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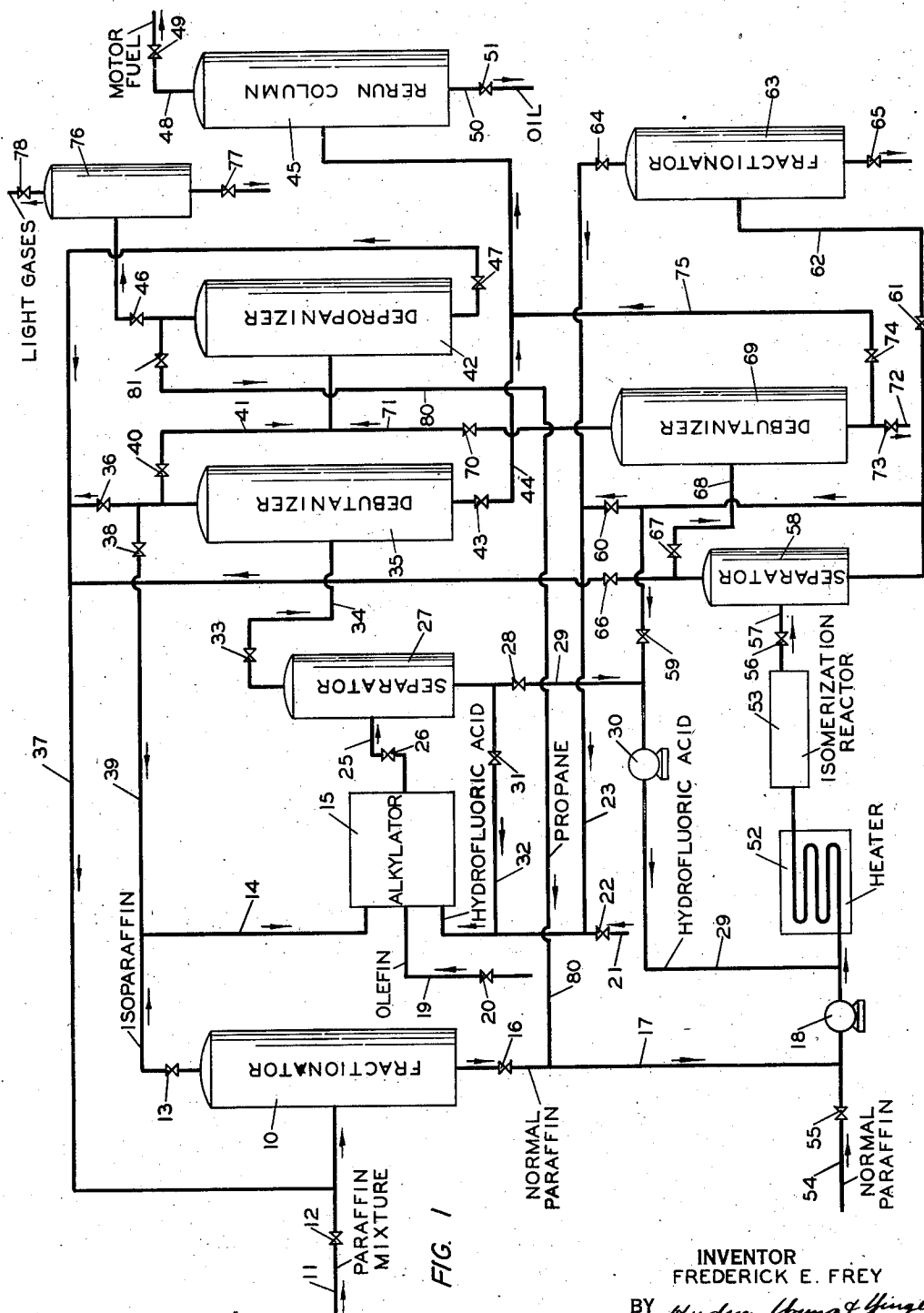
F. E. FREY

2,404,483

PRODUCTION OF MOTOR-FUEL HYDROCARBONS

Filed March 12, 1942

2 Sheets-Sheet 1



INVENTOR
FREDERICK E. FREY
BY *Hudson, Young & Young*
ATTORNEYS

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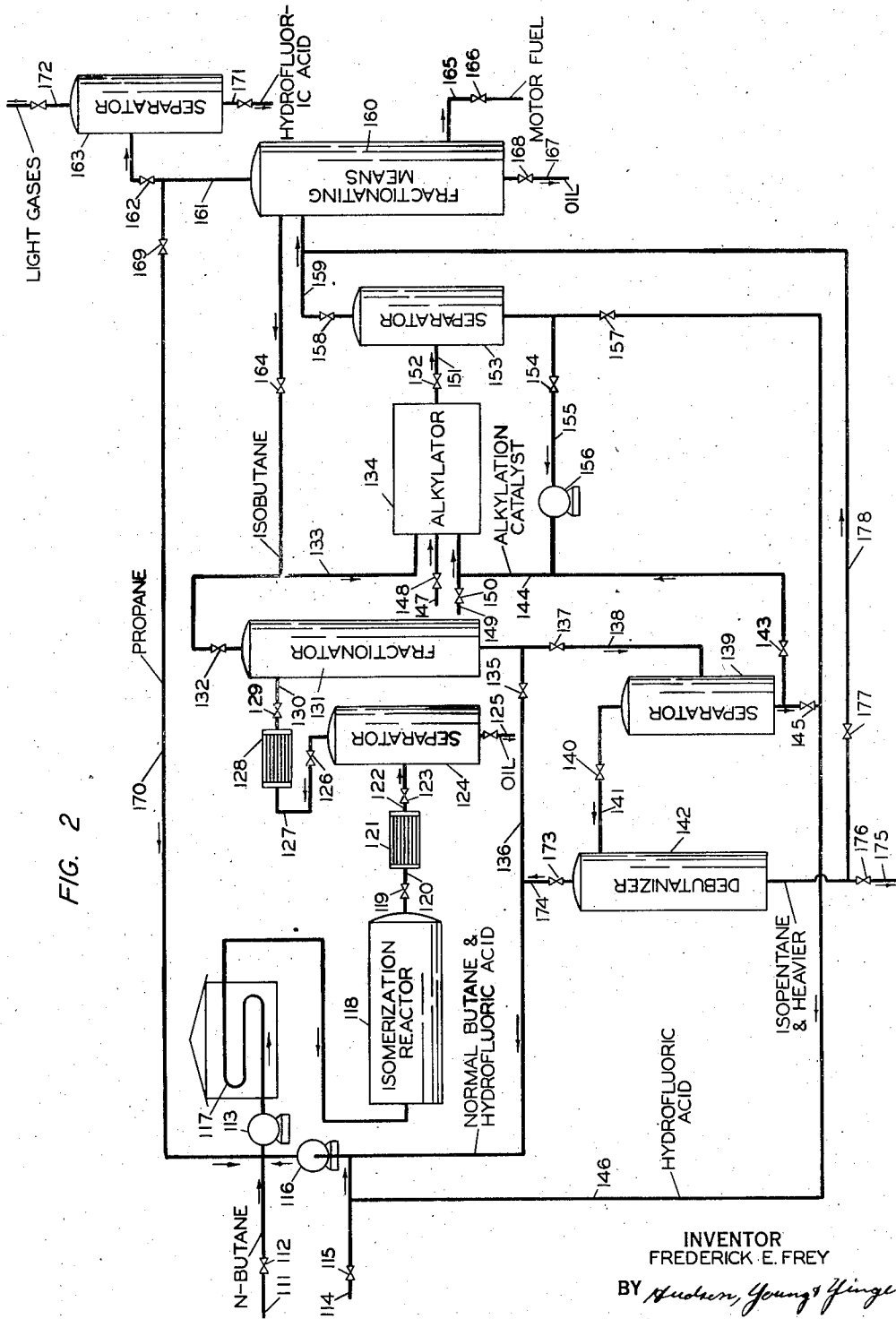
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UNITED STATES PATENT OFFICE

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PRODUCTION OF MOTOR-FUEL
HYDROCARBONSFrederick E. Frey, Bartlesville, Okla., assignor to
Phillips Petroleum Company, a corporation of
Delaware

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9 Claims. (Cl. 260—683.4)

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This invention relates to the conversion of hydrocarbons. More particularly, it relates to the production of motor-fuel hydrocarbons from relatively low-boiling hydrocarbons by a process in which hydrofluoric acid is used as a catalyst. This application is a continuation-in-part of my co-pending application, Serial No. 426,627, filed January 13, 1942, and Serial No. 432,679, filed February 27, 1942.

An object of this invention is to convert relatively low-boiling normal paraffin hydrocarbons, such as normal butane and/or normal pentane, to higher-boiling saturated hydrocarbons.

Another object of this invention is to produce a motor fuel stock from relatively low-boiling paraffins by a process in which used hydrofluoric acid catalyst from an alkylation step is used as a catalyst for isomerizing normal paraffins to isoparaffins suitable for use in the alkylation step.

A specific object is to combine, in a process for converting normal butane to motor fuel, an isomerizing step with an alkylating step in such a way that the material charged to the alkylating step is substantially free from normal paraffins.

Another specific object is to produce a motor fuel of high octane number in increased yield and of increased volatility as compared to that which is produced by ordinary alkylation processes.

A specific object of this invention is to produce a motor fuel stock from relatively low-boiling paraffins by a combination isomerization-alkylation process in which an azeotropic mixture of hydrofluoric acid and an isoparaffin is distilled from the effluent from an isomerizing step and is passed to an alkylating step.

Other objects and advantages of this invention will be apparent from the accompanying description and discussion.

Isoparaffins of relatively low molecular weight, such as isobutane and isopentane, can be reacted in the presence of an alkylation catalyst, such as concentrated hydrofluoric acid, at a comparatively low reaction temperature, for example, in the range of 0 to 200° F., with alkylating reactants such as olefins having 3 to 5 carbon atoms per molecule and corresponding alkyl compounds such as alkyl halides, alcohols, ethers, esters, and the like, preferably those of secondary or tertiary structure, to produce hydrocarbons in the motor-fuel range which have high antiknock values and that are suitable for use in aviation gasoline. Normal paraffins, such as normal butane and normal pentane, can also be alkylated, but only under considerably more drastic conditions, so that

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the product usually is of lower quality in respect to octane number and is produced in lower yield than that obtained by alkylating the corresponding isoparaffins.

In such alkylation processes, the hydrofluoric acid eventually becomes so spent or deactivated by acid-soluble and/or fluoro-organic by-products that it is unsuited for continued use; the spending or deactivation is especially rapid at elevated temperatures, such as those required for the alkylation of normal paraffins. Disposal of the spent acid is a considerable problem, because of the corrosive nature of the acid; furthermore, heretofore no use for the spent acid has been known, so that in the past it has been necessary to provide acid-recovery steps, such as distillation to recover the free hydrogen fluoride, and thermal decomposition and distillation to liberate and recover the organically combined fluorine as hydrogen fluoride.

The product obtained by catalytic alkylation usually consists of primary alkylation products, for example when alkylating isobutane with butylenes the product usually consists predominantly of octanes with relatively small proportions of low-boiling hydrocarbons such as pentanes and hexanes. Because of this fact, it is usually necessary to increase the volatility of the product, so that it may be efficiently used as in aviation gasoline, by adding additional relatively low-boiling hydrocarbons, such as isopentane and branched hexanes.

I have now found that spent or partly deactivated hydrofluoric acid from an alkylating step can be advantageously used as a catalyst in an isomerizing step to convert relatively low-boiling normal paraffins, such as normal butane and/or normal pentane, into isoparaffins, such as isobutane and/or isopentane, that are suitable for conversion to motor-fuel hydrocarbons in the alkylating step. I have also found that appreciable proportions of motor-fuel hydrocarbons are formed by secondary reactions in this isomerizing step, and that these hydrocarbons can be advantageously added to the product of the alkylating step to increase the yield and the volatility of aviation-grade motor fuel. Further, I have found that from the effluent from such a conversion can be distilled a low-boiling or azeotropic mixture comprising isobutane and hydrogen fluoride, which is suitable for use as feed material to an alkylating step.

In one specific embodiment, for example, the present invention comprises isomerizing normal butane by the isomerizing action of hydrofluoric

acid previously used in an alkylation step, using the resulting isobutane for conversion to motor-fuel hydrocarbons by hydrofluoric acid-catalyzed alkylation, and combining the products boiling above the butane range in such manner as to obtain a motor fuel of desirably high anti-knock rating and volatility.

An advantageous feature of my invention is an azeotropic-distillation step, interpositioned between an isomerizing step and an alkylating step, for separating isobutane and lighter hydrocarbons from normal butane and heavier hydrocarbons. By this particular step, an efficient separation of isobutane from normal butane is effected with a minimum of fractionating equipment. The resulting overhead mixture comprises, as well as isobutane, a substantial proportion of hydrofluoric acid in a relatively active and anhydrous condition, in which it is suitable for use as catalyst in an alkylating step; this overhead mixture is advantageously charged directly to the alkylating step with no prior treatment other than condensing and cooling to a suitable temperature.

Another advantageous feature of my invention is the blending of low-molecular-weight normally liquid hydrocarbons, chiefly isopentane and isomeric hexanes, which are produced by side and secondary reactions in an isomerizing step, with the alkylate produced in an alkylation step to increase the volatility of the alkylate. These low-molecular-weight normally liquid hydrocarbons are preferable to natural-gasoline fractions of a corresponding boiling range, which are sometimes blended in motor fuel to increase its volatility, because they comprise relatively larger proportions of branched-chain paraffins and hence have higher octane numbers than those of the natural-gasoline fractions.

An understanding of some aspects of my invention may be aided by a consideration of the accompanying drawings, in which Figure 1 is a schematic flow-diagram of one arrangement for practicing the invention and Figure 2 a schematic flow-diagram of another arrangement for practicing my invention.

Referring now to Figure 1, a low-boiling hydrocarbon material, for example a mixture of normal butane and isobutane, is admitted to fractionator 10, as through inlet 11 having valve 12 and/or through conduit 37. By fractionator 10 it is separated into a concentrated isobutane fraction, which is passed through valve 13 and conduit 14 to alkylator 15, and into a normal butane fraction, which is passed through valve 16 and conduit 17 to pump 18.

In alkylator 15, the isobutane is mixed under alkylating conditions with an alkylating reactant, such as an olefin of three to five carbon atoms per molecule, preferably butylene, which may be admitted through inlet 19 and valve 20, and with concentrated hydrofluoric acid, preferably anhydrous, which may be admitted through inlet 21 and valve 22 and/or through conduit 23 as the alkylation catalyst.

In the composite feed to alkylator 15, the weight ratio of isoparaffins to olefins, or other alkylating reactant, preferably is in the range of 2:1 to 20:1 or more, and the weight ratio of hydrofluoric acid to total hydrocarbons preferably is in the range 0.2:1 to 4:1. The olefin preferably is introduced into the reaction mixture under conditions of high turbulence and/or in multipointwise fashion, so that it is rapidly mixed and diluted with the isoparaffin reactant. This procedure is ad-

vantageous in order to favor the desired olefin-isoparaffin junctures, or alkylation reactions, and to hinder undesirable olefin-olefin junctures, or polymerization reactions. Preferred operating conditions in alkylator 15 are a temperature in the range of 30 to 150° F., a pressure sufficient to maintain all components in the liquid phase, and a reaction time of about 1 to 30 or more minutes; but if desired other conditions may be used in particular cases without passing beyond the scope of this invention.

The resulting mixture passes through conduit 25 having valve 26 to separator 27, wherein it is separated into two liquid phases as by cooling and gravitational or centrifugal means.

The heavier or hydrofluoric acid phase is passed through valve 28, and conduit 29 to pump 30. If desired, however, part of the acid may be recycled to alkylator 15 through valve 31 and conduit 32.

The lighter or hydrocarbon phase from separator 27 is passed through valve 33 and conduit 34 to debutanizer 35. An overhead fraction, which is usually predominantly isobutane but which at times may comprise other gases and vapors, such as hydrofluoric acid, propane, and normal butane, may be passed from debutanizer 35 through valve 36 and conduit 37 to fractionator 10; if little or no normal butane is present, this fraction preferably is passed directly to alkylator 15, as through valve 38 and conduit 39. Preferably also, when there is some excess propane and incidental difficultly condensible gases, such as methane and ethane, part of the debutanizer overhead is passed through valve 40 and conduit 41 to depropanizer 42, from which these gases are passed through valve 46 to separator 46, and from which the resulting concentrated butanes are passed to fractionator 10 through valve 47. A normally liquid kettle product from debutanizer 35 is passed through valve 43 and conduit 44 to rerun column 45 wherein it is separated into two fractions: (1) a major motor-fuel fraction comprising hydrocarbons suitable for use in aviation gasoline, which is withdrawn through outlet 48 having valve 49, and (2) a bottom fraction comprising hydrocarbons boiling above the motor-fuel range, which is withdrawn through outlet 50 having valve 51.

Normal butane from fractionator 10 and hydrofluoric acid from separator 27 are forced by pumps 18 and 30, respectively, through heating coil 52 to reactor 53, wherein the normal butane is isomerized to isobutane to a substantial extent. If desired, additional normal butane may be admitted, as through inlet 54 and valve 55; at times such normal butane may be the sole paraffin feed to the process.

In the feed to reactor 53, the ratio of hydrofluoric acid to hydrocarbon is preferably in the range of about 0.2:1 to 4:1 or more by weight; usually, operating with an acid-to-hydrocarbon ratio within this range will effect the maximum conversion of normal paraffins to isoparaffins. The exact ratio desired for any particular case may be obtained by controlling the relative proportions of spent acid from separator 27 that pass through valves 28 and 31, respectively.

The temperature in reactor 53 may be within the range of about 250 to 1000° F. A temperature in the range 400 to 800° F. is usually preferred; at low temperatures the rate of reaction is low, and at high temperatures some cracking and carbon formation occurs. The pressure may be within the range of atmospheric to 5000 pounds per square inch or more; usually it is preferred,

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for reasons of economy in equipment and operating costs, to use a pressure in the range of 250 to 2000 pounds per square inch. The reaction time may be within the range of about 1 to about 300 minutes depending chiefly upon the temperature; the time required decreases with increase in temperature. If the reaction time is very short, such as 1 to 5 minutes, the reaction can be completed in coil 52 or an extension thereof; whereupon reactor 53 may be by-passed or removed from the system by means not shown. Preferably, the reaction zone is packed with a contact mass, such as steel turnings, alumina, bauxite, or other material resistant to corrosion by hydrofluoric acid and suitable for promoting the reaction and/or heat transfer.

The resulting mixture from reactor 53 is passed through valve 56 and conduit 57 to separator 58, wherein it is separated into two liquid phases as by cooling and gravitational or centrifugal means.

Although the heavier or hydrofluoric acid phase from separator 58 may be recycled to coil 52 and/or alkylator 15, as through valve 59 and/or valve 60, at least a part of it is preferably passed through valve 61 and conduit 62 to fractionator 63. In this fractionator it is separated into (1) an overhead fraction comprising substantially anhydrous hydrofluoric acid, which is passed through valve 64 and conduit 23 to alkylator 15, and (2) a bottom fraction, or sludge, comprising acid-soluble materials, which may be withdrawn through valved outlet 65.

The lighter or hydrocarbon phase from separator 58 may be passed through valve 66 and conduit 37 to fractionator 10; however, in order to recover valuable normally liquid hydrocarbons produced in the isomerizing step by secondary reactions, it is preferably passed through valve 67 and conduit 68 to debutanizer 69, wherein it is separated into fractions. The overhead fraction, which comprises propane, normal butane, and isobutane, and generally some hydrofluoric acid, is passed through valve 70 and conduit 71 to depropanizer 42; the bottom fraction, which comprises isopentane, hexanes, and other hydrocarbons, may be withdrawn through outlet 72 having valve 73, but is preferably passed, at least in part, through valve 74 and conduit 75, together with normally liquid alkylation products from debutanizer 35, to rerun column 45.

In separator 76 hydrofluoric acid is separated as a liquid phase from the overhead fraction from depropanizer 42, as by cooling and gravitational means. The acid may be withdrawn through valved outlet 77, but preferably is recycled to alkylator 15 or coil 52 by means not shown. Propane and other light gases are withdrawn through valved outlet 78. A part or all of the propane-containing fraction removed from the top of depropanizer 42 may be passed directly to the isomerization step through conduit 80, controlled by valve 81, to conduit 17 and heater 52.

Referring now to Figure 2 a suitable hydrocarbon material, such as a mixture comprising chiefly normal paraffins, preferably normal butane, is admitted through inlet 111, valve 112, and pump 113. To this hydrocarbon material is added hydrofluoric acid previously used in the alkylation step, from acid-recycle conduit 146, by pump 116; if desired, additional acid may be admitted through inlet 114 and valve 115. The resultant acid-hydrocarbon mixture is passed through heater 117 to reactor 118. The operation of heater 117 and reactor 118 are substantially as described for heater 52 and reactor 53.

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The resulting mixture in reactor 118 is passed through valve 119 and conduit 120 to partial condenser 121, wherein, by a suitable cooling means, relatively high-boiling material, such as hydrocarbons boiling above approximately the pentane range, heavy hydrofluoric acid-soluble material, and the like, are condensed or liquefied. Suitable conditions in partial condenser 121 are a temperature in the range of 125 to 400° F. and a corresponding pressure in the range of 15 to 400 pounds per square inch. The optimum conditions are readily determinable by trial and/or from well-known vapor-pressure relationships of the various constituents. Conditions outside the ranges given above may be used, if desired or necessary for any particular case.

The resulting partly liquefied mixture from partial condenser 121 is passed through conduit 122 and valve 123 to separator 124, wherein it is separated into a gas phase and a liquid phase. The temperature and the pressure should be as nearly as possible the same as those in partial condenser 121. The liquid phase which comprises mainly hydrocarbons and acid-soluble substances boiling approximately in the hexane range and above, is withdrawn through valved outlet 125. The gas phase is passed through valve 126 and conduit 127 to condenser 128.

In condenser 128, the gas phase from separator 124 is cooled and liquefied. The resulting liquid mixture of acid and hydrocarbon phases, which comprises hydrofluoric acid, isoparaffins, and unreacted normal paraffins, is passed through valve 129 and conduit 130 to fractionating means 131.

Two fractions are withdrawn from fractionating means 131. The overhead fraction, which comprises a low-boiling azeotropic mixture of hydrofluoric acid and isobutane, and usually some lower-boiling material such as propane, is passed through valve 132 and conduit 133 to alkylator 134. The bottom product, which comprises hydrofluoric acid and hydrocarbons boiling above isobutane, may be recycled in part through valve 135 and conduit 136 to coil 117; preferably, however, most of it is passed through valve 137 and conduit 138 to separator 139.

In separator 139 the kettle fraction from fractionator 131 is separated into two liquid phases as by cooling and gravitational means. The lighter or hydrocarbon phase is passed through valve 140 and conduit 141 to debutanizer 142. The heavier or hydrofluoric acid phase may be passed in part through valve 143 and conduit 144 for use as catalyst in alkylator 134, but preferably most or all of it is recycled through valve 145 and conduit 146 to pump 116.

In alkylator 134 the overhead mixture comprising hydrofluoric acid and isobutane from fractionator 131 is mixed under alkylating conditions with an alkylating reactant, such as an olefin having from 3 to 5 carbon atoms per molecule, or an equivalent alkyl compound, which is introduced through inlet 147 and valve 148. Since the overhead mixture usually contains insufficient hydrofluoric acid for effecting with desirably high efficiency the alkylation of the isobutane, additional alkylation catalyst is admitted through inlet 149 and valve 150 and/or through conduit 144. Such additional alkylation catalyst may be any of the alkylation catalysts that are operative in the presence of hydrofluoric acid, but for the sake of simplicity and of eliminating otherwise necessary subsequent catalyst-segregating steps, it may be taken to be addi-

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tional hydrofluoric acid, which is preferred. Usually the hydrofluoric acid admitted through inlet 149 may be the sole catalyst feed to the system.

In the feeds to alkylator 134 the weight ratio of isobutane to olefin, or other alkylating reactant, is preferably in the range of 2:1 to 20:1 or more, and the weight ratio of hydrofluoric acid to total hydrocarbons is preferably in the range 0.2:1 to 4:1. The olefin is preferably introduced into the reaction mixture under conditions of high turbulence and/or in multipointwise fashion, so that it is rapidly mixed with the isobutane. This procedure is advantageous in order to favor the desired olefin-isoparaffin junctures, or alkylation reactions, and to hinder undesirable olefin-olefin junctures, or polymerization reactions. Preferred operating conditions in alkylator 134 are a temperature in the range of 30 to 150° F., a pressure sufficient to maintain all components in the liquid phase, and a time of about 1 to 30 or more minutes; however, conditions outside of these ranges may also be used in particular cases without passing beyond the scope of this invention.

The resulting mixture passes through conduit 151 and valve 152 to separator 153, wherein it is separated into two liquid phases as by cooling and gravitational or centrifugal means.

Part of the heavier or hydrofluoric acid phase may be recycled through valve 154, conduit 155, and pump 156 to alkylator 134; preferably an amount of acid approximately equivalent to, or somewhat greater than, that introduced to the alkylator in the overhead fraction from fractionator 131 is passed through valve 157 and conduit 146 to pump 116 for use in the isomerizing step. It is a particular feature of this invention that the catalyst used for effecting the isomerization reaction is a hydrofluoric acid which is discharged from the alkylation step as spent alkylation catalyst.

The lighter or hydrocarbon phase from separator 153 is passed through valve 158 and conduit 159 to fractionating means 160, in which it is separated into the following four fractions: (1) a low-boiling fraction comprising propane and hydrogen fluoride with minor proportions of incidental gases, such as methane and ethane, which may be passed through conduit 161 and valve 162 to separator 163; (2) a major fraction comprising isobutane, which is recycled via valve 164 and conduit 133 to alkylator 134; (3) a fraction of highly branched paraffinic reaction products boiling within the motor-fuel range, which is withdrawn through outlet 165 having valve 166; and (4) a relatively high-boiling hydrocarbon residue, which is withdrawn through outlet 167 having valve 168. Preferably, to increase the over-all yield, part of the propane-rich low-boiling fraction is recycled through valve 169 and conduit 170 to coil 117 of the isomerizing step.

In separator 163, by cooling and gravitational means, a liquid hydrofluoric acid phase is separated out. This hydrofluoric acid phase may be withdrawn through valved outlet 171, or it may be recycled to alkylator 134 or to coil 117 by means not shown in the drawings. The hydrocarbon residue (gas and/or liquid) is withdrawn through valved outlet 172 and disposed of in any suitable manner.

In debutanizer 142 the hydrocarbon phase from separator 139 is separated by distillation into two fractions. The overhead fraction, which comprises mostly normal butane with some hydro-

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fluoric acid, is recycled through valve 173 and conduit 174 to the isomerizing step. The bottom fraction, which comprises low-boiling normally liquid hydrocarbons, such as isopentane, hexanes, and heptanes, may be withdrawn through outlet 175 having valve 176; preferably, however, at least a part of it is passed through valve 177 and conduit 178 to fractionating means 160, wherein it becomes blended with the liquid alkylation products.

A few of the many aspects of my invention are illustrated by the following examples, which are illustrative, but not necessarily limitative, of the invention.

Example I

In an arrangement similar to that illustrated in Figure 1, a mixture of approximately equal proportions of normal butane and isobutane is charged to a fractional-distillation column, from which an overhead fraction consisting chiefly of isobutane is passed to an alkylation step, and from which a bottom fraction consisting chiefly of normal butane is passed to an isomerization step. Butylenes and concentrated hydrofluoric acid are separately charged to the alkylation step. In this alkylation step, conditions are approximately as follows: temperature, 85° F.; pressure, 125 pounds per square inch; reaction time, 6 minutes; isobutane-to-olefin molal ratio (in the materials entering the alkylation reactor), 10:1; hydrocarbon-to acid weight ratio, 1.5:1; and rapid mixing to maintain intimate contact between the acid and hydrocarbon phases.

The resulting effluent from the alkylation step is separated by gravity into two liquid layers. The heavier or acid layer is passed to the isomerization step. The lighter or hydrocarbon layer is debutanized; the overhead fraction, comprising chiefly unreacted isobutane and hydrofluoric acid, is recycled to the alkylation step; the bottom fraction, comprising normally liquid hydrocarbons, is passed to a rerun column.

In the isomerization step, conditions are approximately as follows: temperature, 500° F.; pressure, 750 pounds per square inch; time, 45 minutes; hydrocarbon-to-acid ratio, about 1:1 by weight; and a contact mass comprising steel turnings in the reactor.

The effluent from the isomerization step is cooled and separated into two liquid phases. The heavier or acid phase is fractionally distilled to recover hydrofluoric acid, which is returned to the alkylation step. The lighter or hydrocarbon phase is also fractionally distilled; it has a hydrocarbon composition about as follows, in per cent by weight: propane, 10; isobutane, 26; normal butane, 51; pentanes (mostly isopentane), 10; hexanes, 3. An azeotropic mixture of propane and hydrofluoric acid is recycled to the isomerization step; the excess propane is withdrawn from the process; the isobutane is passed to the alkylation step; the normal butane is recycled to the isomerization step; and the normally liquid material heavier than butane is passed to the rerun column.

In the rerun column, the mixture of normally liquid hydrocarbons from both the alkylation and the isomerization steps is fractionally distilled to yield an overhead fraction of aviation-range motor-fuel hydrocarbons and a bottom fraction of higher-boiling hydrocarbons. The yield of motor-fuel hydrocarbons is about 205 per cent by weight of the butylenes charged to the alkylation step. The motor-fuel product has an octane number of about 91 and a desirably high volatility.

Example II

In an arrangement similar to that illustrated in Figure 2, normal butane and concentrated hydrofluoric acid are charged to an isomerization stage. The isomerizing conditions are approximately as follows: temperature, 425° F.; pressure, 2000 pounds per square inch (mixed-phase or liquid-and-gas conditions); reaction time, 60 minutes; acid-to-hydrocarbon ratio, 1.5:1. The resulting isomerization effluent comprises a hydrocarbon mixture of approximately the following composition in per cent by weight: propane, 10; isobutane, 26; normal butane, 51; hydrocarbons boiling higher than normal butane, 13.

From the isomerization effluent is withdrawn, by partial cooling and gravitational settling, a liquid product which comprises substantial proportions of pentanes and hexanes. The remaining material is passed to a fractionator from the bottom of which a mixture of hydrofluoric acid and hydrocarbons (mostly normal butane) boiling above isobutane is recycled to the isomerizing stage, and from the top of which a low-boiling mixture comprising chiefly propane, isobutane, and hydrofluoric acid is passed to an alkylator. The composition of this low-boiling mixture is usually about 20 to 30 per cent by weight hydrogen fluoride and 70 to 80 per cent hydrocarbons. Sufficient additional or recycle hydrofluoric acid is introduced to the alkylator to bring the acid-to-hydrocarbon weight ratio up to about 1.1. A relatively small proportion of mixed butylenes, preferably below about 20 per cent by weight of the isobutane, is introduced as alkylating reactant into the alkylator.

The conditions in the alkylator are as follows: temperature, 95 to 125° F.; pressure, 150 to 200 pounds per square inch; average reaction time, 4 minutes; and rapid agitation to maintain intimate contact between acid and hydrocarbon phases.

The resulting effluent mixture from the alkylator is passed to a settler in which it is separated into an acid phase and a hydrocarbon phase. Of the acid phase, a proportion equivalent to that passing from the isomerizing stage to the alkylator is recycled to the isomerizing step; the remainder is recycled to the alkylator. The hydrocarbon phase is passed to a fractionating means, from which are obtained various products and recycle fractions, such as those indicated on the drawings as being obtained from fractionation means 160. The motor-fuel fraction has a clear octane number of about 90 and is suitable for use in aviation gasoline.

There are numerous modifications of my invention, which will be obvious to those skilled in the art of hydrocarbon conversion. For example, if the paraffinic feed material comprises normal paraffins but substantially no isoparaffins, it is advantageously admitted in the modification of Figure 1 to the isomerizing step through inlet 54 and valve 55 instead of to fractionator 10 through inlet 11 and valve 12. Also, if desired, in order to inhibit the formation of low-boiling hydrocarbons in the isomerizing step, a propane-rich fraction, such as that from the top of depropanizer 42 may be recycled to coil 52 through conduit 50 and valve 51. Various catalyst modifiers that do not enter the alkylation reaction under the prevailing conditions, such as organic or inorganic compounds of the type of primary halides or alcohols, polyhalides, sulfur dioxide, organic nitrogen compounds, and the like, may be added to the

hydrofluoric acid. Some change in the flow scheme that will be obvious to those skilled in the art may be advantageous to facilitate the use of such modifiers.

Additional pumps, valves, conduits, coolers, fractionators, and other equipment, such as are well-known in the art of hydrocarbon conversion, may be used wherever they are necessary or convenient for obtaining the results indicated in any particular case. The scope of my invention should not be unduly limited by specific numerical values recited herein.

I claim:

1. A process for producing motor-fuel hydrocarbons, which comprises: isomerizing a low-boiling normal paraffin of four to five carbon atoms per molecule in the presence of concentrated hydrofluoric acid in an isomerization step; separating the effluent from said isomerization step by distillation into an overhead fraction comprising hydrofluoric acid and an isoparaffin of four to five carbon atoms per molecule, and into a bottom fraction comprising hydrofluoric acid and a normal paraffin having four to five carbon atoms per molecule; passing said bottom fraction to said isomerization step; passing said overhead fraction to an alkylating step and alkylating said isoparaffin with an added alkylating reactant in the presence of said accompanying hydrofluoric acid to produce motor-fuel hydrocarbons; and withdrawing the resulting motor-fuel hydrocarbons.

2. The process of claim 1, in which said effluent is freed from material boiling approximately above the pentane range by partial condensation prior to said distillation.

3. The process of claim 1, in which said normal paraffin is normal butane.

4. A process for producing a normally liquid isoparaffinic hydrocarbon material boiling in the motor fuel range from lower-boiling normal paraffin hydrocarbons of at least four carbon atoms per molecule, which comprises subjecting such a normal paraffin to catalytic isomerization in the presence of hydrofluoric acid as the isomerization catalyst to produce low-boiling isoparaffin hydrocarbons, separating from effluents of said isomerization used hydrofluoric acid catalyst and an isobutane fraction and a volatile normally liquid hydrocarbon fraction boiling in the motor fuel range, reacting said isobutane fraction with butenes under alkylation conditions and in the presence of said used hydrofluoric acid catalyst to produce isoparaffins of higher molecular weight and in the motor fuel range, separating an isoparaffinic hydrocarbon fraction comprising predominantly isooctanes so produced, and blending said isooctane fraction and said volatile liquid hydrocarbon fraction separated from the isomerization step to produce a composite motor fuel product.

5. A process for producing normally liquid isoparaffinic hydrocarbons from a lower-boiling normal paraffin hydrocarbon of at least four carbon atoms per molecule which comprises subjecting such a normal paraffin in an isomerization step to catalytic isomerization in the presence of hydrofluoric acid as the isomerization catalyst to produce low-boiling isoparaffin hydrocarbons, subjecting effluents of said isomerization to fractional distillation to produce a low-boiling fraction containing isobutane and hydrofluoric acid and a higher-boiling fraction containing low-boiling normal paraffins and hydrofluoric acid, returning said higher-boiling fraction to said iso-

merization step, passing said low-boiling fraction to an alkylation step and reacting isobutane contained therein with an alkylating reactant in the presence of hydrofluoric acid as the alkylation catalyst to produce isoparaaffins of higher molecular weight, and recovering a hydrocarbon fraction containing higher boiling isoparaaffins so produced.

6. The process of claim 5 in which at least a portion of the spent hydrofluoric acid alkylation catalyst is passed to the isomerization step as the isomerization catalyst.

7. A process for producing an isoparaaffinic motor fuel stock containing both low-boiling and high-boiling isoparaaffinic hydrocarbons from low-boiling normal paraaffins, which comprises subjecting such a normal paraffin to catalytic conversion in the presence of hydrofluoric acid as the conversion catalyst to produce isobutane and low-boiling normally liquid isoparaaffins, separating from effluents of said conversion a mixture containing substantial quantities of isobutane and substantially anhydrous hydrofluoric acid, separating also a low-boiling liquid isoparaaffinic hydrocarbon fraction, adding to said isobutane-hydrofluoric acid mixture an alkylating reactant and subjecting the combined mixture to alkylation conditions to produce high-boiling normally liquid isoparaaffins boiling in the motor fuel range, separating from effluents of said alkylation spent hydrofluoric acid catalyst and passing at least a substantial portion of same to said conversion, separating also from effluents of said alkylation a normally liquid isoparaaffinic hydrocarbon fraction containing said high-boiling isoparaaffins

so formed, and blending the last said hydrocarbon fraction with the aforesaid low-boiling hydrocarbon fraction to produce a composite motor fuel stock as a product of the process.

8. A process for producing motor fuel, which comprises in combination; alkylating isobutane with an olefin of three to five carbon atoms per molecule in the presence of concentrated hydrofluoric acid in an alkylation step; separating from the resulting effluent from said alkylation step a hydrofluoric acid fraction, an unreacted isobutane fraction, and a normally liquid hydrocarbon fraction; mixing said hydrofluoric acid fraction with normal butane; subjecting the resulting acid-butane mixture to such conditions in an isomerization step that said normal butane is isomerized to isobutane to a substantial extent by hydrofluoric acid; separating from the resulting effluent from said isomerization step used hydrofluoric acid catalyst and an isobutane fraction, an unreacted normal butane fraction, and a normally liquid by-product fraction; recycling said unreacted normal butane fraction to said isomerization step; passing said used hydrofluoric acid catalyst, said unreacted isobutane fraction and said isobutane fraction to said alkylation step; mixing together said normally liquid hydrocarbon fraction and said normally liquid by-product fraction; separating from the resulting normally liquid mixture a motor-fuel fraction; and withdrawing from the process said motor-fuel fraction.

9. The process of claim 8 in which said olefin is at least one butylene.

FREDERICK E. FREY.