

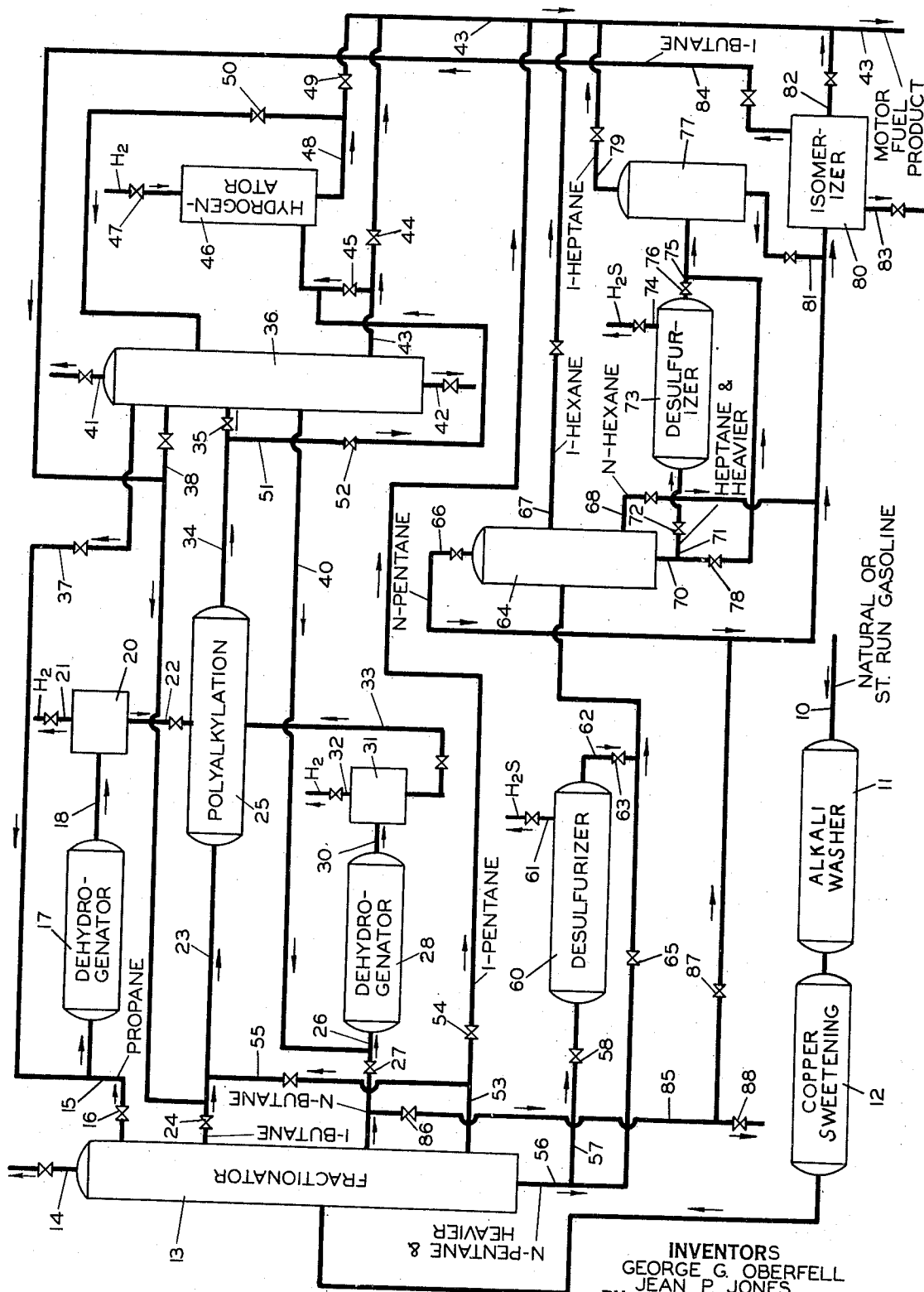
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TREATMENT OF LIGHT HYDROCARBONS

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TREATMENT OF LIGHT HYDROCARBONS

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This invention pertains to the treatment of hydrocarbons to produce hydrocarbons of higher molecular weight and of greatly improved anti-knock and volatility characteristics, suitable for use as motor and aviation fuels, and as blending components in such fuels. It relates more particularly to the molecular rearrangement and molecular combination of hydrocarbons of low molecular weight having three to seven carbon atoms or more per molecule, through two or more of a series of reactions known as isomerization, dehydrogenation, polymerization, alkylation and hydrogenation, to produce higher molecular weight hydrocarbons of more complex structure possessing higher anti-knock properties and volatilities within the motor and aviation fuel range.

This application is a continuation-in-part of our application Serial No. 383,430, filed March 14, 1941.

In the production and refining of crude petroleum and natural gas large amounts of both saturated and unsaturated low-boiling hydrocarbons of molecular weights up to seven or eight carbon atoms and higher are produced. The lighter of these hydrocarbons, those containing three and four carbon atoms, are relatively high in anti-knock rating but their volatilities are too high for inclusion in motor or aviation fuels used by present-day internal combustion engines. The heavier hydrocarbons mentioned are generally of the simpler, straight-chain structure, low in anti-knock properties. Those possessing branched-chain structure are of the simpler type, and those of six or more carbon atoms per molecule are generally also of low anti-knock properties. As a general rule the more complex a hydrocarbon molecule which boils in the motor fuel range the higher its anti-knock rating and the more valuable it is for such fuel. Therefore a process which offers a cheap, economical and efficient means for converting hydrocarbons of low molecular weight and anti-knock properties into those having the desired volatility and anti-knock characteristics is of great commercial importance to the industry. Such an economical, efficient process is the basis of this invention.

As to reactivity the straight-chain paraffin hydrocarbons show the least tendency to enter into reaction with other hydrocarbons or into any sort of reaction with any other chemical. In order to increase the reactivity of these straight-chain hydrocarbons it is necessary to change them into isoparaffinic structure, or to dehydrogenate them to olefinic structure having fewer hydrogen atoms per molecule than has the paraffin of the same number of carbon atoms. Both the isoparaffins and the olefins show greatly increased reactivity as compared with the normal paraffins and processes are well known in the industry by which

these changes in molecular structure may be effected.

Furthermore, in production of these light hydrocarbons in the modern refinery or natural gasoline plant, the proportions of normal and isomeric paraffins and of olefins may vary widely. In the alkylation process to be described later, wherein isoparaffins are reacted, it is necessary that one molecule of an olefin be present to combine with each molecular of isoparaffin reacted. Therefore, unless the proportions of isoparaffin to olefin in the light products from a refinery are in the desired ratio it is necessary to provide additional material of the molecular structure required to supply the deficiency of one or the other. This deficiency may be made up from an outside source if such is available, otherwise it is necessary to change the molecular structure or configuration of some of the material which is available in excess or that excess of material cannot be utilized.

Also, as stated before, the normal paraffins enter very reluctantly into reaction unless their molecular structure is changed by suitable methods. Therefore the normal paraffin content of these light hydrocarbons is often practically unutilizable unless treated to change it to a more reactive form. This is accomplished either by dehydrogenation or by isomerization, or both. In the simple dehydrogenation of paraffins to olefins a molecule of hydrogen is released for each olefin molecule produced. To exercise the greatest economy and conservation of resources it is desirable to bring this hydrogen again into combination with the hydrocarbons produced by polymerization of the olefins insofar as is possible, a step which is accomplished by hydrogenation, preferably with the aid of efficient catalysts.

One main object of this invention therefore is to provide a process of utmost flexibility to convert to more useful hydrocarbons suitable for premium aviation and motor fuels light hydrocarbons of two to seven carbon atoms per molecule, or more, which may contain normal and isomeric paraffins, and/or olefins in any proportions and to so process these hydrocarbons that the entire available production may be utilized to the greatest advantage.

Another object is to provide methods by which the molecular structure of available hydrocarbons may be changed and altered so as to produce the desired proportions of the different types of hydrocarbons to meet the requirements of the products and to provide the widest flexibility in operation regardless of the composition of the original materials available.

A further object of our invention is to produce a normally liquid hydrocarbon mixture having characteristics of vapor pressure, volatility, boiling range, octane number, sulfur content, etc., to

suit it for use as an automobile or aviation fuel.

Other objects and advantages will become apparent to one skilled in the art from the accompanying disclosure and discussion.

As one modification of our process alkylation and polymerization reactions are carried out in the same reaction vessel, simultaneously. Using a suitable catalyst or combination of catalysts and a suitable correlation of reaction conditions, the two reactions occur concurrently where a charge stock is utilized containing some isoparaffin and an excess of olefin over and above that which enters into an alkylation reaction with the isoparaffin present. Such catalysts include aluminum chloride or ferric chloride in the presence or absence of added hydrogen halides, phosphoric acid and metal phosphates, sodium chloroaluminate, and other suitable materials. Catalysts such as concentrated sulfuric acid and concentrated hydrofluoric acid may also be used, although a proper correlation of other reaction conditions to produce both alkylation of isoparaffins and an appreciable amount of polymerization, so that the product contains an appreciable amount of olefinic polymers, is often somewhat difficult to maintain.

Heretofore, in the preparation of premium motor fuels, it has been considered desirable to have essentially paraffinic products, or at least products essentially free of unsaturates such as olefins, cycloolefins, and the like. However, it has more recently been found that when using liquid-cooled engines, especially in service requiring frequent and sometimes sustained acceleration, the presence of such unsaturates is not only permissible but often even desirable. In such an instance advantage may be taken of this modification of our invention to produce, in a single operation, aliphatic hydrocarbon material containing substantial and controllable amounts of isoparaffins and isoolefins, both of high octane number. At the same time alkylation equipment designed to produce a given amount of a completely paraffinic product can produce greater amounts per unit time of such a mixed product by reason of the greater throughput permitted by a shorter reaction time. When a more highly paraffinic product is desired than that resulting from such an operation, the product, or fractions thereof, may be subjected to non-destructive hydrogenation. Such an operation is simple and can be carried out in simple equipment with hydrogen produced in a previous dehydrogenation step in the process, so that often the net result is an increased yield of a paraffinic product from existing equipment at less expense of money and time than would result from a similar increase in capacity by installation of additional alkylation equipment.

Such an alkylation-polymerization operation, or polyalkylation, is carried out under conditions such that the concentration of unreacted olefins in the reaction zone is higher than is permitted in usual paraffin alkylation operations, and at somewhat higher temperatures. Generally a greater flow rate, or lower reaction time, is also used. Preferably the concentration of unreacted olefin is maintained above ten per cent by weight, although it should not be above about 40 or 45 per cent by weight. The reaction time, temperature and pressure will be dependent, in each case, upon the catalyst used, its activity, and the reactants, and can be readily determined and established for any particular instance by one skilled in the art. These conditions are best cor-

related to give a normally liquid product containing 10 to 60 per cent by weight of olefinic products of the reaction. Under suitable conditions the initial step of isomerization of normal paraffins present in a mixture of hydrocarbons also may be carried out along with the other steps mentioned above, preferably catalytically in the first section of the combined reaction zone. Such a method permits the utilization of a mixture of normal and isomeric paraffins and olefins with a minimum of equipment in a simple manner and with the fewest steps. The olefinic polymer formed during the combined reaction may be retained in the mixture of products and used as such, or may be partially or completely hydrogenated catalytically with hydrogen from any source to yield a saturated product of greatly enhanced anti-knock properties.

Another method of handling a mixture of normal and isomeric paraffin hydrocarbons is to fractionate the mixture to separate the straight-chain or normal paraffin from the isoparaffin. After separation of the normal paraffin this stream may be split, part of it being dehydrogenated with a suitable catalyst to supply additional olefin charge for the alkylation reaction with the isoparaffins recovered, while the other part of the normal hydrocarbon stream is isomerized catalytically and added to the original isomer stream for use in the alkylation step. With any charge stock of light hydrocarbons of any given composition the operator skilled in the art can easily calculate the proportion of the normal paraffin stream to be isomerized and that to be dehydrogenated. The entire straight-chain fraction may be dehydrogenated and included with the isomer fraction which will combine with the theoretical portion of the olefin in the alkylation reaction, the remainder of the olefin present being polymerized in the same or a different step, and hydrogenated in another step if desired, with the hydrogen freed during the dehydrogenation step. The proportion of olefin may be any percentage, preferably above ten per cent, in the alkylation-polymerization step.

Reference will now be made to the drawing which forms a part of the specification and which illustrates diagrammatically by use of a flow sheet an arrangement of apparatus in which our invention may be practiced together with various modifications thereof. The description of this drawing will serve to exemplify our invention and optimum conditions will be given for operation of various process steps.

Referring now to the drawing, a suitable hydrocarbon mixture such as a raw natural gasoline having a composition as indicated in the following table, is passed through pipe 10 to an alkali washer 11.

	Mol per cent
Ethane	1.2
Propane	46.9
Isobutane	8.4
N-butane	26.4
Isopentane	5.4
N-pentane	4.9
Isohexane	2.9
N-hexane	1.9
Heptane	2.0
	100.0

The hydrocarbon material may contain substantial amounts of organic sulfur compounds such as mercaptans which are not indicated

in the table just mentioned, but which will be distributed throughout the various fractions shown, particularly those of the C_4 and heavier hydrocarbons. In the alkali washer 11 such a sulfur-containing material is contacted with aqueous solution of a suitable alkali such as sodium hydroxide or sodium carbonate which will remove any residual hydrogen sulfide and also any lower boiling mercaptans, particularly methyl mercaptan. From alkali washer 11 the hydrocarbon material may be passed through copper sweetening unit 12 wherein mercaptans are converted to disulfides. This operation may be a so-called solid copper sweetening unit in which the liquid hydrocarbon material is contacted with an absorbent such as fuller's earth on which is an aqueous solution containing copper and chloride ions, such as is found in a solution of copper sulfate and sodium chloride. Other sweetening treatments known to the art may be used instead, however we have found the one just described to be the simplest and most efficient.

From copper sweetening unit 12 the hydrocarbon material is passed to suitable separating means represented by fractionator 13. By means of such a fractionator, which in reality includes a series of fractionating columns together with normally occurring auxiliary apparatus, the hydrocarbon material is separated into various fractions as will be discussed. Low boiling hydrocarbons such as ethane and perhaps a portion of the propane can be discharged from the system through valved pipe 14. A propane fraction is removed through pipe 15 controlled by valve 16 to a dehydrogenation step, which is preferably catalytic, carried out in dehydrogenator 17. A suitable catalyst may comprise chromium oxide, preferably a black unglowed chromium oxide, which may be associated with other constituents such as alumina or zirconia or the like and which is preferably on a supporting material such as pumice, dehydrated bauxite, etc. Dehydrogenation can be carried out at a temperature within the range of about 900 to 1100° F. with a contact time such as to produce from 15 to 40% of olefins in the effluent material. From dehydrogenator 17 the effluent is passed through pipe 18 to separating means 20. In separating means 20 hydrogen is separated from hydrocarbon constituents and may be discharged through valved pipe 21. In some instances it may be found desirable to include also apparatus for separating paraffins from olefins as by selective solvent extraction, as is known to the art. A propylene-containing material is passed from separating means 20 through valve 21 to conduit 22 for reacting in the polyalkylation step to be described.

An isobutane fraction is removed from fractionator 13 through pipe 23 and valve 24 to a suitable alkylation unit or polyalkylation unit 25. A normal butane fraction is removed from fractionator 13 through pipe 26 and is passed at least in part through valve 27 to dehydrogenator 28 wherein dehydrogenation is effected to form principally butenes. This dehydrogenation is preferably catalytic and may be carried out in the presence of a catalyst such as has been discussed in connection with the operation of dehydrogenator 17 and under similar conditions. The temperature range within which the dehydrogenation is carried out may be somewhat lower, such as within the range of about 800 to 1050° F. with a similar extent of conversion. From dehydrogenator 28 effluents are passed through pipe 30 to

separating means 31, the operation of which will be similar to that just discussed for separating means 20. Hydrogen is discharged through valved pipe 32. A butene-containing material is passed through valved pipe 33 to unit 25. The operation in unit 25 may be entirely one of alkylation to produce as highly a paraffinic product as possible under alkylation conditions, preferably in the presence of a catalyst such as will be readily ascertained by one skilled in the art. However, we prefer to operate unit 25 as a polyalkylation unit under conditions such as have been discussed hereinbefore to produce a product which contains both normally liquid paraffin hydrocarbons resulting from alkylation and normally liquid olefin hydrocarbons resulting from polymerization of olefins charged through pipes 22 and/or 33. Thus, we may maintain a relatively high olefin concentration such as one substantially above 10% by weight and react the material charged in the presence of a catalyst comprising sodium chloroaluminate at a temperature between about 300 and 450° F. Effluents of the polyalkylation step pass through pipe 34 and are preferably passed through valve 35 to separating means such as fractionator 36. From fractionator 36 propane may be removed through valved pipe 37 and returned to pipe 15 and dehydrogenator 17 for dehydrogenation. An isobutane fraction may be removed through valved pipe 38 and returned to pipe 23 and unit 25. A normal butane fraction may be removed through valved pipe 39 to pipe 26 and dehydrogenator 28. Undesirable low boiling material may be discharged through valved pipe 41, and undesired high boiling material may be discharged through valved pipe 42. One or more normally liquid hydrocarbon fractions boiling in the motor fuel range may be removed through suitable pipes represented by pipe 43 and may be passed directly through valve 44 for inclusion in a final motor fuel product. When unit 25 is operating as a polyalkylation unit such fractions will include both paraffin and olefins as discussed. If the olefin content is higher than that desired, the fractions may be subjected to partial or complete saturation with hydrogen by being passed from pipe 43 through valve 45 to hydrogenator 46. In hydrogenator 46 a hydrocarbon material is reacted with free hydrogen, which may be introduced with valved pipe 47, in the presence of a suitable hydrogenation catalyst such as metallic nickel deposited on a support such as pumice. The reaction may be satisfactorily carried out at a temperature of about 200 to 450° F. Hydrogen introduced through pipe 47 is preferably secured from one of the previous dehydrogenation steps and discharged through pipes 21 and/or 32. The hydrogenated material is passed from hydrogenator 46 through pipe 48 and may be passed through valve 49 to pipe 43 for inclusion in motor fuel products. If it is desired to fractionate this material, it may be sent to suitable fractionating equipment such as by being passed from pipe 48 through valve 50 back to separating means 36. In some instances it may be found expedient to subject the hydrocarbon effluent of unit 25 to hydrogenation without a previous fractionation, in which case the effluent may be passed from pipe 34 through pipe 51 and valve 52 directly to hydrogenator 46, in which case separating means 36 may have as the charge only material which is effluent from hydrogenator 46.

An isopentane fraction is removed from fractionator 13 through pipe 53 and may be passed

through valve 54 to pipe 43 for direct inclusion in the final motor fuel produced. If desired, a portion of this material may be passed from pipe 53 through valved pipe 55 to pipe 23 and unit 25 for alkylation.

When a sulfur-containing natural gasoline or straight-run gasoline is charged through pipe 10 and is given the preliminary treatment indicated for units 11 and 12, the amount of sulfur compounds which will be present in the fractions just discussed will generally be negligible and all of the sulfur will be concentrated in the heavier fractions. Some of this sulfur may or may not in particular cases be in the lower boiling portions of these fractions. When sulfur compounds are present in the lower boiling fractions a normal-pentane-and-heavier fraction is removed through pipe 56 from fractionator 13 and may be passed through pipe 57 and valve 58 to desulfurizer 60. In desulfurizer 60 sulfur is removed by many suitable means, preferably by passing the stock in the vapor phase into contact with a catalytic material such as bauxite, brucite, etc. at a temperature between about 500 and 750° F. for a time such as to effect a substantially complete decomposition of sulfur compounds, primarily into hydrogen sulfide and olefins with at most only a slight decomposition of hydrocarbon constituents. Hydrogen sulfide may be separated from the effluents by suitable means, such as distillation or alkali wash, and removed through valved pipe 61, and the desulfurized hydrocarbon material may be passed through pipe 62 and valve 63 to fractionator 64. If the low boiling fractions do not contain sufficient sulfur compounds to warrant desulfurization at this point, the fraction of normal-pentane-and-heavier may be passed directly through valve 65 to fractionator 64 with desulfurizer 60 omitted. From fractionator 64 a normal pentane fraction is removed through valved pipe 66 and may be passed directly to isomerizer 80. An isohexane fraction may be removed from fractionator 64 and passed through valved pipe 67 to pipe 43 for inclusion in the final motor fuel product. A normal hexane fraction may be removed through valved pipe 68 and passed to pipe 66 and isomerizer 80. A heptane-and-heavier fraction is removed through pipe 70. If further desulfurization is desired at this point, or desulfurizer 60 has been by-passed, this heptane-and-heavier fraction may be passed through pipe 71 and valve 72 to a desulfurizer 73 which can be operated under conditions similar to those described for desulfurizer 60. Hydrogen sulfide may be removed through valve pipe 74 and a desulfurized material is passed through pipe 75 and valve 76 to fractionator 77. When desulfurizer 60 has been previously used and has effected a satisfactory extent of desulfurization, desulfurizer 73 may be omitted and the heptane-and-heavier fraction passed through valve 78 directly to fractionator 77. An iso-heptane fraction is removed from fractionator 77 through valved pipe 79, and is passed to pipe 43 for inclusion in the motor fuel product. A normal-heptane-and-heavier fraction is removed through valved pipe 81 and is passed to pipe 66 and isomerizer 80. In some instances it may be desirable to remove from the material passed through valved pipe 81, an isooctane fraction, in which case additional fractionating equipment, not shown, can be included for use in the process. However, in many instances further fractionation cannot be economically justified and the operation indicated will be found most satisfactory.

In isomerizer 80 the various hydrocarbon materials charged through pipe 66 are subjected to the action of an isomerization catalyst and converted primarily into paraffin hydrocarbons having more highly branched molecular structure. Such isomerization may be carried out in the presence of a catalyst such as aluminum chloride, aluminum bromide, ferric chloride and the like known to the art, preferably in the presence of small amounts of the corresponding hydrogen halide. Concentrated hydrofluoric acid is also an effective and efficient catalyst for this operation. The reaction temperature will generally be in the range of about 200 to 350° F. and the pressure may be such as to maintain a liquid phase or a gas phase as may be found most suitable in any particular instance. The reaction should be conducted with a reaction time such that about 30 to 50% of the paraffins charged undergo reaction. The resulting isoparaffinic fraction may be removed from isomerizer 80 through valve 82 and passed to pipe 43 for inclusion in the final motor fuel products. Undesired heavy material may be discharged through valved pipe 83. Low boiling isoparaffins primarily isobutane, may be passed through valved pipe 84 to pipes 38 and 23 and unit 25. Such isobutane may result from decomposition reaction of higher boiling hydrocarbons in isomerizer 80. In some instances it may be desirable to charge normal butane to isomerizer 80 by removing a portion of the stream passing through pipe 26 through pipe 85 and valve 86, and passing it through valve 87 to pipe 66 and isomerizer 80. In such a case at least a considerable portion of the isobutane which is passed through pipe 84 will be a product of the isomerization of normal butane. If desired a substantial amount of normal butane may be recovered as an independent product of the process through valve 88. If desired some normal butane so removed may be included in the final motor fuel product to produce a desired vapor pressure.

It will be appreciated that the various separating and fractionating units 13, 36, 64 and 77 will be operated so as to effect a production of the fractions having substantially the composition of the hydrocarbons used to identify them, particularly for the lower-boiling fractions. Each such fraction may be associated with small amounts of hydrocarbons in adjacent boiling ranges but such other hydrocarbons should not be present in quantities so large that the fraction cannot be satisfactorily identified as indicated. In some instances the individual fraction may comprise the indicated hydrocarbon in a purity of about 95% or more. It has also been found that some of the fractions of some natural gasolines and also some straight-run gasolines will include cycloparaffins and this is particularly true in connection with some of the higher boiling isoparaffinic fractions. Such cycloparaffins often contribute to the desired characteristics of the final motor fuel product. In some types of motor fuels aromatic hydrocarbons are desirable, particularly alkyl benzenes in aviation gasolines. One or more of the dehydrogenation steps may be directed to the production of such aromatics. The various normal paraffin fractions have been shown as being isomerized in a single operation, but it will be understood that one or more fractions may be treated individually in this manner. As a variant, one or more of such fractions, particularly the normal heptane or the normal octane fraction, may be subjected to aromatiza-

tion to form alkyl benzenes for inclusion in the final product.

Many other modifications and variations of this invention may obviously be used and can be adapted by one skilled in the art without departing from the spirit of the disclosure. It will be understood that the flow diagram is schematic, that only essential pieces of equipment and conditions have been described, and the reactions and modifications are discussed in sufficient detail to serve as efficient guides.

We claim:

1. A process for converting a natural, sulfur-bearing saturated hydrocarbon mixture containing propane and heavier hydrocarbons including normally liquid hydrocarbons into a substantially sulfur-free normally liquid motor fuel product, which comprises washing said mixture with an alkali to remove low-boiling mercaptans, subjecting the washed mixture to a sweetening treatment to convert remaining mercaptans to higher boiling disulfides which are higher-boiling than hexanes, subjecting the sweetened mixture to fractional distillation and removing therefrom a propane fraction, an isobutane fraction, a normal butane fraction, an isopentane fraction, a normal pentane fraction, an isohexane fraction, a normal hexane fraction, and a heptanes-and-heavier fraction, subjecting said heptanes-and-heavier fraction to a catalytic desulfurization at an elevated temperature to convert organic sulfur compounds into hydrogen sulfide and removing same from the process, subjecting the desulfurized material to fractional distillation and removing therefrom an isoheptane fraction, a normal heptane fraction, an isooctane fraction, and a normal octane fraction, each of which is substantially sulfur-free, subjecting said propane fraction to dehydrogenation to form propylene, subjecting at least a portion of said normal butane fraction to dehydrogenation to form butylenes, reacting said propylene and said butylenes with said isobutane fraction in a catalytic alkylation step to form normally liquid hydrocarbons boiling in the motor fuel range, subjecting said normal pentane, normal hexane, normal heptane and normal octane fractions to isomerization in the presence of an isomerization catalyst to form more highly branched normally liquid paraffin hydrocarbons, and blending products of said alkylation, products of said isomerization, said

isopentane fraction, said isohexane fraction, said isoheptane fraction and said isooctane fraction to form a normally liquid hydrocarbon mixture having motor fuel characteristics of vapor pressure, volatility, and boiling range, and having high antiknock characteristics and a low sulfur content.

2. A process for converting a natural, sulfur-bearing saturated hydrocarbon mixture containing propane and heavier hydrocarbons including normally liquid hydrocarbons into a substantially sulfur-free normally liquid motor fuel product, which comprises washing said mixture with an alkali to remove low-boiling mercaptans, subjecting the washed mixture to a sweetening treatment to convert remaining mercaptans to higher boiling disulfides which are higher-boiling than hexanes, subjecting the sweetened mixture to fractional distillation and removing therefrom a propane fraction, an isobutane fraction, a normal butane fraction, an isopentane fraction, a normal pentane fraction, an isohexane fraction, a normal hexane fraction, and a heptanes-and-heavier fraction, subjecting said heptanes-and-heavier fraction to a catalytic desulfurization at an elevated temperature to convert organic sulfur compounds into hydrogen sulfide and removing same from the process, subjecting the desulfurized material to fractional distillation and removing therefrom an isoheptane fraction and a heavier motor-fuel-range fraction, each of which is substantially sulfur-free, dehydrogenating said propane fraction to form propylene, dehydrogenating at least a portion of said normal butane fraction to form butylenes, reacting said propylene and said butylenes with said isobutane fraction in a catalytic alkylation step to form normally liquid hydrocarbons boiling in the motor fuel range, subjecting said normal pentane, normal hexane, and heavier motor-fuel-range fractions to isomerization to form more highly branched normally liquid paraffin hydrocarbons, and blending products of said alkylation, products of said isomerization and said isopentane, isohexane and isoheptane fractions to form a normally liquid hydrocarbon mixture having motor fuel characteristics of vapor pressure, volatility, and boiling range, and having high antiknock characteristics and a low sulfur content.

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