

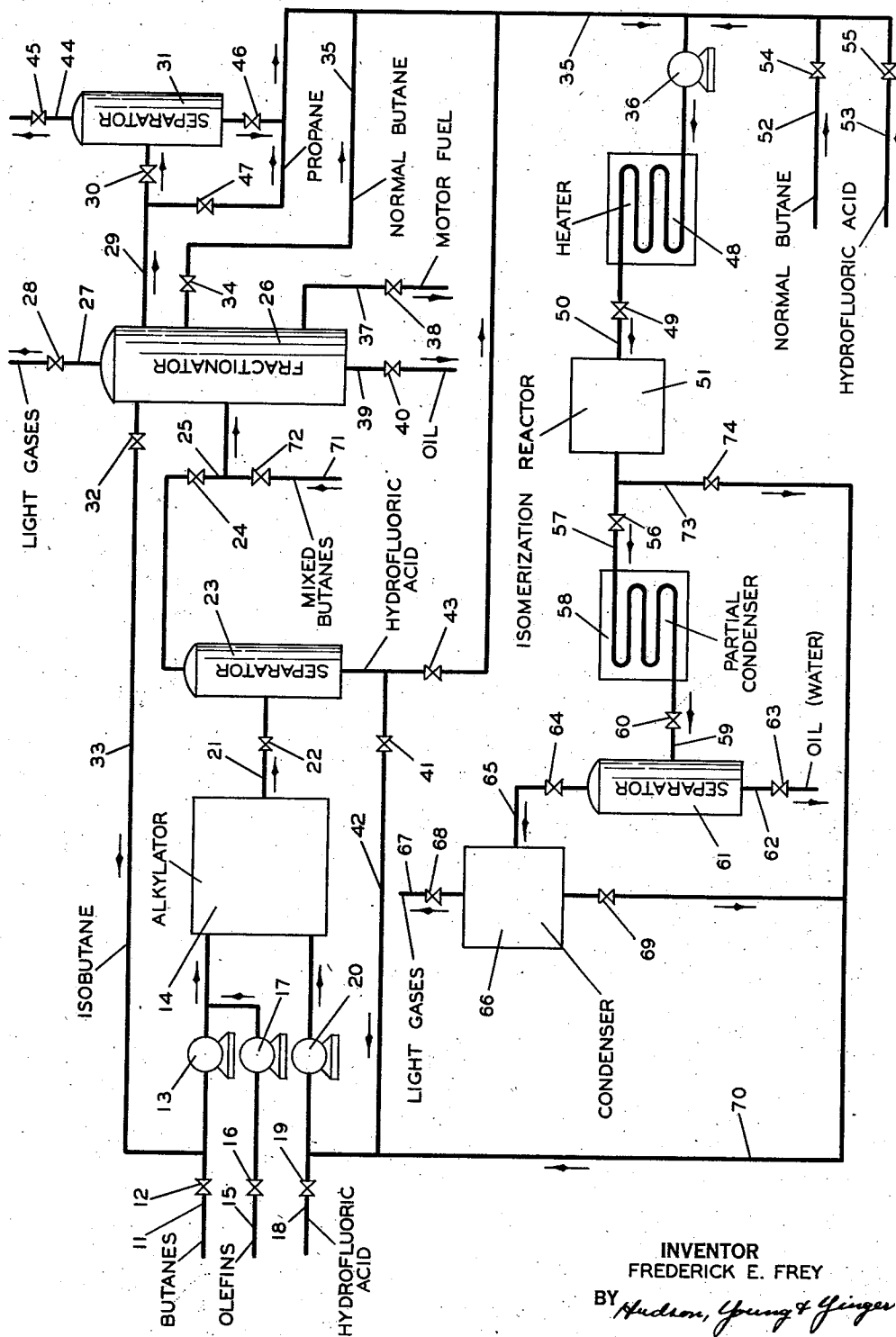
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PRODUCTION OF MOTOR FUEL

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## PRODUCTION OF MOTOR FUEL

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This invention relates to the conversion of hydrocarbons. More particularly, it relates to the production of motor fuel 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 copending application, Serial No. 315,063, filed January 22, 1940 (Patent No. 2,322,300), and Serial No. 426,627, filed January 13, 1942.

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

A specific 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 the isoparaffins required for the alkylation step.

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

In the prior art of hydrocarbon conversion, it has been shown that isoparaffins of relatively low molecular weight, such as isobutane and/or isopentane can be reacted in the presence of concentrated hydrofluoric acid at a comparatively low 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, esters, ethers, and the like, preferably those of secondary or tertiary structure, to produce motor-fuel hydrocarbons that have high antiknock values and that are suitable for use in aviation gasoline. Normal paraffins, such as normal butane and/or normal pentane, can also be alkylated, but only under considerably more drastic conditions, so that the product obtained by alkylating normal paraffins 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 organic and fluoro-organic material 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. Therefore, in commercial alkylation, it is necessary to provide acid-recovery steps, such

as distillation, to recover the free hydrogen fluoride, and/or thermal decomposition and distillation, to recover the organically combined fluorine as hydrogen fluoride.

I have now found that spent or partly deactivated hydrofluoric acid from the alkylating step can be advantageously used as an isomerizing catalyst to convert relatively low-boiling normal paraffins, such as normal butane and/or normal pentane, into isoparaffins, such as isobutane and/or isopentane. I have also found that the effluent from such a conversion can be used as feed to an alkylation step, wherein the isoparaffins are converted to higher-boiling motor-fuel hydrocarbons. Furthermore, I have found that the acid from the isomerizing conversion can be purified in a relatively simple manner so that it can be re-used in the alkylation step.

An understanding of some aspects of my invention may be aided by the accompanying drawing, which is a schematic flow-diagram of one arrangement of equipment for practicing the invention.

In the alkylating step of this invention, a suitable hydrocarbon material, for example a mixture of normal butane and isobutane, is admitted to alkylator 14, as through inlet 11, valve 12, and pump 13 and/or through conduit 70 and pump 20. In alkylator 14, it is mixed under alkylating conditions with an alkylating reactant, which may be admitted through inlet 15, valve 16, and pump 17, and with concentrated hydrofluoric acid, preferably anhydrous, which may be admitted through inlet 18, valve 19, and pump 20 and/or through conduit 70 and pump 20.

In the feeds to this alkylating step 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 with the isoparaffin reactant. 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. Suitable operating conditions in alkylator 14 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.

The resulting mixture passes through conduit 21 and valve 22 to separator 23, 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 41 and conduit 42 to pump 20; preferably, however, most of it is passed through valve 43 and conduit 35 to pump 36 for use as catalyst in an isomerization step to be described.

The lighter or hydrocarbon phase from separator 23 is passed through valve 24 and conduit 25 to fractionating means 26, in which it is separated into the following six fractions: (1) a relatively minor fraction of relatively inert and difficultly condensable gases, which is removed through outlet 27 having valve 28; (2) a fraction comprising propane and hydrogen fluoride, which is passed through conduit 29 and valve 30 to separator 31; (3) one or more fractions comprising isoparaffins, such as isobutane and/or isopentane, and at times also some hydrofluoric acid, which are recycled to pump 13, as through valve 32 and conduit 33; (4) one or more fractions comprising normal paraffins, such as normal butane and/or normal pentane, which are passed to pump 36, as through valve 34 and conduit 35; (5) a fraction of highly branched paraffinic reaction products boiling within the motor-fuel range, which is withdrawn through outlet 37 having valve 38, and (6) a relatively high-boiling hydrocarbon residue, which is withdrawn through outlet 39 having valve 40. Fractionating means 26 comprises whatever distilling columns and auxiliary equipment are necessary or convenient for effecting the separations indicated, as will be readily appreciated by those skilled in the art.

In separator 31 the fraction comprising propane and hydrofluoric acid is separated into two phases as by cooling and gravitational or centrifugal means. The lighter or propane phase may be withdrawn through outlet 44 having valve 45; the heavier or hydrofluoric acid phase is passed through valve 46 and conduit 35 to pump 36. If desired, separator 31 may be by-passed, the hydrogen fluoride and the propane then passing through valve 47 and conduit 35 directly to pump 36.

In the isomerizing step of this invention, the materials from the alkylating step that come to pump 36 through conduit 35, that is, a mixture of normal paraffins, such as propane, butane, and normal pentane, with used or spent hydrofluoric acid, is forced by pump 36 through heating coil 48, valve 49, and conduit 50 to reactor 51.

In the feed to reactor 51, 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. These proportions are obtained by controlling the relative proportions of spent acid from separator 23 which pass through valves 41 and 43, respectively. Also, if desired, additional normal paraffin and/or hydrofluoric acid may be admitted to the system, as through inlets 52 and/or 53 and valves 54 and/or 55, respectively.

The reaction temperature in reactor 51 may be within the range of about 250 to 1000° F. A temperature within 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, for reasons of economy in equip-

ment and operating costs, to use a pressure in the range of 250 to 1000 pounds per square inch. The reaction time may be within the range of from about 1 to about 300 minutes, depending chiefly upon the temperature, since 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 48 or an extension thereof; whereupon reactor 51 may be by-passed or removed from the system. Preferably, the reaction zone is packed with a contact mass, such as steel turnings, alumina, or other material resistant to corrosion by hydrofluoric acid and suitable for aiding the reaction and heat transfer.

The resultant mixture from reactor 51 may be passed through valve 56 and conduit 57 to partial condenser 58, wherein, by a suitable cooling means, relatively high-boiling material, such as hydrocarbons boiling above about the pentane range, water, acid-soluble material, and the like, are liquefied. Suitable conditions in the partial condenser 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 for any particular case 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.

The resulting mixed-phase mixture from partial condenser 58 is passed through conduit 59 and valve 60 to separator 61, wherein it is separated into a gas phase and a liquid phase, as by gravitational or centrifugal means. The temperature and pressure conditions should be, as nearly as possible, the same as in partial condenser 58. The liquid phase, which comprises mainly hydrocarbons and acid-soluble substances boiling approximately in the hexane range and above, is withdrawn through outlet 62 having valve 63. The gas phase is passed through valve 64 and conduit 65 to condenser and separator 66.

In condenser and separator 66, the gas phase from separator 61 is cooled and liquefied. The resulting mixture of acid and hydrocarbon phases, which comprises the isoparaffins produced in reactor 51, is passed through valve 69 and conduit 70 to pump 20 for use as feed in the alkylation step. Incidental noncondensable gases may be removed from condenser 66 through outlet 67 having valve 68.

The above method employed for the separation of the effluents of the isomerization step has the advantage of simplicity while, at the same time, heavy impurities are removed from the catalyst and from the system. The material passed through valve 69 and conduit 70 to the alkylation step therefore contains isoparaffins and also concentrated hydrofluoric acid in a purified state suitable for catalyzing the subsequent alkylation reaction. In some instances it may be possible to pass a portion, or all, of the isomerization effluent directly to the alkylation step, as through conduit 73 and valve 74, with valve 56 partially or completely closed. Such a procedure may be followed when the impurities in the effluent from the isomerization are small, or negligible, in amount. At other times it may be desirable to subject the isomerization effluent to more complete separation, obtaining thereby in various separate fractions low-boiling isoparaffins, unreacted normal paraffins, hydrofluoric acid, impurities, and the like. This may be done by passing the isomerization effluents to other, or additional, separation

equipment, not shown, as will be appreciated by those skilled in the art. Any fraction so recovered may be used in other steps of the process, and may be introduced thereto through one or more appropriate conduits.

It is contemplated that the hydrofluoric acid can be, and in many instances will be, the isomerization catalyst, and I have obtained satisfactory isomerization and disproportionation of aliphatic hydrocarbons using hydrofluoric acid as the sole catalytic material. However, in the broadest concept of the present invention, it is to be understood that the isomerization may be carried out in the presence of other material in addition to hydrofluoric acid. Such other materials may serve to enhance the catalytic activity of hydrofluoric acid, such as material which provide large surfaces, to promote the activity of hydrofluoric acid, or to cooperate with the hydrofluoric acid, members of this latter group having, themselves, independent isomerization catalyzing activity. Included among these groups, for use together with hydrofluoric acid, are the oxides and halides of beryllium, sulfur, tungsten, magnesium, aluminum, zinc, titanium, thorium, iron, copper, tin, vanadium, antimony, arsenic, chromium, molybdenum, manganese, nickel and cobalt, their salts of difficultly volatilizable acids, either synthetic or natural. Of the naturally occurring materials, I prefer those of large surface such as various clays, bauxite, brucite, etc. Sometimes activated charcoal may also be used to advantage. These various materials, or various ones of the materials mentioned may be used in granular form, as a powder, or may be pelleted, as may be found most effective or desirable in any particular instance.

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

In an arrangement similar to that illustrated in the accompanying drawing, normal butane is charged to the isomerization stage, as through inlet 52; normal butylenes and concentrated hydrofluoric acid are separately charged to the alkylation stage, as through inlets 15 and 18, respectively. All of the acid used in the alkylation step is passed as catalyst to the isomerization step.

The alkylating conditions are approximately as follows: temperature, 102° F.; pressure, 150 pounds per square inch; time, 5 minutes; isobutane-to olefin molal ratio (in the incoming materials to the alkylation reactor), 11.5; hydrocarbon-to-acid weight ratio, 1.0; and rapid mixing to maintain intimate contact between the acid and hydrocarbon phases.

The isomerizing conditions are approximately as follows: temperature, 850° F.; pressure, 2,000 pounds per square inch; time, 10 to 30 minutes.

From this process, there is produced in a yield of about 160 per cent, based on the weight of olefins charged, an aviation motor fuel which has a clear octane number of about 90.

In this process, the acid effluent from the alkylation step is used as catalyst in the isomerization step; it is then purified by partial condensation, as in condenser 58, and is returned to the alkylation step.

My invention provides a process for utilizing normal paraffins, particularly low-boiling paraffins such as normal butane and/or normal pentane, to produce relatively high-boiling saturated hydrocarbons of high antiknock value that are

suitable for use as aviation gasoline. Concentrated hydrofluoric acid used as a catalyst in one step (alkylation) is used subsequently as catalyst in another step (isomerization); it is then freed from material boiling above about the pentane range by partial condensation, and is returned for use in the first step without being subjected to a separate acid-recovery fractional-distillation step.

There are numerous modifications of my invention, which will be obvious to those skilled in the art of hydrocarbon conversion. For example, if the hydrocarbon feed material comprises relatively large proportions of normal paraffins and only small proportions of isoparaffins, it is preferably introduced to fractionating means 26, as through inlet 71 having valve 72, instead of directly to alkylator 14; whereupon the isoparaffins are separated out and passed to alkylator 14, and the normal paraffins are passed to the isomerization step. In another modification, the paraffinic feed material, instead of being admitted directly to alkylator 14, or to fractionating means 26, is admitted through inlet 52, valve 54, and pump 36 to the isomerization step; this modification is particularly advantageous when the feed material has mostly low-boiling normal paraffins but practically no low-boiling isoparaffins. 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. The scope of my invention should not be unduly limited by the numerical values discussed herein.

I claim:

1. In a process for alkylating an isoparaffin in the presence of hydrofluoric acid, the improvement which comprises mixing a normal paraffin with used hydrofluoric acid from an alkylating step, subjecting the resulting mixture to isomerizing conditions in an isomerizing step, and using at least part of the effluent from the isomerizing step as feed material in the alkylating step.

2. In the process of claim 1, cooling the effluent from the isomerizing step to remove by partial condensation material which boils above about the pentane range prior to using said effluent as feed material in the alkylating step.

3. A process for producing motor fuel, which comprises: alkylating a low-boiling isoparaffin of four to five carbon atoms per molecule with an olefin of three to five carbon atoms per molecule in the presence of concentrated hydrofluoric acid in an alkylation step; separating the effluent from said alkylation step into a hydrofluoric acid fraction, at least one low-boiling isoparaffin fraction, at least one low-boiling normal paraffin fraction, a motor-fuel fraction, and a heavier-than-motor-fuel fraction; removing from the process said motor-fuel and heavier-than-motor-fuel fractions; recycling said low-boiling isoparaffin fraction to the alkylation step; passing said hydrofluoric acid and low-boiling normal paraffin fractions to an isomerization step in which such conditions are maintained that normal paraffins are isomerized to a substantial extent by hydrofluoric acid into isoparaffins; freeing the resulting effluent from the isomerization step from material boiling above about the pentane range by partial condensation; and passing the thus freed effluent to said alkylation step.

4. A process for producing normally liquid isoparaffinic hydrocarbons 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 concentrated hydrofluoric acid to produce a low-boiling isoparaffin hydrocarbon, reacting said isoparaffin so produced with an alkylating reactant in the presence of concentrated hydrofluoric acid as the alkylation catalyst to produce normally liquid isoparaffins of higher molecular weight, separating from effluents of said alkylation a hydrocarbon fraction containing liquid isoparaffins so produced as a product of the process, separating also from effluents of said alkylation a hydrofluoric acid fraction, and passing said fraction to said isomerization.

5. A process for producing normally liquid isoparaffinic hydrocarbons 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 concentrated hydrofluoric acid as the isomerization catalyst to produce a low-boiling isoparaffin hydrocarbon, reacting said isoparaffin so produced with an alkylating reactant in the presence of concentrated hydrofluoric acid as the alkylation catalyst to produce normally liquid isoparaffins of higher molecular weight, separating from effluents of said alkylation a hydrocarbon fraction containing liquid isoparaffins so produced as a product of the process, separating also from effluents of said alkylation a hydrofluoric acid fraction, and passing said fraction to said isomerization as the isomerization catalyst.

6. A process for producing normally liquid isoparaffinic hydrocarbons from a mixture of low-boiling isoparaffins and normal paraffins of at least four carbon atoms per molecule, which comprises separating an isoparaffin fraction and a normal paraffin fraction from said mixture, reacting said isoparaffin fraction in an alkylation step with an alkylating reactant in the presence of concentrated hydrofluoric acid as the alkylation catalyst to produce higher-boiling isoparaffins, separating from effluents of said alkylation higher-boiling isoparaffins so produced as products of the process, separating also from effluents of said alkylation an impure liquid hydrofluoric acid, passing said liquid hydrofluoric acid together with the aforesaid normal paraffin fraction to an isomerization step to isomerize said normal

paraffins and form low-boiling isoparaffins, and recovering low-boiling isoparaffins so formed and passing same to said alkylation step.

7. A process for producing normally liquid isoparaffinic hydrocarbons from lower boiling paraffin hydrocarbons, which comprises subjecting a low-boiling normal paraffin hydrocarbon of at least four carbon atoms per molecule to isomerization in the presence of hydrofluoric acid as the isomerization catalyst at a temperature within the range of 250 to 1000° F. and a super-atmospheric pressure to produce low-boiling isoparaffins, subjecting the effluent of said isomerization to cooling and partial condensation to condense material boiling above pentanes and removing material so condensed from the system, subjecting uncondensed material to further cooling and condensation to condense hydrofluoric acid and low-boiling isoparaffins, separating material so condensed from uncondensed gases, passing the last said condensed material to an alkylation zone and reacting isoparaffins contained therein with an added alkylating reactant in the presence of said hydrofluoric acid and as the alkylation catalyst to produce normally liquid isoparaffins, separating from the effluent of said alkylation a liquid hydrofluoric acid phase, and passing said hydrofluoric acid phase to said isomerization.

8. In a process for producing paraffin hydrocarbons boiling in the motor fuel range from lower-boiling paraffin hydrocarbons, the improvement which comprises subjecting a normal paraffin of four to five carbon atoms per molecule in an isomerization step to catalytic isomerization in the presence of used hydrofluoric acid obtained from a subsequent alkylation step, separating from effluents of said isomerization a low-boiling isoparaffin so produced, reacting said isoparaffin in an alkylation step with an alkylation reactant in the presence of concentrated hydrofluoric acid as the alkylation catalyst to produce paraffins boiling in the motor fuel range, passing effluents of said alkylation to a separator and effecting a separation between a hydrocarbon phase and a hydrofluoric acid phase, and passing at least a portion of said hydrofluoric acid phase to said isomerization step.

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