

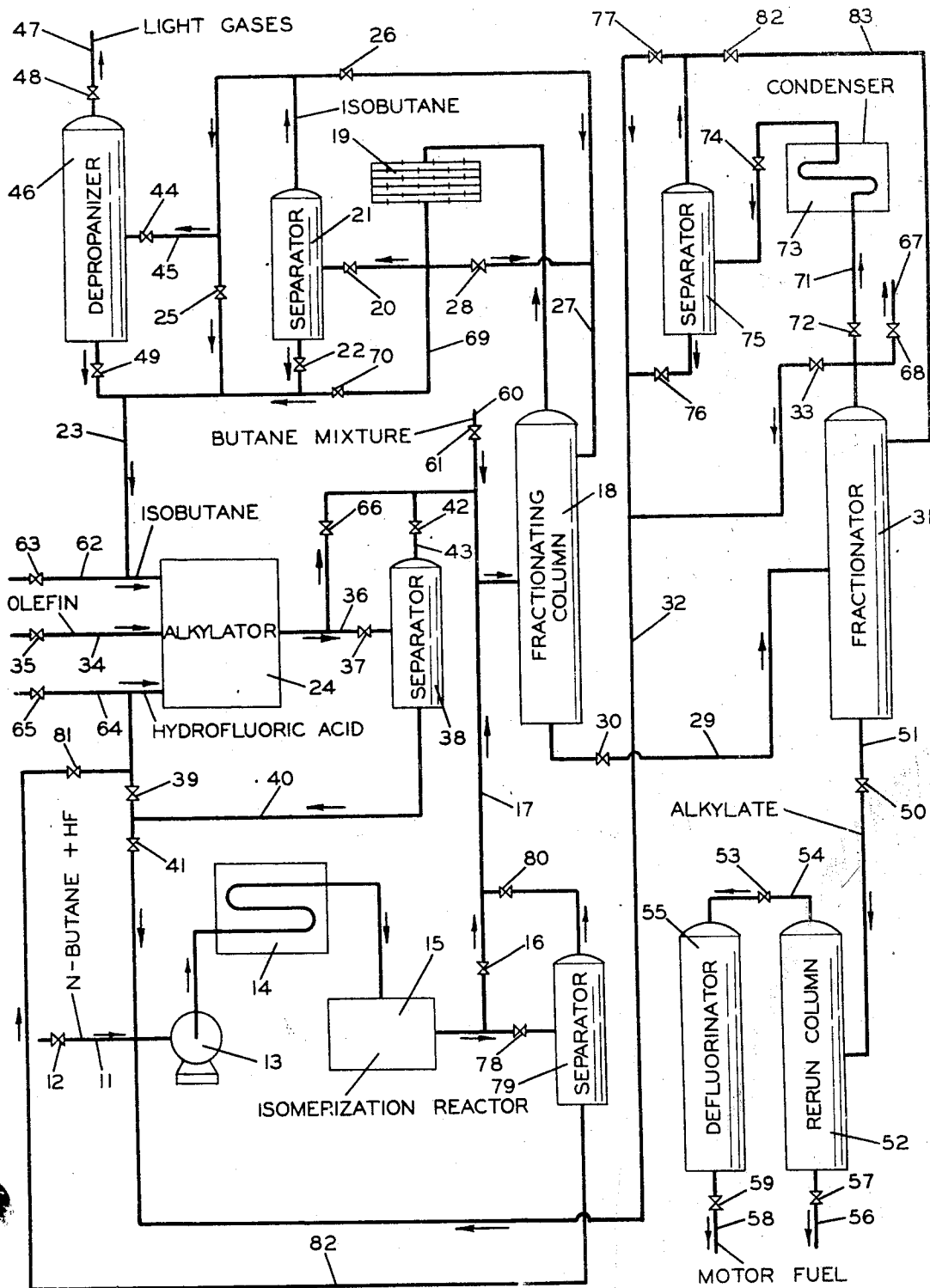
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J. D. GIBSON

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TREATMENT OF MIXTURES OF HYDROCARBONS AND HYDROFLUORIC ACID

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INVENTOR
JAMES D. GIBSON

BY *Hudson, Young & Young*
ATTORNEYS

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TREATMENT OF MIXTURES OF HYDROCARBONS AND HYDROFLUORIC ACID

James D. Gibson, Bartlesville, Okla., assignor to
Phillips Petroleum Company, a corporation of
Delaware

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This invention relates to the treatment of mixtures which comprise hydrofluoric acid and hydrocarbons. More particularly it relates to the production of hydrocarbon-hydrofluoric acid mixtures of desired proportions. It relates further to the production of liquid paraffins from low-boiling normal paraffins.

In processes in which hydrofluoric acid is used as a catalyst or reagent, such as alkylation of hydrocarbons to produce motor fuel and reconstruction of hydrocarbons to produce other hydrocarbons having a chemical structure different from that of the feed material, there is frequently produced, at some stage in the process, a mixture which comprises hydrofluoric acid and one or more saturated hydrocarbons. Often, acid-soluble materials such as unsaturated hydrocarbons and fluorinated organic compounds are also present. At times it is desired to separate such mixtures into several fractions, among which may be a fraction containing hydrofluoric acid and one or more specific hydrocarbons, such as isobutane or normal butane, in desired proportion for use in a subsequent step.

In feeds to a process such as the alkylation of isobutane in the presence of hydrofluoric acid as catalyst, it is desirable to have a mixture of hydrofluoric acid and isobutane that comprises more than 25 per cent hydrofluoric acid by weight; for example, acid-to-isobutane ratios of 0.4:1 to 4:1 or more are ordinarily needed in alkylating steps.

An object of this invention is to provide an improved process for converting relatively low-boiling hydrocarbons to motor fuel hydrocarbons in the presence of hydrofluoric acid as a catalyst.

Another object is to produce by distillation, from a two-liquid-phase mixture comprising hydrofluoric acid and one or more hydrocarbons, a fraction comprising hydrofluoric acid and isobutane in controlled proportions and suitable for use as feed to an alkylating step.

Another object is to produce by distillation, from a two-liquid-phase mixture comprising hydrofluoric acid and one or more hydrocarbons, a fraction comprising hydrofluoric acid and normal butane in controlled proportions and suitable for use as feed in a reconstructing or isomerizing step.

Other objects and advantages of this invention will become apparent from the accompanying disclosure and discussion.

In accordance with one aspect of this invention, a mixture comprising isobutane, normal

butane, and hydrofluoric acid in excess of that required to form an azeotropic mixture with all the isobutane is treated to produce a mixture consisting of hydrofluoric acid and isobutane in desired proportions by distilling the mixture while retaining the normal butane in the kettle, cooling and separating the overhead distillate into two liquid phases, withdrawing substantially all of the lower or hydrofluoric acid phase and a desired limited proportion only of the upper or isobutane phase, and returning the remainder of the upper phase as reflux to the distillation column. This procedure is especially advantageous in a combination isomerization-alkylation process in which normal butane is isomerized to isobutane in the presence of hydrofluoric acid; the resulting reaction mixture is distilled; and the distilled hydrofluoric acid and isobutane, in any desired proportion whereby the acid-to-isobutane ratio is greater than that in a corresponding azeotropic mixture, are passed to an alkylating zone.

Further, in a process in which a mixture comprising normal butane, hydrocarbons boiling higher than normal butane, and hydrofluoric acid in excess of that required to form an azeotropic mixture with all the normal butane, is distilled in such a way that normal butane is distilled overhead and hydrocarbons boiling higher than normal butane are retained in the kettle, I have found that it is advantageous to cool and separate the overhead distillate into two liquid phases, withdrawing substantially all of the lower or hydrofluoric acid phase and any desired proportion, greater than zero and less than 100 per cent, of the upper or hydrocarbon phase and returning the remainder of the upper phase as reflux to the distillation column. This procedure is especially advantageous in a combination isomerization-alkylation process in which normal butane is isomerized to isobutane in the presence of hydrofluoric acid as a catalyst; the resulting reaction mixture is cooled and separated into two liquid phases, of which the heavier or hydrofluoric acid phase is passed as catalyst to an alkylating zone, and of which the lighter or hydrocarbon phase is passed together with the total effluent from the alkylating zone to a fractionator; from this fractionator an overhead azeotropic mixture of isobutane and hydrofluoric acid is passed (after depropanization if necessary) to the alkylating zone, and a kettle fraction comprising normal butane, hydrocarbons boiling above normal butane, and hydrofluoric acid in excess of that required to form an azeotropic

mixture with all the normal butane, is passed to a distillation column; and the distilled hydrofluoric acid and normal butane, in any desired proportion whereby the acid-to-butane ratio is greater than that in a corresponding azeotropic mixture, are passed to an isomerizing zone.

An understanding of some aspects of my invention may be aided by reference to the accompanying drawing, which is a schematic flow-diagram of one arrangement for practicing my invention in a combination isomerization-alkylation process for producing motor fuel hydrocarbons. By omitting part of the equipment shown and making other minor changes, as will be described hereinafter, the process may be operated as an alkylation process without an isomerizing step.

In the arrangement shown, a mixture of a suitable hydrocarbon, for example, normal butane, and hydrofluoric acid is admitted through inlet 11, valve 12, pump 13, and heating coil 14 to reactor 15, wherein a substantial proportion of the normal butane is converted to isobutane, and, to some extent, to higher-boiling hydrocarbons, such as pentanes and hexanes.

In reactor 15, the ratio of hydrofluoric acid to hydrocarbon is preferably in the range from 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. Preferably most of the acid comes from other steps (to be described hereinafter), and only enough fresh or make-up acid is introduced through inlet 11 to maintain a desired quantity in the system. The reaction temperature may vary from about 250 to 1000° F. A temperature in the range 300 to 900° 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 about atmospheric to 5000 pounds per square inch or more; usually, it is preferred, 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 vary from 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 heating coil 14 or in an extension thereof; whereupon reactor 15 may be by-passed or removed from the system. Preferably the reaction zone is packed with a contact mass, such as steel turnings, alumina, bauxite, or other material resistant to destruction by hydrofluoric acid and suitable for aiding the reaction and/or heat transfer.

The resulting mixture of hydrofluoric acid and hydrocarbons is passed from reactor 15 through valve 16 and conduit 17 to distillation column 18, wherein it is subjected to distillation in accordance with this invention to produce, as an overhead product, a mixture of isobutane and hydrofluoric acid in which the proportion of hydrofluoric acid is greater than that in an azeotropic mixture and which is suitable for use as feed to an alkylating step. An overhead mixture of hydrofluoric acid and isobutane (some propane may also be present at times) from the top of column 18 is cooled, liquefied, and separated into two liquid phases, as by passing it through cooling coil 19 and valve 20 to separator 21. This will be substantially an azeotropic mixture. Substan-

tially all of the lower or acid phase is passed through valve 22 and conduit 23 to alkylator 24, together with any desired proportion, less than 100 per cent and greater than zero, of the upper or hydrocarbon phase (mostly isobutane), which is passed through valve 25, the resultant mixture passing through conduit 23 being the aforesaid overhead product. The remainder of the hydrocarbon phase is returned through valve 26 and conduit 27 as reflux to the top of column 18. If desired part of the effluent from cooling coil 19 may be recycled through valve 28 and conduit 27 for use as additional reflux in column 18, or a part may be passed directly to the alkylation step through conduit 69 and valve 70.

The kettle fraction from column 18 comprises normal butane, motor-fuel-range hydrocarbons, small proportions of higher-boiling hydrocarbons, and acid-soluble materials; in some cases, when not all the hydrofluoric acid is distilled overhead hydrofluoric acid will also be present. This fraction is preferably passed through conduit 29 and valve 30 to fractionator 31 for producing an overhead fraction comprising normal butane, which is passed through conduit 32 and valve 33 to pump 13.

Under some conditions of operation, it is advantageous to remove propane and other relatively low-boiling inert material from the system by passing part of the hydrocarbon phase from the top of separator 21 through valve 44 and conduit 45 to depropanizer 46, from which an overhead fraction comprising mainly material boiling below isobutane is withdrawn through outlet 47 having valve 48, and from which a kettle fraction comprising mainly isobutane is passed via valve 49 and conduit 23 to alkylator 24.

In alkylator 24, the mixture of isobutane and hydrofluoric acid is mixed under alkylating conditions with an alkylating reactant, such as an olefin having from 3 to 5 carbon atoms per molecule, an alkyl compound, such as an alcohol or a halide, or an olefinic polymer, which is introduced through inlet 34 and valve 35.

In the total feed to alkylator 24, 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 will generally be even higher in the reaction zone, and the weight ratio of hydrofluoric acid to total hydrocarbons is preferably in the range of 0.4:1 to 4:1. The olefin or other alkylating reactant 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 24 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 without passing beyond the scope of this invention.

After a suitable reaction time, the resulting mixture passes from alkylator 24 through conduit 36 and valve 37 to separator 38, wherein, as by cooling and gravitational or centrifugal means, it is separated into two liquid phases. Part of the heavier or hydrofluoric acid phase may be recycled through valve 39 and conduit 40 to alkylator 24; preferably, however, most of it is passed through conduit 40 and valve 41 to pump 13 for

use as catalyst in the isomerizing step. The lighter or hydrocarbon phase from separator 38 is passed through valve 42 and conduit 43 to column 18, in which, together with the effluent from the isomerizing step, it is separated into two fractions as already described.

The kettle fraction from fractionator 31, which comprises mainly branched-chain motor-fuel hydrocarbons or "alkylate" is passed through valve 50 and conduit 51 to rerun column 52. In this column it is separated into two fractions: (1) a major motor-fuel-range fraction, which is passed through valve 53 and conduit 54 to defluorinator 55; and (2) a bottom fraction comprising hydrocarbons boiling above the motor-fuel range, which is withdrawn through outlet 56 having valve 57.

Fluorine remover or defluorinator 55 comprises a chamber containing a contact mass having hydrogenation and/or dehydrogenation properties, such as bauxite, alumina, or other similar catalyst. Usually suitable operating conditions are a temperature in the range of 75 to 500° F. and a space velocity in the range of 1 to 50 volumes of liquid hydrocarbon material per volume of catalyst per hour. Under such conditions, which may be particularly selected by trial for any particular case, organically combined fluorine is substantially completely removed from the hydrocarbon material, which then is withdrawn through outlet 58 having valve 59.

Under some conditions other modifications of the foregoing general scheme will be preferable. For example, if the available paraffinic feed material comprises appreciable proportions of isobutane, it is advantageous to introduce this feed to column 18 through inlet 60 having valve 61. If auxiliary supplies of isobutane are available, it is advantageous to introduce them directly to alkylator 24 through inlet 62 and valve 63. If desired, additional or make-up acid may also be introduced to alkylator 24, as through inlet 64 and valve 65.

My invention is also applicable to a simple alkylation process, such as that used if adequate supplies of isobutane are available without isomerization of normal butane. Such a process may also be illustrated by the accompanying drawing, with the following changes in operation:

The isobutane-containing feed material preferably is admitted through inlet 62 having valve 63 to alkylator 24. Make-up hydrofluoric acid is introduced through inlet 64 having valve 65. Part of the total effluent from alkylator 24, preferably at least one-fourth or more, is by-passed around separator 38 directly through valve 66 and conduit 43 to column 18. The amount of alkylation effluent so by-passed is adjusted or regulated so that the material returning to alkylator 24 through conduit 23 has the desired proportion of hydrofluoric acid needed for the alkylation and so that the kettle product from column 18 is free from hydrofluoric acid. Appropriate valves, such as valves 16, 33, and 44, are closed to remove from use equipment not necessary to the alkylation step. Normal butane may be withdrawn from the system through outlet 67 having valve 68. Hydrofluoric acid from the bottom of separator 38 is recycled through valve 39 to alkylator 24. Proceeding in this manner has the advantage that column 18 serves to regenerate continuously hydrofluoric acid spent in the alkylation step.

Many other modifications and/or applications of my invention will be obvious to those skilled in the art of hydrocarbon conversion. For exam-

ple, in a combination isomerization-alkylation process, similar to that already described, total effluent from an alkylator, together with hydrocarbon effluent from an isomerizing step, may be passed to a distilling column from which an overhead mixture of hydrofluoric acid and isobutane is passed or recycled to the alkylator, and from which a kettle fraction comprising normal butane, motor-fuel hydrocarbons, and hydrofluoric acid is passed to an azeotropic distilling column used in the same manner as that hereinbefore described for column 18. From this column there is produced an overhead fraction comprising hydrofluoric acid and normal butane in controlled proportions, such as in the range of 0.4:1 to 4:1 by weight, suitable for use as feed to the isomerizing step. Hydrofluoric acid from the isomerizing step is passed as catalyst to the alkylating step. For this modification it is desirable to make the following changes: Column 18 is operated as an ordinary azeotrope column, sending an overhead azeotropic mixture of isobutane and hydrofluoric acid through line 69 and valve 70 to alkylator 24; valve 20 is closed. Hydrofluoric acid, normal butane, and alkylate pass from the kettle of column 18 through valve 36 to fractionator 31, which is now operated in the manner that is a special feature of this invention. That is, valves 33 and 68 are closed; an overhead azeotropic mixture of normal butane and hydrofluoric acid is passed through line 71 and valve 72 to condenser 73, from which it is passed through valve 74 to settler or separator 75 for separation into two liquid phases. The heavier or acid phase is passed through valve 76 and conduit 32 to pump 13. Any desired portion less than 100 per cent of the lighter or normal butane phase is passed through valve 77 and conduit 32 to pump 13; the remainder of the butane phase is passed as reflux through valve 82 and conduit 33 to column 31. Valve 16 is closed, and the isomerizer effluent from reactor 15 is passed through valve 78 to separator 79, in which it is separated into two liquid phases. The lighter or hydrocarbon phase is passed through valve 80 and conduit 17 to column 18; the heavier or hydrofluoric acid phase is passed through valve 81 and conduit 82 for use as catalyst in alkylator 24.

My invention is very advantageous for use in applications similar to the foregoing in that no separate acid-distilling equipment is necessary. For example, acid-soluble materials dissolved in the acid passed into column 18 remain in the kettle fraction and subsequently act to increase the yield of motor fuel, or are removed from the system in the oil withdrawn through outlet 56 having valve 57. Thus, the acid is continuously purified, and the yield of hydrocarbon products is simultaneously increased. Also by the practice of my invention, the separation of isobutane from normal butane is facilitated, and control of the relative proportions of hydrofluoric acid and desired low-boiling hydrocarbons in recycle fractions is easily effected. Other normal paraffins than normal butane may be treated in the isomerization step, particularly normal pentane, and isoparaffins so formed and including isopentane may be alkylated. In isomerizing normal pentane a substantial amount of isobutane is generally also produced, and in such a case the combined isobutane and isopentane may be subjected to alkylation.

To further illustrate some of the many aspects of my invention, the following specific example is given:

In an arrangement similar to that illustrated in the accompanying drawing, normal butane and concentrated or substantially anhydrous hydrofluoric acid are charged to an isomerizing step. The isomerizing conditions are approximately as follows: temperature 350° F.; pressure, 1500 pounds per square inch (liquid-phase conditions); reaction time 200 minutes; acid-to-hydrocarbon ratio, 3:1 by weight. The total effluent from the isomerizing step is cooled and passed to an azeotropic distilling column having a special refluxing arrangement whereby the overhead fraction is separated by cooling and gravity into two liquid phases. The lower or acid phase and a part of the upper or hydrocarbon phase are withdrawn in a weight ratio of about 2:1; the remaining part of the upper phase is returned as reflux to the top of the column. The hydrocarbon portion withdrawn is passed through a depropanizer wherefrom most of the propane and incidental low-boiling materials are removed by distillation; the residual isobutane and the hydrofluoric acid withdrawn are passed together as feed to an alkylating step, wherein the isobutane is alkylated under alkylating conditions with an alkylating agent, such as a mixture of butylenes.

The conditions in the alkylator are as follows: temperature 90 to 115° F.; pressure, 125 to 175 pounds per square inch; average reaction time, 6 minutes, rapid agitation to maintain intimate contact between acid and hydrocarbon phases, isobutane-to-alkylating agent ratio, about 6:1 by weight, acid-to-hydrocarbon ratio, about 2:1 by weight.

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. The acid phase is passed to the isomerizing step for use as catalyst, and the hydrocarbon phase, which comprises isobutane and motor-fuel hydrocarbons, is passed to the aforementioned azeotropic distilling column. From the bottom of this column motor-fuel hydrocarbons produced by alkylation, together with normal butane and higher-boiling hydrocarbons originating in the isomerizing step, are passed to a debutanizing column for separating normal butane, which is recycled to the isomerizing step. The remaining material, which is mainly highly branched paraffinic hydrocarbons suitable for use in aviation gasoline, is subjected to another distillation step to remove relatively high-boiling impurities, and to a defluorination treatment to remove organic fluorine. The resulting motor-fuel fraction is substantially completely saturated, has a clear octane number of about 91, and is suitable for use in aviation gasoline.

It is not intended that mention of specific apparatus or of specific applications should be taken to limit unduly the scope of my invention. The special distilling and refluxing features of my invention are applicable, for example, to any case wherein it is desired to produce a distillation product of controlled proportions of a low-boiling saturated-type hydrocarbon and hydrofluoric acid in which product the proportion of hydrofluoric acid is greater than that in a corresponding azeotropic mixture. The invention should not be limited otherwise than as specified in the appended claims.

What I claim is:

1. In a combination isomerization-alkylation process in which there is produced a mixture comprising isobutane, normal butane, hydrocarbons boiling higher than normal butane, and hydro-

fluoric acid in excess of that required to form azeotropic mixtures with all the isobutane and with all the normal butane, the steps which comprise distilling the mixture to produce an overhead azeotropic mixture comprising isobutane and hydrofluoric acid and a bottom fraction comprising normal butane, hydrocarbons boiling higher than normal butane, and hydrofluoric acid in excess of that required to form an azeotropic mixture with all the normal butane; passing said overhead azeotropic mixture comprising isobutane and hydrofluoric acid to an alkylating zone; passing said bottom fraction to a second distilling column and distilling an azeotropic mixture of hydrofluoric acid and normal butane overhead and retaining hydrocarbons boiling higher than normal butane in the kettle; cooling and separating the overhead distillate into two liquid phases, withdrawing substantially all of the hydrofluoric acid phase and a substantial proportion of the normal butane phase; passing these withdrawn materials to an isomerizing zone; and returning the remainder of the normal butane phase as reflux to the distillation column.

2. In a combination isomerization-alkylation process in which there is produced a mixture comprising isobutane, normal butane, and hydrofluoric acid in excess of that required to form an azeotropic mixture with all the isobutane, the steps which comprise distilling at least a part of the mixture in such a way that an azeotropic mixture comprising isobutane and hydrofluoric acid is distilled overhead and normal butane is retained in the kettle; cooling and separating the overhead distillate into two liquid phases, withdrawing substantially all of the hydrofluoric acid phase and a substantial proportion of the isobutane phase; passing these withdrawn materials to an alkylating zone; and returning the remainder of the isobutane phase as reflux to the distillation column.

3. In a process for isomerizing normal butane to form isobutane and for alkylating isobutane so formed, the improvement which comprises isomerizing normal butane in the presence of concentrated hydrofluoric acid as the isomerization catalyst to form isobutane, passing effluents of said isomerization to a fractional distillation column, removing from said fractional distillation column a low-boiling mixture comprising isobutane and hydrofluoric acid, cooling and condensing at least a portion of said mixture to form a liquid isobutane phase and a liquid hydrofluoric acid phase, returning a portion of said liquid isobutane phase to said fractional distillation column, passing a further portion of said isobutane phase together with said hydrofluoric acid to an alkylation zone, reacting said isobutane with an added alkylation reactant in the presence of said hydrofluoric acid as the alkylation catalyst, separating from effluents of said alkylation a major part of the hydrofluoric acid, passing a residual hydrocarbon material containing only a minor part of hydrofluoric acid to said fractional distillation column, and removing as a high boiling fraction from said fractional distillation column a hydrocarbon material substantially free from isobutane.

4. In a process for isomerizing a low-boiling normal paraffin of at least four carbon atoms per molecule and for alkylating resulting low-boiling isoparaffins, the improvement which comprises isomerizing a low-boiling normal paraffin of at least four carbon atoms per molecule in the presence of concentrated hydrofluoric acid as the isomerization catalyst to form low-boiling isoparaffins, passing effluents of said isomerization to a

fractional distillation means, passing from said distillation means to an alkylating zone a low-boiling isoparaffin and hydrofluoric acid, reacting in said alkylation zone said isoparaffin with an added alkylating reactant in the presence of said hydrofluoric acid to form higher-boiling isoparaffins, separating from effluents of said alkylation

zone a hydrocarbon material substantially free from hydrofluoric acid, passing said hydrocarbon material to the aforesaid fractional distillation means, and recovering also from said distillation means a normally liquid isoparaffinic hydrocarbon material so produced.

JAMES D. GIBSON.