentane and isopentane from said remaining hydrocarbons, and fractionating facilities for separating normal pentane from isopentane. The particular sequence or method is not critical so long as normal pentane and normal hexane are segregated for isomerization. The zone may, of course, include debutanization facilities, although such facilities are usually not required or desired. It is readily apparent, however, that the combination of the present invention requires no more separation equipment than a recycle isomerization unit alone.

Processes for use in our hydroforming zone and isomerization zone may comprise any of the prior art. The method of the present invention, however, is most advantageously employed with platinum catalyst hydroforming processes. In such processes the catalyst usually consists essentially of alumina, 0.05 to 1 percent by weight of platinum, and 0.1 to 2 percent by weight of a halogen, based on dry Al_2O_3. Hydroforming conditions are a temperature in the range of about 800 to 1050° F., a pressure in the range of about 100 to 1000 pounds per square inch gage, a space velocity of about 0.5 to 10 pounds of hydrocarbon charge per hour per pound of catalyst, and a hydrogen rate in the range of about 1000 to 10,000 standard cubic feet per barrel of hydrocarbon charge.

A preferred form of platinum catalyst process for use in the combination of the present invention is Ultraforming (Petroleum Engineer, vol. XXVI, No. 4, April 1954, at page C–35). Ultraforming operates at low pressure, i.e., a pressure in the range of about 100 to 400 pounds per square inch gage, e.g., 300 pounds per square inch gage, a temperature in the range of about 850 to 1000° F.; a weight-hourly space velocity of about 0.5 to 5, and a hydrogen rate in the range of about 3,000 to 8,000 standard cubic feet per barrel.

With respect to the isomerization zone any process capable of substantial conversion of normal pentane and normal hexane to branched-chain paraffins may be used, including processes employing noble metal catalyst, e.g., supported-platinum, supported-ruthenium, and the like. Usually a low temperature process is preferred so as to minimize the amount of recycling required. Low temperature shifts the equilibrium in favor of greater isomerization. Because the present invention embodies recycling, however, isomerization processes operating at relatively high temperatures may also be used.

A particularly advantageous process for use in the isomerization zone in the Isomate Process (World Petroleum, vol. 27, No. 8, July 15, 1956, at page 68), which features both low temperature and a very active catalyst. The isomate process utilizes 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. Preferred catalyst is an aluminum-chloride-hydrocarbon complex. The process operates at a temperature in the range of about 100 to 350° F., preferably about 150 to 300° F., a pressure in the range of about 500 to 1000 pounds per square inch gage, preferably about 600 to 900 pounds per square inch gage, a space velocity in the range of about 0.1 to 10 pounds of hydrocarbon charge per hour per pound of catalyst, preferably about 0.5 to 5 pounds per hour per pound, and a hydrogen addition rate in the range of about 20 to 200 standard cubic feet of hydrogen per barrel of hydrocarbon charge, preferably about 50 to 150 standard cubic feet per barrel.

Hydrocarbons to be up-graded by the method of the present invention are preferably hydrogen treated beforehand in the presence of a hydrogenation catalyst to saturate any olefins and reduce sulfur and nitrogen content. When hydrogen-treating facilities are provided, thermal, cokestill, and/or cat-cracked naphthas as well as virgin naphthas may be treated by the method of the present invention. Hydrogen for such treatment is preferably obtained from the excess hydrogen produced in the hydroforming zone. Examples of hydrogenation catalyst include bauxite, fuller's earth, group VI metal oxides on alumina such as chromia-on-alumina, group V and VI metal oxide mixtures on alumina such as nickel tungstate, cobalt molybdate or even a platinum-on-alumina catalyst. Alumina-supported cobalt-molybdate catalyst is preferred. Conditions for hydrogenation may preferably be a temperature in the range of about 600 to 850° F., a pressure in the range of about 100 to 1200 pounds per square inch gage, a space velocity in the range of about 1 to 20 liquid volumes of said hydrocarbon streams per volume of catalyst. Hydrogen requirements depend on the degree of unsaturation, sulfur and nitrogen contents, and the like.

In a preferred embodiment of our invention we upgrade hydrocarbon naphthas by the method which comprises charging said hydrocarbon naphthas to a hydrogenation zone in the presence of hydrogen and a hydrogenation catalyst and under hydrogenation conditions adapted to saturate olefins and to hydrogenate sulfur, sulfur compounds, and nitrogen compounds, charging the hydrocarbon effluent from said hydrogenation zone to a fractionation zone wherein hydrocarbons are separated into at least a first fraction containing any hydrocarbons boiling substantially above about 400° F., a second fraction boiling below about 400° F. and above about 180° F., a third fraction boiling below about 180° F. and above about 40° F., and a fourth fraction boiling below about 40° F., charging said second fraction to a hydroforming zone in the presence of an alumina-

supported platinum catalyst at a temperature in the range of about 850 to 1000° F., a pressure in the range of about 100 to 1000 pounds per square inch gage, a space velocity in the range of about 0.5 to 10 pounds of hydrocarbon charge per hour per pound of catalyst, and a hydrogen rate in the range of about 1000 to 10,000 standard cubic feet per barrel of hydrocarbon charge, whereby a reformate product of higher octane is produced with a net production of hydrogen and additional hydrocarbons boiling below about 180° F., withdrawing as a product said reformate, recycling a portion of said hydrogen to said hydroforming zone, directing another portion of said hydrogen to said hydrogenation zone, charging said additional hydrocarbons boiling below about 180° F. to said fractionation zone, charging said third fraction to a separation zone wherein at least a substantial portion of normal pentane and normal hexane in said third fraction is separated therefrom, withdrawing as a product from said separation zone the remaining hydrocarbons boiling below about 180° F., charging the separated normal pentane and normal hexane to an isomerization zone in the presence of an aluminum chloride-hydrocarbon complex catalyst, formed by the reaction of anhydrous aluminum chloride with a hydrocarbon in the presence of hydrogen chloride, at a temperature in the range of about 100 to 300° F., a pressure in the range of about 500 to 1000 pounds per square inch gage, a space velocity in the range of about 0.1 to 10 pounds of hydrocarbon charge per hour per pound of catalyst, and a hydrogen addition rate, from said hydroforming zone to said isomerization zone, of about 20 to 200 standard cubic feet of hydrogen per barrel of hydrocarbon charge, whereby at least a substantial portion of said normal pentane and normal hexane is converted to isomers thereof, and charging the hydrocarbon effluent from said isomerization zone to said fractionation zone.

The invention will be more clearly understood from the following detailed description read in conjunction with the accompanying drawings which form a part of this specification and in which:

Figure 1 is a schematic flow diagram showing a preferred embodiment which includes hydrogen treating and a common fractionation zone for separating C_1—C_4 hydrocarbons from fresh charge and from the products of the isomerization zone and the hydroforming zone,

Figure 2 is a schematic flow diagram of the ultraforming process, which is the preferred process for use in the hydroforming zone of Figure 1, and

Figure 3 is a schematic flow diagram of the isomate process, which is the preferred process for use in the isomerization zone of Figure 1.

The feed stock in this embodiment is typically a Mid-continent naphtha containing about .03 percent by weight of sulfur and having an ASTM end-point in the range of about 400–450° F. It consists chiefly of paraffins and naphthenes, naphthene content being in the range of about 30–50%. Such a charge stock may have a F–1 octane number of about 40–50. It may also contain cracked materials, e.g., thermal, cokestill and/or catcracked naphtha, in which event hydrogen pretreating is necessary to saturate olefins and reduce sulfur and nitrogen content.

Referring to Figure 1, such a full-boiling naphtha from source **10** is charged via line **11** to hydrogen treating zone **12**. In hydrogen treating zone **12** olefins are saturated, and sulfur, sulfur compounds, and nitrogen compounds are hydrogenated in the presence of a hydrogenation catalyst, e.g., alumina-supported cobalt molybdate, at a temperature in the range of about 600–850° F., a pressure in the range of about 100–1200 pounds per square inch gage, a volumetric space velocity in the range of about 1 to 20, and in the presence of hydrogen introduced from line **13**. Stripping facilities (not shown) are preferably employed to remove the hydrogenated sulfur and nitrogen compounds, for which purpose hydrogen from line **13** may also be used. Effluent from hydrogen treating zone **12** is charged via line **14** to fractionation zone **15**, along with effluent from isomerization zone **16**, which is charged to fractionation zone via line **17**, and light hydrocarbons boiling below about 180° F. from hydroforming zone **18**, which are charged via line **19**. While lines **17** and **19** are shown as intersecting line **14**, it should be understood that line **17** and **19** may, alternatively, enter fractionation zone **15** separately.

In fractionation zone **15** light hydrocarbons, primarily C_1—C_4 hydrocarbons boiling below about 40° F., are removed overhead via line **20** as fuel or for other purposes, e.g., alkylation, vapor pressure control, and the like. Heavy hydrocarbons, if any, e.g., hydrocarbon boiling above about 400° F., are removed from fractionation zone **15** via line **24**. Hydrocarbons boiling in the range of about 40 to 180° F., i.e., isopentane, normal pentane, cyclopentane, neohexane, diisopropyl, methyl pentanes, normal hexane, methylcyclopentane and cyclohexane, are removed from fractionation zone **15** via line **21** and charged to separation zone **22**. Hydrocarbons boiling in the range of about 180 to 400° F. are withdrawn from fractionation zone **15** via line **23** and charged to hydroforming zone **18** for octane improvement. Hydroforming zone **18** is preferably a platinum catalyst reforming process of the low-pressure type, e.g., ultraforming, which will be described in Figure 2 in greater detail. It should be understood that in the case of other reforming processes which are end-point sensitive, or where product specifications limit end-point of reformate product, the width of the fraction, i.e., the end-point, leaving fractionation zone **15** via line **23** may be tailored accordingly. Thus, the fraction may be, for example, 180 to 360° F., and hydrocarbons boiling above about 360° F., if any, would then be removed via line **24**. It should also be understood that hydroforming zone **18** may also include extraction facilities and/or fractionation facilities for recycling operations.

The cut-point of about 180° F. in fractionation zone **15** removes, for example, cyclohexane from reformer charge. This is usually preferred because the effective or "blended" research octane number of cyclohexane may be higher than that of benzene, to which cyclohexane would be converted with some shrinkage in hydroforming zone **18**. The blending octane of any particular hydrocarbon depends in part, of course, on the nature of the base stock into which it is blended. In some blends the "blended" octane of cyclohexane may be lower than that of benzene, just as the "unblended" octane is lower. In such cases, or in the case of petrochemical manufacture, it may be desirable to include cyclohexane in charge to hydroforming zone **18**. In this event fractionation zone **15** is adjusted so that hydrocarbons boiling in the range of about 170 to 400° F., rather than 180 to 400° F., are charged to hydroforming zone **18**. Likewise, only hydrocarbons boiling below 170° F. would be returned via line **19**, and such operation should be considered within the scope of the present invention. In no case should the cut points be lowered to the point where any substantial amount of the normal hexane is charged to hydroforming zone **18**.

Effluent from hydroforming zone **18** comprises high-octane reformate boiling above about 180° F., which is removed via line **25** and is one of the high-octane base stocks forming a product of the present invention. This high-octane product may be further up-graded, of course, by additional processing, e.g., thermal reforming, or may be extracted and/or fractionated for petrochemical manufacture, e.g., aromatics production. Light hydrocarbons, i.e., hydrocarbons boiling below about 180° F., which were produced in hydroforming zone **18**, are removed via line **19** and charged to fractionation zone **15** via line **14**. While all hydrocarbons boiling below about 180° F. are shown as leaving hydroforming zone **18** via line **19**, it should be understood that the method of the pres-

ent invention requires that only hydrocarbons boiling in the range of about 40 to 180° F. be removed and charged to separation zone 22, preferably via fractionation zone 15. If hydroforming zone 18 contains stabilization facilities for removing C_1—C_4 hydrocarbons, a 40 to 180° F. fraction may be charged directly via lines 19, 19*a*, and 21 to separation zone 22, thereby by-passing fractionation zone 15. Likewise, if separation zone 22 contains stabilization facilities for removing butane and lighter hydrocarbons, all hydrocarbons boiling below about 180° F. from hydroforming zone 18 may be charged directly via line 19, 19*a*, and 21 to separation zone 22.

Separation zone 22 comprises facilities for removing normal pentane and normal hexane from the total charge entering separation zone 22 via line 21. This charge contains hydrocarbons boiling in the range of about 40 to 180° F. separated from other hydrocarbons in fractionation zone 15 and may also include stabilized light hydrocarbons from hydroforming zone 18 charged directly via line 19 and 19*a* and/or stabilized product from isomerization zone 16 charged directly via lines 17 and 17*a*. The usual and, in the case of isomerization zone effluent, preferred operation, however, is to charge these materials via fractionation zone 15.

In Figure 1 separation zone 22 comprises depentanizer 26, deisopentanizer 27, and deisohexanizer 28. Isopentane and normal pentane are separated from the remaining heavier hydrocarbons in depentanizer 26 and are charged via overhead line 29 to deisopentanizer 27. Here, isopentane is removed as an overhead product via line 30, and normal pentane is removed as bottoms via line 31 and charged via line 32 to isomerization zone 16. Bottoms from depentanizer 26 are charged via line 33 to deisohexanizer 28. In deisohexanizer 28 hydrocarbons boiling below about 150° F., i.e., cyclopentane, neohexane, diisopropyl and methylpentanes (2-methyl pentane and 4-methyl pentane) are removed overhead via line 34. Material boiling in the range of about 150–160° F., i.e., normal hexane, is removed via line 35 and charged to isomerization zone 16 via line 32. For maximum octane, it may sometimes be desirable to charge methylpentanes, along with the normal hexane, to isomerization, in which event hydrocarbons boiling below about 140° F. are removed overhead via line 34, and hydrocarbons boiling in the range of about 140 to 160° F. are charged via lines 35 and 32 to isomerization zone 16. Material boiling above about 160° F., primarily methylcyclopentane and cyclohexane is removed via line 36 and may be combined with other high-octane product components in line 37. If particular feed stocks from source 10 contain essentially no methylcyclopentane and cyclohexane, and if Isomate product and material boiling below 180° F. from hydroforming zone 18 are charged to separation zone 22 via fractionation zone 15, there may be little incentive to separate out a bottoms fraction in diisohexanizer 28. In such case, all material boiling above about 150° F. (or, alternatively, 140° F.) from separation zone 22 may be charged via line 32 to isomerization zone 16.

While separation zone 22 is shown in this embodiment as hereinabove described, it should be understood that alternative arrangements, requiring substantially no more process equipment, are possible. Thus, feed from line 21 to separation zone 22 could be charged directly to deisohexanizer 28, from which the product fractions would be the same as described above except that the overhead material leaving via line 34 would also include normal pentane and isopentane. This overhead material would then be charged to other fractionating facilities for removing and separating normal and isopentane. Such equivalent fractionating arrangements are understood to be within the scope of the present invention.

Product from separation zone 22 comprises isopentane from line 30, cyclopentane, neohexane, diisopropyl and methylpentanes from line 34, and methylcyclopentane and cyclohexane from line 36. These streams may be considered separate products or, optionally, may be combined as a high-octane base stock in line 37. Normal pentane which leaves separation zone 22 via line 31 and normal hexane which leaves via line 35 are charged to isomerization zone 16 via line 32. While in this embodiment normal pentane and normal hexane are shown as being combined in line 32, it should be understood that each of these streams could be charged separately to isomerization zone 16, should the isomerization facilities have separate reactors for pentane and hexane.

Isomerization zone 16 may comprise any process capable of converting a substantial portion of normal pentane and normal hexane to isomers thereof. A preferred process for use in isomerization zone 16 is the Isomate Process, which will be described in further detail in Figure 3. Effluent from isomerization zone 16, which contains at least a substantial portion C_5 and C_6 isomers is charged via lines 17 and 14 to fractionation zone 15, wherein materials boiling below about 40° F. are removed via line 20 and materials boiling in the range of about 40 to 180° F. are removed via line 21 to be further separated in separation zone 22. Unconverted normal pentane and normal hexane are thus recycled back to isomerization zone 16 from separation zone 22 via line 32. Heavy Isomate product, i.e., hydrocarbons boiling above about 180° F., which are rich in naphthenes, is charged via line 23 to hydroforming zone 18.

If isomerization zone 16 or separation zone 22 contain stabilization facilities for removing hydrocarbons boiling below about 40° F., i.e., C_1—C_4's effluent from isomerization zone 16 may be charged directly to separation zone 22 via lines 17 and 17*a*, rather than indirectly via fractionation zone 15. This should be avoided, however, because it has the disadvantage of allowing high-boiling hydrocarbons in Isomate product, i.e., hydrocarbons boiling above about 180° F. to pass out of the system via line 36, rather than via fractionation zone 15, and line 23 to hydroforming zone 18.

Hydrogen for use in isomerization zone 16 is obtained from hydroforming zone 18 via lines 38, 39 and 40. Hydrogen is also recycled to hydroforming zone 18 via lines 38 and 41 and may also be utilized via lines 38, 39, and 13 as a reactant and for stripping purposes in hydrogen treating zone 12. Excess hydrogen, if any, may be withdrawn from the system at any convenient point.

While reference has been made in this embodiment to specific hydrocarbons and/or specific boiling ranges and cut points, it should be understood that such references are used for descriptive purposes only. It should be understood that perfect fractionation is not an essential of the present invention and should not be considered as such. Economic considerations will influence the design of the fractionation and separation facilities. Thus, for example, where it is shown in Figure 1 that C_1—C_4's leave fractionation zone 15 via line 20, that 40–180° F. hydrocarbons leave fractionation zone 15 via line 21, that 180–400° F. material leaves fractionation zone 15 via line 23, and that heavy ends leave fractionation zone 15 via line 24, it should be understood that there will be a certain amount of "slop-over" among the respective fractions. Likewise, such slop-over will occur in the fractionation facilities of separation zone 22. The degree of separation which is economic in any particular installation would have to be analyzed in the light of the types and relative amounts of the hydrocarbon streams being treated, the particular hydroforming and isomerization processes utilized, and the like. It should also be understood that overlap in fractionation may be deliberately utilized for particular purposes. Thus, for example, to adjust Reid Vapor Pressure of the base stock leaving separation zone 22 via line 37, some C_4's could be slopped-over in fractionation zone 15 so that they leave fractionation zone 15 via line 21 rather than line 20, and ultimately pass via depentanizer 26, line

29, diisopentanizer 27, and line 30 to line 37. Likewise, methyl pentanes can be slopped over in deisohexanizer 28 so that at least some are removed with normal hexane via line 35 for charging to isomerization zone 16. Also, cyclohexane can be slopped over in fractionation zone 15 so as to be included in material leaving via line 23 to hydroforming zone 18.

Figure 2 shows a schematic flow diagram of the Ultraforming Process, which is the preferred hydroforming process for hydroforming zone 18. Ultraforming uses an alumina-supported platinum catalyst, in which the platinum content is in the range of about 0.05 to 1 percent by weight. The catalyst is loaded in a series of fixed-bed reactors, usually 3 to 6 in number. A spare or "swing" reactor is usually provided along with suitable manifolding lines and valves so that when catalyst in any of the onstream reactors becomes deactivated, the swing reactor may be temporarily substituted for it. The deactivated catalyst is then regenerated by special techniques which fully restore activity. Typical ultraforming conditions are temperature in the range of about 850 to 1000° F., pressure in the range of about 100 to 400 pounds per square inch gage, hourly-weight space velocity in the range of about 0.5 to 5, and hydrogen recycle rate in the range of about 3000 to 8000 standard cubic feet per barrel of naphtha charge stock.

In Figure 2 catalyst in swing reactor 42 is being regenerated, while naphtha is being processed in on-stream reactors 43, 44, and 45. Naphtha feed boiling above about 180° F., from line 23 and hydrogen-rich recycle gas from line 41 are passed through furnace 42*a* where they are heated to reaction temperature, e.g., 920° F. Naphtha vapors and recycle gas are then mixed in line 46 and passed via lines 47 and 48 to reactor 43, thence via line 49, reheat furnace 50, and lines 51, 52 and 53 to reactor 44, and finally via line 54, reheat furnace 55, and lines 56, 57, and 58 to tail reactor 45. Reheat furnaces 50 and 55, which, along with furnace 42*a*, may be sections of a single furnace, are required because of the overall endothermic nature of the ultraforming reactions.

Effluent from reactor 45 passes via lines 59 and 60 to separator 61, from which is flashed a hydrogen-rich gas via line 38. A portion of this hydrogen-rich gas is recycled via line 41 to furnace 42*a*. Another portion of hydrogen-rich gas passes via line 39 to isomerization zone 16 and hydrogen-treating zone 12, as shown in Figure 1. Hydrocarbons from separator 61 are passed through a second separator 62, from which product reformate boiling above about 180° F. is removed via line 25, and hydrocarbons boiling below about 180° F. are removed overhead via line 19 and charged to fractionation zone 15 via line 14, as shown in Figure 1. Under certain circumstances it may be desirable to remove light ends, i.e., material boiling below about 180° F., at an intermediate point on the hydroforming chain, e.g., after the first reactor. This would prevent any further cracking of these light ends in subsequent reactors.

When activity of catalyst in a particular reactor declines, that reactor is temporarily isolated from the naphtha processing system, and its place is taken by the swing reactor, said substitution of reactors being made possible by valved manifolds 63, 64, 65 and 66. Deactivated catalyst is reactivated using air from source 67, and inert gas from source 68 (usually an inert gas generator), which are heated in furnace 69 and passed via the appropriate manifolding to the reactor containing deactivated catalyst. Reactivation usually comprises a carbon burn-off and/or additional oxygen treats under controlled conditions, i.e., an oxygen partial pressure above about 0.4 atmosphere and a temperature above about 950° F. Excess flue gas is removed from the regeneration system via line 70. After regeneration, the reactor with regenerated catalyst is again placed back on-stream and swing reactor 42 is held in readiness until catalyst in another reactor needs regeneration.

Figure 3 shows a schematic flow diagram of the Isomate Process. The reaction is conveniently carried out in a simple, cement-lined drum, which is mounted vertically and contains a pool of the liquid catalyst. The catalyst is preferably a highly-selective liquid complex of aluminum chloride and hydrocarbon. Hydrogen is also introduced to suppress cracking and catalyst contamination. The naphtha rises through the catalyst as an insoluble phase and its composition in the effluent is close to equilibrium. High catalyst activity is maintained by periodically injecting a slurry of fresh aluminum chloride in naphtha. Reaction conditions are typically a temperature in the range of about 150–300° F., a pressure of 600 to 900 pounds per square inch gage, and a hydrogen addition rate of about 50 to 150 standard cubic feet per barrel.

Referring to Figure 3, feed naphtha, i.e., normal pentane and normal hexane (and, optionally, methyl pentanes), enters via line 32 to dryer 72, and thence via line 73 to HCl absorber 74, where it picks up hydrogen chloride, said hydrogen chloride entering from line 75. Gas (excess hydrogen) to fuel or for other purposes leaves HCl absorber 74 via line 76. Feed stock containing absorbed HCl leaves absorber 74 via line 77 and is charged via pump 78, exchanger 79, and line 80 to reactor 71. About 50–150 standard cubic feet of hydrogen per barrel of feed from line 40 is mixed with feed in line 80 prior to entering reactor 71. A slurry of fresh aluminum chloride in naphtha from source 81 enters reactor 71 via pump 82 and line 83. Spent catalyst leaves reactor 71 via line 84.

Product effluent from reactor 71 leaves via line 85 and cooler 86 and is flashed into a settler 87 for separation of entrained catalyst, said entrained catalyst leaving by valved line 88. The liquid product leaves settler 87 via line 89 and enters HCl stripper 90 for removal of HCl. Gases from settler 87 and stripper 90 leave via lines 91 and 92 respectively and are recycled via line 75 to the HCl adsorber, along with a small amount of make-up hydrogen chloride from source 93. Liquid product leaves HCl stripper 90 via line 94 and is joined in line 95 with caustic introduced from source 96 for washing in caustic wash vessel 97. Residue is removed from caustic vessel 97 via line 98 and liquid product is removed via line 99 for further washing in water wash vessel 100, water for which is introduced from source 101. Residue from water wash vessel 100 is removed via line 102, and isomerization zone product is removed via line 17 and returned to fractionation zone 15 via line 14 as shown in Figure 1.

If stabilization facilities are available for removal of C_1—C_4 hydrocarbons in isomerization zone 16 effluent from isomerization zone 16 may pass directly via line 17, 17*a* and 21 to separation zone 22. Even if such stabilization facilities are available, however, the preferred operation is to charge isomerization zone effluent via lines 17 and 14 to fractionation zone 15 so that higher-boiling hydrocarbons, i.e. hydrocarbons boiling above about 180° F., which are highly naphthenic and thus highly desirable as hydroforming charge stock, are removed and charged via line 23 to hydroforming zone 18. If isomerization zone effluent were charged directly via lines 17, 17*a*, and 21 to separation zone 22, such naphthenic heavy hydrocarbons would be removed via line 36 without further up-grading.

As can be seen from the hereinabove specific embodiment, use of a unitized and integrated fractionation and separation zone, combined with hydrogen treating, hydroforming, and isomerization, has a number of advantages. For example, hydrogen from hydroforming zone 18 is used in isomerization zone 16 and hydrogen treating zone 12. The same fractionation zone 15 stabilizes and fractionates charge naphtha, light hydrocarbons from hydroforming zone 18, and effluent from isomerization zone 16. Use of such integrated fractionation facilities not only minimizes equipment and operating costs but also, and more importantly, effectively

segregates in one operation desired hydroforming charge from incoming fresh naphtha and from isomerization zone effluent. Separation zone 22 segregates desirable isomerization zone feed, i.e., normal pentane and normal hexane, from fresh light hydrocarbons, hydroforming zone product, and isomerization zone product. At the same time, the separation zone eliminates from each of these streams particular hydrocarbon fractions, e.g., cyclopentane, methylcyclopentane, and cyclohexane, which are not considered desirable isomerization zone charge stock.

In brief, the method of the present invention optimizes combined hydroforming-isomerization operations with the attendant advantages of maximum octane potential, highest yield-octane relationship, and the flexibility of providing several high-octane blending stocks with superior octane and volatility blending characteristics at a minimum in operating and investment costs. For example, application of combined hydroforming-isomerization to a typical refinery situation, as a substitute for incremental hydroforming, results in both a higher octane motor fuel pool and lower costs per incremental octane.

While we have described our invention with reference to certain specific embodiments thereof, it is to be understood that such embodiments are illustrative only, and not by way of limitation.

Having thus described our invention, we claim:

1. A combination process for producing high octane gasoline blending stocks from lower octane naphtha, which process comprises charging said naphtha to a fractionation zone, separating said naphtha in said zone into at least a first naphtha fraction rich in hydrocarbons boiling below about 170–180° F. and a second naphtha fraction rich in hydrocarbons boiling above about 170–180° F., hydroforming said second naphtha fraction in a hydroforming zone in the presence of platinum-alumina hydroforming catalyst, whereby there is produced a net amount of hydrogen and a hydroformate having a higher octane than said second naphtha fraction, recycling a first portion of said hydrogen to said hydroforming zone, separating said hydroformate into a first hydroformate fraction rich in hydrocarbons boiling below about 170–180° F. and a second hydroformate fraction rich in hydrocarbons boiling above about 170–180° F. having a higher octane than said second naphtha fraction and suitable for use as a gasoline blending stock, charging said first naphtha fraction and said first hydroformate fraction to a separation zone, separating from the charge to said separation zone at least a substantial portion of the normal pentane and normal hexane in the charge to said separation zone, withdrawing from said separation zone as a gasoline blending stock the remaining hydrocarbons from the charge to said separation zone, charging said normal pentane and normal hexane and a second portion of said hydrogen to an isomerization zone maintained under isomerizing conditions adapted to convert at least a substantial proportion of said normal pentane and normal hexane to higher octane isomers thereof, and charging the hydrocarbon effluent from said isomerization zone to said separation zone.

2. The improved combination process of claim 1 wherein at least a portion of the hydrocarbon effluent from said isomerization zone is charged to said fractionation zone.

3. The improved combination process of claim 1 wherein at least a portion of the hydrocarbon effluent from said isomerization zone is charged to said fractionation zone and at least a portion of said first hydroformate fraction is charged to said fractionation zone.

4. The improved combination process of claim 1 wherein said naphtha, prior to being charged to said fractionation zone, and a portion of said hydrogen is charged to a hydrogenation zone.

5. In a combination process for producing high octane gasoline blending stocks from lower octane naphtha, which process comprises charging said naphtha to a fractionation zone, separating said naphtha in said zone into at least a first naphtha fraction rich in hydrocarbons boiling below about 170–180° F. and a second naphtha fraction rich in hydrocarbons boiling above about 170–180° F., hydroforming said second naphtha fraction in a hydroforming zone in the presence of a platinum-alumina hydroforming catalyst, whereby there is produced a net amount of hydrogen and a hydroformate having a higher octane than said second naphtha fraction, recycling a first portion of said hydrogen to said hydroforming zone, charging said first naphtha fraction to a separation zone, separating from the charge to said separation zone at least a substantial proportion of the normal pentane and normal hexane in the charge to said separation zone, withdrawing from said separation zone as a gasoline blending stock the remaining hydrocarbons in the charge to said separation zone, charging said normal pentane and normal hexane and a second portion of said hydrogen to an isomerization zone maintained under isomerizing conditions adapted to convert at least a substantial proportion of said normal pentane and normal hexane to higher octane isomers thereof, and withdrawing a hydrocarbon effluent from said isomerization zone suitable for use as a gasoline blending stock, the improved combination which comprises separating said hydroformate into a first hydroformate fraction rich in hydrocarbons boiling below about 170–180° F. and a second hydroformate fraction rich in hydrocarbons boiling above about 170–180° F. suitable for use as a gasoline blending stock, charging said first hydroformate fraction to said separation zone, and charging the hydrocarbon effluent from said isomerization zone to said separation zone.

6. The improved combination process of claim 5 wherein at least a portion of the hydrocarbon effluent from said isomerization zone is charged to said fractionation zone.

7. The improved combination process of claim 5 wherein at least a portion of the hydrocarbon effluent from said isomerization zone is charged to said fractionation zone and at least a portion of said first hydroformate fraction is charged to said fractionation zone.

8. The improved combination process of claim 5 wherein said naphtha, prior to being charged to said fractionation zone, and a portion of said hydrogen is charged to a hydrogenation zone.

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