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PROCESS FOR UPGRADING DESULFURIZED NAPHTHAS

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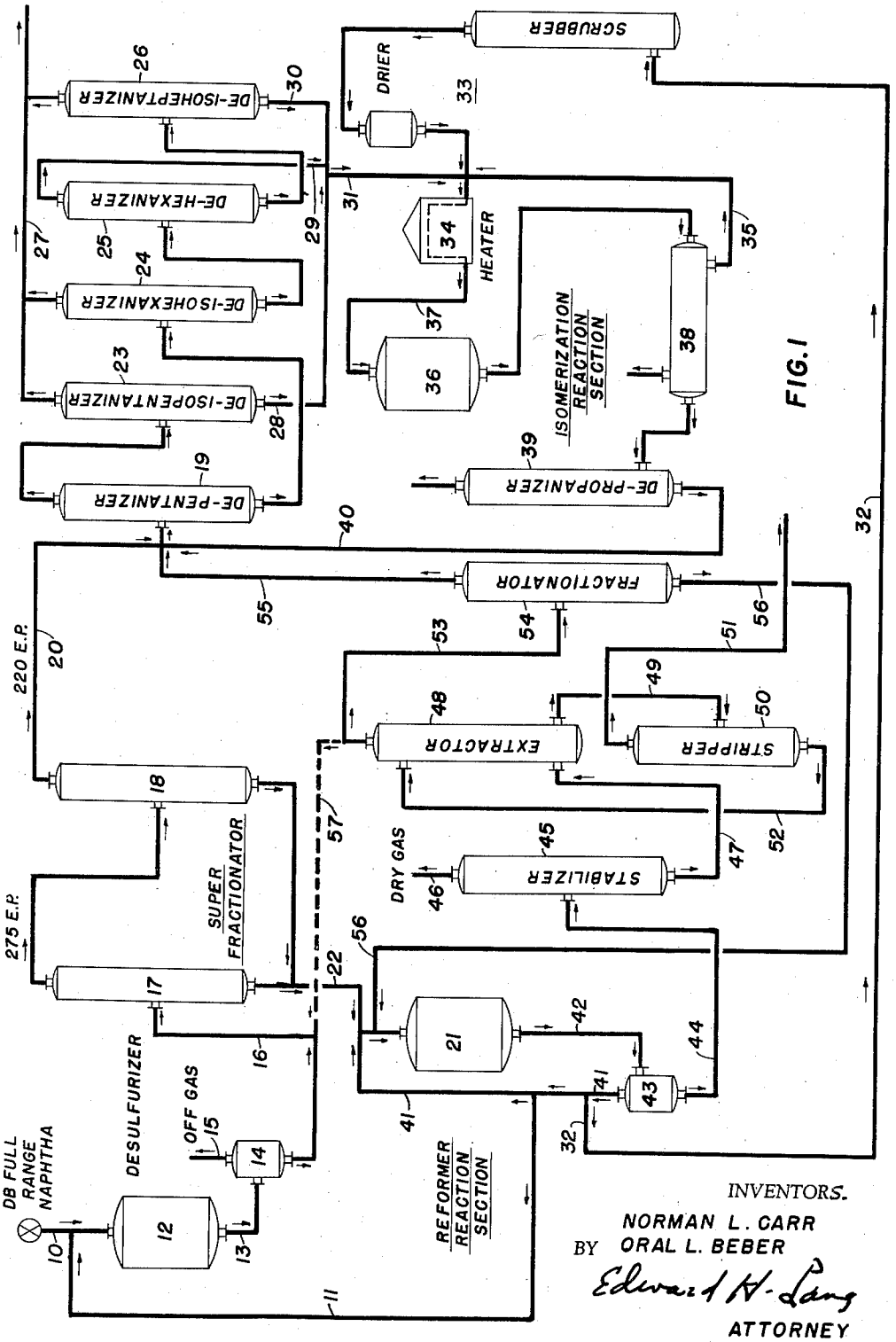


FIG. 1

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PROCESS FOR UPGRADING DESULFURIZED NAPHTHAS

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4 Claims. (Cl. 208—65)

This invention relates to the production of high-octane gasolines. It is more specifically concerned with the processing of full-boiling-range, virgin, petroleum distillates having an ASTM end-point of about 400° F. to produce high-quality gasoline motor fuels.

In a refining situation wherein such factors as the high cost of crude petroleum oils, and upward trends in the quality of gasoline-type motor fuels are present, it is essential, from an economic standpoint, that consideration be given to upgrading the several gasoline components that have inferior performance characteristics. The C_2 and heavier, normally gaseous olefins can be polymerized or alkylated to produce blending stocks of high octane number. The virgin naphtha fraction containing heptane and higher boiling hydrocarbons, having an end boiling point of about 400° F., normally is subjected to catalytic reforming to provide an aromatic blending material having an improved octane number. The fuel requirements of high-output, high-speed, spark-ignited, interal combustion engines with high compression ratios make it necessary to refine more selectively the various liquid, hydrocarbon constituents boiling in the gasoline range. Because n-pentane is an important single component which degrades the octane number of gasolines, refining processes have been developed for the isomerization of a n-pentane fraction which is fractionated from a debutanized, full-boiling-range naphtha to produce a high-octane-number, iso-pentane-containing blending stock. The remainder of the fraction containing, inter alia, n-hexane and n-heptane is then converted in conventional catalytic reforming processes. Under optimum operating conditions, some latitude in octane number is available, depending upon the degree of severity at which the reforming is carried out. Regardless of the severity of the reforming operation, however, n-hexane and n-heptane fractions are hydrocracked to compounds of lower molecular weight upon being subjected to reforming conditions, with only an insignificant amount being converted to aromatic hydrocarbons. As a compromise process, there has been developed a reforming process of relatively low severity, employing platinum- or palladium-containing catalysts, e.g., the U.O.P. Rexforming Process. In this process, the reformate is extracted with a selective solvent, viz, diethylene glycol and water, in which the aromatic and low-boiling, non-aromatic components of the reactor effluent are soluble. The soluble, higher-boiling, non-aromatics are recovered for reprocessing. These higher boiling components can be subsequently upgraded by processing this low-octane fraction in a thermal reforming unit, or by recycling it to the catalytic reforming section. High contents of aromatic hydrocarbons in gasolines, however, although desirable from an octane rating aspect, often induce other operational difficulties, such as depreciation of road octane values at high speeds, and at part throttle, O and GJ 45 (60) 84. Accordingly, excessive concentrations of aromatics generally are to be avoided.

It is, therefore, the primary object of this invention to

provide a novel, integrated refining process for the upgrading of virgin naphthas containing pentanes and higher-boiling hydrocarbons and having an end-boiling-point of about 400° F. naphthas in which the deleterious effect on liquid yield due to hydrocracking of the n-hexane and n-heptane constituents of the feed stock is minimized, and a gasoline blending stock having excellent road performance, and containing a desirable content of aromatic hydrocarbons, is produced. This and other objects will be made more apparent from the following detailed description of this invention.

Figure 1 is a schematic flow diagram of a preferred embodiment of the invention. For simplicity and ease of understanding, only essential major processing equipment and flow lines are shown. Conventional pumps, heat exchangers, tanks,etc., that are not shown are understood to be used throughout where required.

According to this invention, a low-sulfur feed stock, which is herein termed a "full-boiling-range naphtha," viz., a debutanized, petroleum-derived naphtha having an ASTM boiling range of about 90°–400° F., is initially fractionated to produce a low-boiling fraction consisting essentially of n-heptane and lighter hydrocarbons, and a high-boiling, residual fraction containing methylcyclohexane and heavier hydrocarbons. The low-boiling fraction is further separated into isomeric and normal paraffinic fractions. The branched-chain hydrocarbons are withdrawn as product and the normal hydrocarbons, containing five through seven carbon atoms per molecule, are subjected to catalytic isomerization in the presence of a preconditioned, refractory, acidic, mixed oxides base-hydrogenation agent composite isomerization catalyst, prepared in accordance with Norman L. Carr's patent application entitled Catalysts and Process, Serial Number 619,376, filed October 31, 1956. The reaction effluent from the isomerization step is fractionated to separate normal paraffins from their isomers. The isomeric fractions which are recovered are combined with the isomeric constituents from the fresh feed to form the finished isomeric hydrocarbon-containing blending stock. The higher-boiling, residual fraction is subjected to reforming, over a catalyst containing platinum or palladium, at a low level of severity to produce a reformate. The reformate then is extracted with a selective solvent to separate an essentially aromatic extract fraction, and a non-aromatic raffinate fraction. The aromatic fraction, upon being separated from the solvent, is withdrawn as a finished product. The non-aromatic raffinate fraction is fractionated into a distillate fraction containing n-heptane and lighter hydrocarbons, and a residual fraction containing hydrocarbons heavier than n-heptane. The distillate fraction is combined with the feed to the isomerization unit. The residual fraction is recycled to the reformer. The finished isomerization product, containing isomeric compounds originally present in the full-range naphtha and those produced in the isomerization unit, is then blended with the finished aromatics from the reforming unit to form a superior motor fuel.

Referring to Figure 1 for a more detailed description, a high-sulfur, full-boiling-range, naphtha is introduced into the process through line **10**. Hydrogen from a suitable source hereinafter described is added through line **11** and the combined feed treated in a conventional catalytic hydrodesulfurization section **12** which preferably contains a cobalt-molybdena catalyst. The reaction effluent leaving the reactor **12** through line **13** contains hydrogen sulfide and is separated from the desulfurized, effluent naphtha in separator **14**. The hydrogen sulfide is vented through line **15** for use as fuel or a chemical intermediate in the synthesis of other chemical by-products. The desulfurized naphtha is transferred through line **16** to a superfractionator comprising fractionator **17** and re-

run tower 18 where is is sharply fractionated into two streams. The distillate from rerun tower 18 is a sharply defined fraction containing n-heptane and lighter hydrocarbons, and the combined residues from the two towers is a sharply defined fraction containing methylcyclohexane and heavier hydrocarbons. The distillate goes to depentanizer 19 through line 20, and the residue stream goes to reforming reactor 21 through line 22.

Depentanizer 19, de-isopentanizer 23, de-isohexanizer 24, dehexanizer 25, and de-isoheptanizer 26 form a consolidated fractionation system to separate isomeric compounds from the straight-chain hydrocarbons. The combined isomers are removed as product through line 27. The predominantly straight-chain hydrocarbons removed from the systems through lines 28, 29, and 30 are combined in line 31 to provide the liquid feed for the isomerization phase. Any make-up hydrogen required is introduced through line 32 and purified in the hydrogen purification system 33 comprising a caustic scrubber and a drier where residual hydrogen sulfide and water are removed. These streams join the recycle hydrogen introduced through line 35 and the combined reactor feed is heated to reaction temperature in heater 34. The heated feed is directed into isomerization reactor 36 by means of line 37. The make-up hydrogen is sufficient in quantity to replace hydrogen lost from the system. The effluent emitted from reactor 36 is freed of gas in reaction effluent separator 38 and depropanized in depropanizer 39. The bottoms from this tower passes through line 40 for isomer recovery in the consolidated fractionation system hereinbefore described. Using this technique, straight-chain hydrocarbons containing seven or less carbon atoms are recycled to extinction in this section of the process.

The combined residues from naphtha fractionator 17 and rerun tower 18, passing through line 22, admix with the recycle hydrogen introduced through line 41. This admixure is fed into reforming reactor 21. Effluent leaving the reactor system through line 42 is freed of gas by flash separation in separator 43 and the liquid reformate is transferred through line 44 to be stabilized to a desired extent in stabilizer 45. In the course of the reforming reaction there is produced a net excess of hydrogen in sufficient amounts to provide hydrogen for use in the hydrodesulfurization unit and hydroisomerization process. Dry gas comprising normally gaseous, C_3 and lighter hydrocarbons from stabilizer 45 is transferred through line 46 to a fuel gas system or other use. Stabilized reformate flows from stabilizer 45 via line 47 to the aromatic separation section which in this illustrative embodiment is a solvent extraction process where the reformate stream is contacted with a selective solvent which absorbs the aromatics produced in the reforming section 21. The aromatic extract leaving extractor 48 by means of line 49 is freed of solvent in stripper tower 50 and the aromatic extract is removed as a finished product via line 51. The solvent is recycled in line 52 for reuse in extraction tower 50. Raffinate from extractor 48 passing through line 53, is predominantly paraffinic and is fractionated in fractionating tower 54 to produce a distillate containing n-heptane and lighter hydrocarbons and a residue containing hydrocarbons of eight or more carbon atoms which is transferred by means of line 55 for further fractionation in the consolidated feed preparation fractionation system. The distillate joins the fresh light feed and isomerate to form the charge to depentanizer 19. The residual fraction containing C_8 and heavier hydrocarbons is recycled to reformer 21 through line 56. In the alternative, fractionator 54 could be omitted and the paraffinic raffinate returned to the superfractionator through line 57 for reprocessing.

It is to be noted that in related, prior art processes, the paraffinic raffinate from the extractor 48 conventionally would be recycled in its entirety to the reforming reactor. In contradistinction, in the process of this invention this stream is fractionated into a precise, more readily isomerized fraction and a precise, more readily reformed fraction, and these streams are subsequently upgraded in a specific, highly efficient manner, a procedure which can be used to advantage in employing the preconditioned isomerization catalyst described above. This catalyst, while effectively functioning to facilitate the isomerization of saturated hydrocarbon, has a particular activity for the isomerization of n-heptane. This separation is accomplished in this invention by using a separate precision fractionator, such as tower 54, or by returning the total raffinate stream to precision fractionator 17 and rerun tower 18, through line 5, the same end result being obtained by either means. If this separation is not made, the n-heptane and lighter fraction can be upgraded by reforming only if more severe conditions are employed; then the quality of the other reforming products is adversely affected, as is the yield of reformate. Furthermore, these severe conditions cause the formation of an appreciable quantity of coke on the reforming catalyst which reduces its activity. These problems are avoided by the use of this invention.

To illustrate the instant invention 1000 b.p.d. of a desulfurized, straight run petroleum naphtha having the following characteristics:

Gravity, °API	60
Octane No.	50
ASTM boiling range, °F	90–400
Sulfur content, wt. percent	0.01

is fractionated to produce a low-boiling fraction having an ASTM boiling range of 90–200° F., constituting 20 vol. percent of the feed and containing the n-heptane and lighter constituents of the feed. The residual fraction boiling between 200°–400° F., which constitutes 80 vol. percent of the feed, will contain the methylcyclohexane and heavier constituents of the feed. By processing the low-boiling fraction in the isomerization feed preparation system the isomeric hydrocarbons are substantially separated and recovered. The residual n-pentane and n-hexane components are treated in a first isomerization reactor while the n-heptane fraction is isomerized in a second isomerization reactor. In these reactors the following conditions are employed:

	n-C_5 and n-C_6	n-C_7
Pressure, p.s.i.g.	350	350
Liquid Vol. Hourly Space Velocity	1.0	1.0
Temperature, °F	700	650
H_2/Hydrocarbon mol ratio	2.3	

The catalyst employed in each reactor is a 10% $NiMoO_4$ on 75 silica-25 alumina. This catalyst is prepared by impregnating a silica-alumina support with an aqueous admixture of ammonium paramolybdate and nickel nitrate. The wetted mass is dried and then calcined at an elevated temperature in the presence of hydrogen. The activated catalyst is preconditioned by alternately oxidizing and reducing the composite catalyst at a temperature of 775°–800° F. Complete details for the preparation of this catalyst are set forth in Norman L. Carr's copending application entitled Catalysts and Process, Serial Number 619,404, filed October 31, 1956, now Patent No. 2,917,566. The isomerization effluent is returned to the feed preparation system for recovery of the isomeric hydrocarbon constituents. In processing a feed stock of this nature 584 b.p.d. having a Research Octane Number (clear) of 80 is produced.

The higher-boiling residual fraction containing the methylcyclohexane and heavier constituents is employed as feed stock in a reforming step employing the following conditions and three reactors with requisite reheating:

Pressure, p.s.i.g.	200–500
Inlet temperature, ° F.	900–920
Liquid weight hourly space velocity	2.0
H_2/hydrocarbon mol ratio	4–6

Employing 0.6 wt. percent platinum on an aluminum support as the catalyst, having a surface area of 527 (BET) sq./m. gram and an ignition loss at 1500° F. of 8.0 wt. percent (Sinclair-Baker RD–150 Catalyst, Petroleum Processing, October 1953), an 84 liquid vol. percent yield of a reformate having a Research Octane Number (clear) of 89 is obtained. The reformate containing about 50% aromatic hydrocarbons is solvent-extracted with a solvent admixture of diethylene glycol and water, using a solvent-to-feed ratio of 10 to 1. The extract upon being stripped of solvent by conventional fractional distillation provides 336 b.p.d. of aromatic hydrocarbon blending stock having a Research Octane Number blending value of 116.5. By blending this product with the isomerization product, 884 b.p.d. of gasoline is produced which, having a Research Octane Number (clear) of 93.9 will have a Research Octane Number (3 cc. of T.E.L.) of 100. The raffinate portion of the reformate is then recycled for reprocessing.

As pointed out above, the reforming phase of the process is carried out in the presence of a reforming catalyst comprising platinum or palladium supported on alumina, or on a siliceous cracking catalyst. Catalysts of this type are well-known in the prior art and contain about 0.1 to 1.0% by weight of platinum or palladium on alumina or a siliceous cracking catalyst, such as silica-alumina, silica-zirconia, silica-alumina-zirconia, etc. Complete descriptions of such catalysts are contained in a number of U.S. Patents, e.g., 2,478,916; 2,479,109; 2,550,531; 2,589,189; 2,705,329; and others. If desired the catalyst can have a combined halogen (0.1–8.0 percent of fluorine or chlorine based on the support) incorporated therein.

These catalysts can be prepared in accordance with conventional techniques by wetting the selected support with an aqueous solution of chloroplatinic acid or chloropalladic acid, or with a aqueous solution of the ammonium salts of these acids. The impregnated support is dried at about 210°–250° F. and reduced in a hydrogen atmosphere between about 200°–950° F. (Cf. I & E Chem. 45, 147, 1953). Operating conditions for carrying out the reforming step are selected for producing optimum results. Accordingly, the following conditions are employed:

Adiabatic Reactor Inlet	Range	Preferred Range
Temperature, °F	890 to 920	900 to 910
Pressure, p.s.i.g.	200 to 700	300 to 500
Liquid Weight Hourly Space Velocity	1 to 5	2 to 3
H_2/Hydrocarbon mol ratio	3 to 10	4 to 6

The isomerization of the low boiling fraction of the feed stock containing the n–C_7 and lighter hydrocarbons, is carried out in the presence of a hydrogenation-cracking catalyst composite of improved efficiency prepared in accordance with copending application of Norman L. Carr, viz., U.S. Patent entitled, "Catalyst and process," Serial Number 619,376, filed October 31, 1956, now Patent No. 2,917,565. These catalysts are preconditioned in a certain prescribed manner described in the above-mentioned application prior to use. This technique, in essence, comprises incorporating a minor amount of a hydrogenation component in a refractory, mixed oxides base, composited to evince acidic properties and hydrocarbon cracking activity, substantially in accordance with conventional catalyst preparation techniques. The freshly prepared, "green" catalyst is activated in a reducing atmosphere in accordance with the prior art to effect reduction of the hydrogenation component of the catalyst as far as possible under specific conditions. Thereafter, the catalyst is subjected to the additional activation and conditioning treatment described in the above-mentioned application. In carrying out this preconditioning phase

of the catalyst preparation, the composite catalyst is subjected to an oxidizing atmosphere maintained at a temperature of about 650° F. to 750° F. Following this oxidation, the oxidized catalyst is contacted with hydrogen at the same temperature as that at which the oxidation was carried out to reduce the reducible elements of the composition to their lowest state of valency and produce a composite catalyst of high activity and resistance to degeneration. Catalysts prepared in this manner are those which comprise a refractory, mixed oxides base composited to evince acidic properties and hydrocarbon cracking activity, having incorporated therein 2 to 10% of a hydrogenation component, such as group VIII metals of the iron period oxides of polyvalent metals of groups V, VI and VII and group VIII metal of the iron period salts of oxyacids of polyvalent metals of groups V, VI, and VII. Specific examples of these hydrogenation components include cobalt, nickel, tungsten, oxide, molybdenum oxide, chromium oxide, manganese oxide, vanadium oxide; and cobalt, and nickel salts of the oxyacids of tungsten, molybdenum, chromium, vanadium, and manganese, e.g., nickel tungstate, cobalt molybdate, nickel molybdate, etc. Suitable refractory, acidic, mixed oxide bases include, but are not limited to, SiO_2—Al_2O_3, SiO_2—ZrO_2, SiO_2—TiO_2, SiO_2—B_2O_3, Al_2O_3—ZrO_2, Al_2O_3—BeO, Al_2O_3—B_2O_3, SiO_2—CrO_3, B_2O_3—TiO_2, SiO_2—Al_2O_3—ZrO_2, SiO_2—Al_2O_3—BeO, and acid-treated clays. These mixed oxides, in forming the base, can be either in chemical or physical combination. From a standpoint of activity, it has been found that catalyst carriers, containing 50 to 87% silica and 50 to 13% alumina, having incorporated therein 3 to 5% of the hydrogenation agent, are preferred. To facilitate the description of these catalysts they will be referred to as "preconditioned, refractory, acidic mixed oxides base-hydrogenation agent composite isomerization catalysts" and so designated in the appended claims.

Operating conditions selected for the isomerization phase are those best suited for isomerization of normal pentane, hexane, and heptane. Accordingly, the following conditions are employed:

	Range	Preferred
Temperature, °F	690–750	650–725
Pressure, p.s.i.g.	180–1000	350–750
Liquid Weight Hourly Space Velocity	0.1–2.0	0.5–1.5
H_2/hydrocarbon mol ratio	0.5–4.5	0.5–3.5

As indicated, the net production of hydrogen in the reforming normally suffices to provide the amounts required in the desulfurizing and isomerizing sections. However, if necessary, additional amounts can be introduced in the form of fresh, extraneous hydrogen. Make-up hydrogen should contain not more than a trace of hydrogen sulfide; otherwise, hydrogen from reforming operations is satisfactory, viz., 80–90 mol percent H_2, remainder dry hydrocarbon gases.

The solvent extraction phase of the invention is preferably carried out using conventional liquid-liquid extraction equipment. The solvent employed has a high solubility for aromatics combined with good selectivity. It must be stable at the operating temperature employed, and preferably, has a high boiling point to permit the distillation of the aromatic hydrocarbons therefrom. This latter characteristic greatly reduces utility requirements. Specific solvents employed include glycols, polyglycols and acyl derivatives, etc., such as diethylene glycol, triethylene glycol, phenol, nitrobenzene, furfural, Chlorex, and others. In addition, mixed solvents, such as those having the foregoing characteristics, discussed by Kalichevsky, ACS Monograph #76, Reinhold, can also be employed. Preferably diethylene and triethylene glycols are employed. In accordance with conventional practice,

it is preferred to employ sufficient amounts of water to permit adjusting the selectivity, solubility, and solvency of the solvent to the optimum for the individual case, and at the same time provide a partial pressure of water vapor such that the aromatics may be recovered by stripping or distillation at moderate temperatures and pressures. Generally, 2.5 to 10 volumes of water per volume of solvent can be used. In carrying out the extraction, a solvent/feed volume ratio of 10 to 30 to 1 is used, employing extraction temperatures in the range of 110° to 130° F. Time of contacting should be sufficient for essentially equilibrium conditions, and if necessary, plural-stage extraction should be used. Selection of optimum conditions will depend upon the characteristics of the reformate being treated and can readily be determined experimentally. (Vide U.S. Patent 2,770,664.) Depending upon design requirements, the use of other aromatic-recovering techniques such as adsorption by silica gel or other similar adsorbents, followed by fractional desorption; extractive distillation, azeotropic distillation, etc., can be used to effect the aromatics separation and recycling of the paraffinic fraction.

Feed stocks treated in the process of this invention are debutanized, full-boiling-range, virgin, petroleum naphthas having an ASTM boiling range of about 90° to 400° F. Stocks which are particularly adaptable for processing are those stocks which have a relatively high n-heptane content of about 1 to 1.8 vol. percent of crude. Because this hydrocarbon has a zero octane number, even the presence of small amounts in a gasoline has a deleterious effect on the performance characteristics of the gasoline. Naphthas derived from crudes such as certain Texas, Wyoming and Oklahoma crudes, are relatively high in n-heptane. The process, however, can be used in the processing of naphthas from Mid-Continent, Middle Eastern, and other similar crudes, when, in the processing scheme, n-heptane is produced in the reforming phase. If the full-boiling-range, virgin naphthas have a total sulfur content of less than about 0.003 wt. percent they can be processed without being desulfurized. In the event desulfurization is needed, conventional vapor-phase desulfurization in the presence of such catalysts as bauxite, clay, cobalt molybdate, etc., can be employed. Because of the hydrogen available, hydrodesulfurization employing catalysts such as cobalt, nickel, or iron molybdate, sulfides, and chromites, either alone or supported on alumina, silica, zinc oxide, or chromium oxide is preferred. For general discussions relative to operating conditions, reference is made to U.S. Patents 2,325,034; 2,369,432; 2,417,308, and others.

From the foregoing description of this invention it will be noted that excellent versatility and flexibility in operations allow the control of product quality and quantity in an economically optimum manner for a wide variety of market conditions. In addition, this process provides a higher octane-yield result than can be obtained by reforming conventional reforming stocks and blending virgin light naphtha with the reformate, or reforming plus isomerization with no isomerization of the paraffinic constituents of the reformate. By means of this process, motor fuel having low sensitivity can be produced. Under certain processing conditions, an excess of aromatics is produced which provides a by-product of aromtics, as for the production of petrochemicals. Additional advantages obtain from the use of a "low-severity" reforming phase such as longer catalyst life, non-regenerative-type processing, less loss to dry gas, etc. Relatively severe reforming conditions which can be employed to produce a fuel of sufficiently high octane number but these adversely affect the quality of the fuel in other respects, such as its effect upon engine cleanliness. These severe conditions result in a product containing aromatic, relatively high-boiling ends which markedly contribute to a dirty engine, principally as crankcase oil contamination. Since the reforming section of this process is conducted under comparatively mild conditions, noted above, heavy aromatic ends are at a minimum in the finished aromatics product, and the motor fuel blends made from the two products of this process, viz., isomer product and aromatic product, do not cause excessive crankcase oil contamination.

It is evident that various modifications of this process can be made by those skilled in the art without departing from the scope of this invention. The foregoing examples and embodiments are illustrative and non-limiting and the invention is limited only as defined in the following claims.

We claim:

1. A process for producing a gasoline motor fuel having enhanced road performance characteristics which comprises fractionating a desulfurized, virgin petroleum naphtha boiling between about 90° and 400° F. into a low-boiling fraction consisting essentially of n-C_7 and lower-boiling hydrocarbons present in said naphtha, and a consecutive high-boiling fraction containing substantially all of the hydrocarbons present in said naphtha having a boiling point higher than n–C_7, separating the normal hydrocarbon constituents from the branched chain, hydrocarbon constituents of said low-boiling fraction, isomerizing said normal hydrocarbon constituents in an isomerization zone in the presence of hydrogen and a composite catalyst prepared by impregnating a refractory, acidic, mixed oxides base with a hydrogenation agent, and preconditioned by reduction, followed by oxidation at 650°–750° F., and reduction with hydrogen at 650°–750° F., employing the following reaction conditions:

	Range
Pressure, p.s.i.g	180–1000
Temperature, ° F	600–750
Liquid volume hourly space velocity	0.1–2.0
H_2/hydrocarbon mol ratio	0.1–4.5

to produce an isomerization effluent rich in branched-chain, saturated hydrocarbons, and recovering the branched-chain hydrocarbons from said isomerization effluent; catalytically reforming said high-boiling fraction in a reforming zone in the presence of hydrogen and a catalyst consisting essentially of a noble metal selected from the group consisting of platinum and palladium supported on a suitable carrier at a temperature of 900°–920° F., under reforming conditions to produce a reformed reaction effluent, solvent extracting said reformed effluent to produce a paraffinic fraction and an aromatic fraction, fractionating said paraffinic fraction to produce a distillate fraction consisting essentially of n–C_7 and lower-boiling hydrocarbons and a residual fraction containing hydrocarbons boiling above n-C_7, recycling said residual fraction to said reforming zone, fractionating said distillate fraction to separate the normal hydrocarbon constituents thereof for treatment in said isomerization zone, and recovering the branched-chain hydrocarbons constituents from said distillate fraction, and blending said branched-chain hydrocarbon constituents from said low-boiling fraction, said isomerization effluent, and said distillate fraction with said aromatic fraction to produce a high octane number gasoline.

2. A process in accordance with claim 1 in which said noble metal is platinum supported on a carrier selected from the group consisting of silica-alumina, and alumina.

3. A process in accordance with claim 1 in which said preconditioned isomerization catalyst is $NiMoO_4$ supported on silica-alumina.

4. A process in accordance with claim 1 in which the isomerization catalyst consists essentially of 8–15% reduced nickel molybdate on silica-alumina, the reforming catalyst consists essentially of 0.01–1.0% platinum on alumina, and the solvent extraction of a reformed effluent is carried out using a selective solvent selected from the group consisting of diethylene glycol and triethylene

glycol, having a high solubility and selectivity for aromatic hydrocarbons.

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UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

Patent No. 2,965,561 December 20, 1960

Norman L. Carr et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 3, for "sq./m." read -- sq.m./ --; line 59, for "process" read -- Process --; column 6, lines 13 and 15, for "group", each occurrence, read -- Group --; same column 6, lines 14 and 16, for "groups", each occurrence, read -- Groups --; column 7, line 50, after "2,369,432;" insert -- 2,392,579; --.

Signed and sealed this 23rd day of May 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents