July 9, 1946. F. E. FREY 2,403,650

RECONSTRUCTION OF PARAFFINS

Filed Feb. 6, 1942 2 Sheets-Sheet 1

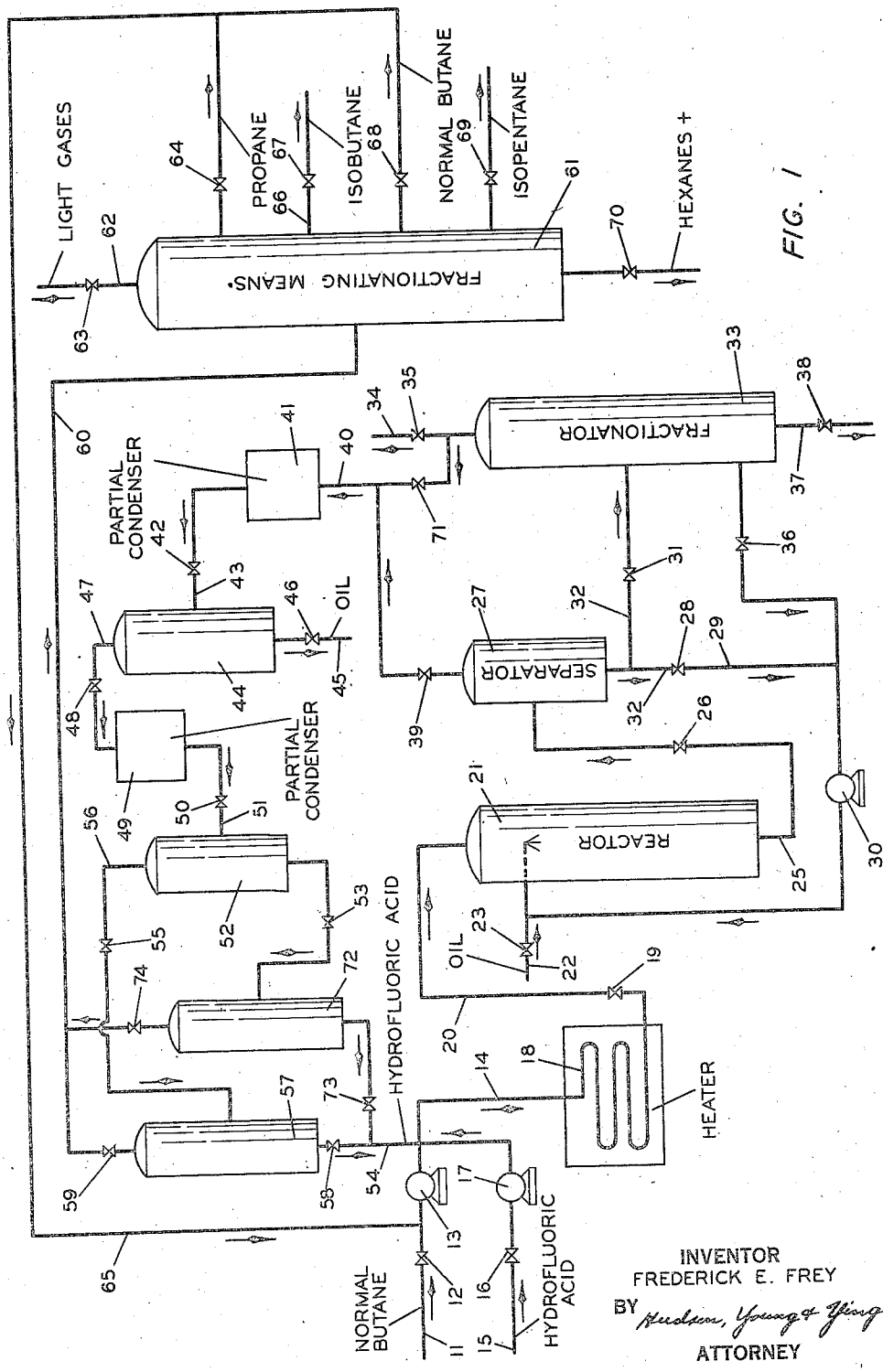



FIG. 1

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RECONSTRUCTION OF PARAFFINS

Filed Feb. 6, 1942 2 Sheets-Sheet 2

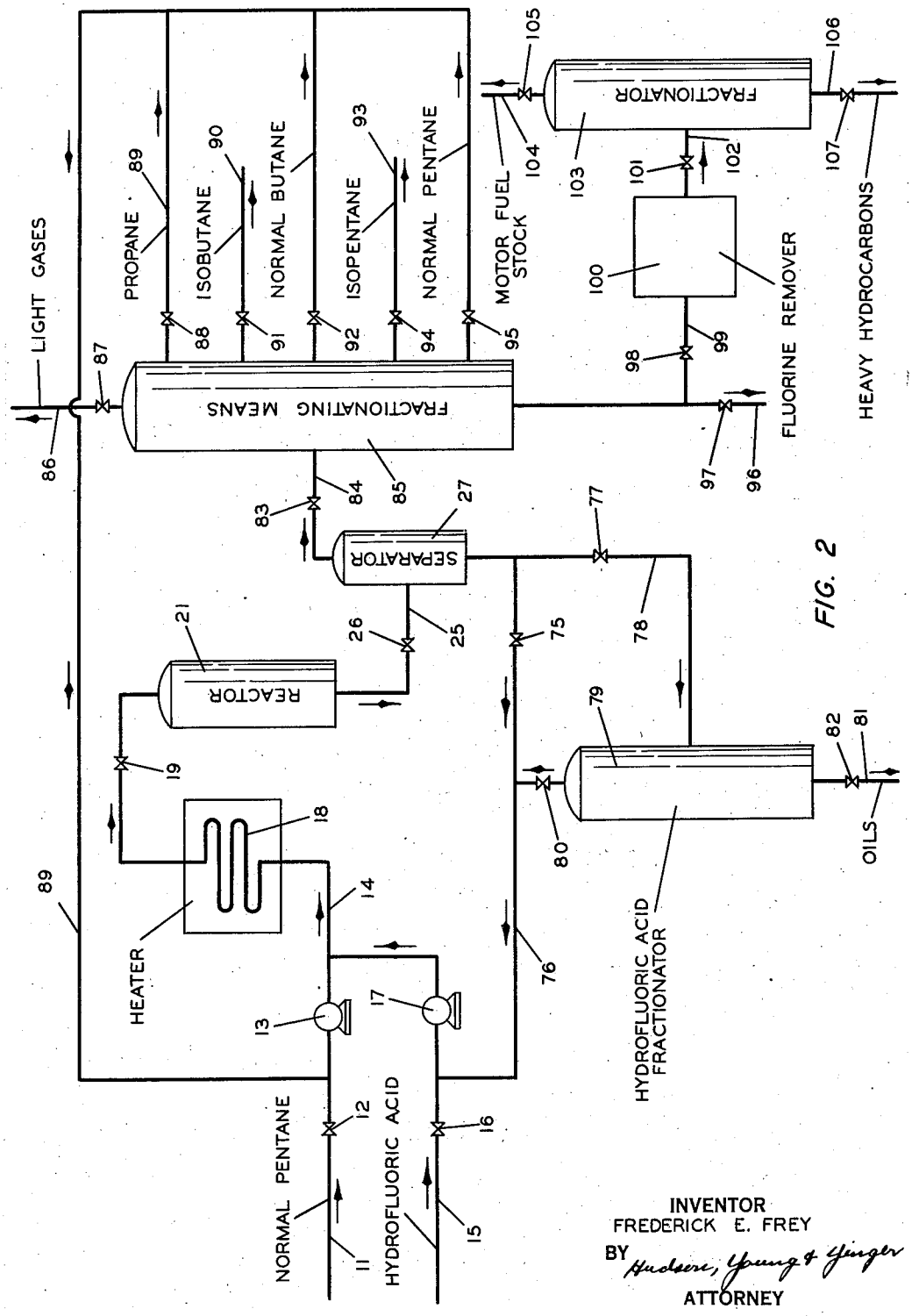



FIG. 2

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# UNITED STATES PATENT OFFICE

2,403,650

## RECONSTRUCTION OF PARAFFINS

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Application February 6, 1942, Serial No. 429,810

13 Claims. (Cl. 260—683.5)

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This invention relates to the conversion of hydrocarbons. More particularly, it relates to chemical reconstruction of paraffins into more highly branched paraffins in the presence of hydrofluoric acid as a catalyst. This application is a continuation in part of my copending application, Serial No. 426,627, filed January 13, 1942.

An object of this invention is to produce branched paraffins from relatively less highly branched paraffins.

A specific object is to control, in a process for converting paraffins in the presence of hydrofluoric acid, the proportions and the molecular weight or volatility of the hydrocarbons produced that differ in molecular weight from the feed material.

Another specific object is to produce low-boiling isoparaffins from normal butane.

Another specific object is to produce low-boiling isoparaffins from normal pentane.

Another specific object is to minimize the deposition of non-volatile material in the reaction zone of a process for converting paraffins in the presence of hydrofluoric acid.

Other objects and advantages of my invention will be apparent from the accompanying description and disclosure.

In the afore-mentioned copending application, I have disclosed a broad process for converting saturated hydrocarbons into saturated hydrocarbons of different skeletal configurations and, in part, of different molecular weight by the action of hydrofluoric acid. This process involves several different types of chemical reactions. The predominating reaction types, as deduced from a consideration of reactants, products, operating conditions, and theoretical aspects relating to the invention, may be exemplified as follows:

(1) $2C_7H_{16} \xrightarrow{HF} C_6H_{14} + C_8H_{18}$
(heptanes) (hexanes) (octanes)

(2) (*a*) n-heptane $\xrightarrow{HF}$ branched heptanes

(*b*) n-butane $\xrightarrow{HF}$ isobutane

(3) $2C_7H_{16} \xrightarrow{HF} C_6H_{12} + 2C_4H_{10}$
(heptanes) (cyclohexane) (butanes)

(4) $C_6H_{12} \xrightarrow{HF} CH_3C_5H_9$
(cyclohexane) (methyl cyclopentane)

The first two reactions, namely, reconstruction to produce both higher- and lower-boiling paraffins, and isomerization, respectively, predominate under relatively mild treating conditions. The yield of cyclics, exemplified in the third equation by cyclohexane, is increased by increasing the temperature and/or the time of reaction. A fourth type of reaction is believed to account for the increase in saturation and stability that occurs when motor fuel comprising some unsaturated material is treated. By this reaction, olefins are converted to cycloparaffins such as cyclohexane and its derivatives. This reaction may be exemplified as follows:

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(5) $C_7H_{14} \xrightarrow{HF} C_6H_{11}CH_3$
(heptylene) (methyl cyclohexane)

Several other types of reactions undoubtedly occur in the reconstruction process; however, the above-mentioned five types appear to account for most of the effects which are produced. The general term "reconstruction" is used herein to denote the production of one or more of the above-mentioned effects and/or of other inherent advantageous effects which result from the practice of my invention.

The present invention is concerned with the gas-phase conversion of predominantly paraffinic hydrocarbons of comparatively low molecular weight into more highly branched isomeric paraffinic hydrocarbons and, in part, into saturated hydrocarbons of lower and higher molecular weight. I have found that, in the presence of substantial proportions of hydrogen fluoride and under suitable conditions of temperature and time, paraffin hydrocarbons of relatievly low molecular weight, such as normal butane and/or normal pentane, can be converted in high yield to isomeric branched paraffins, such as isobutane and isopentane. Further, I have found that paraffins of higher and lower molecular weight can also be produced under similar conditions, concurrently with the production of isomers, and that the proportions and the molecular weights of such products can be controlled by suitable recycling steps; for example, isobutane can be produced as the major product from one or more paraffins having four to five carbon atoms per molecule, of which at least four carbon atoms are in a straight chain. Still further, I have found that relatievly non-volatile material, which is formed in small proportions and which would otherwise be deposited and carbonized upon the surfaces of the reaction zone, can be removed by scrubbing the reaction zone, intermittently or continuously, with a liquid hydro-

carbon which is relatively non-volatile at the reaction temperature.

In general, my investigations have shown that, when a relatively low-boiling paraffin hydrocarbon material having at least four carbon atoms per molecule, in a straight chain, is subjected to the action of substantial proportions of concentrated hydrofluoric acid under suitable reaction conditions, there results a mixture comprising propane, isobutane, normal butane, isopentane, normal pentane, hexanes, and higher-boiling hydrocarbons. Any of these hydrocarbons, especially if present in relatively large proportions in the original mixture or feed material, tends to be converted to hydrocarbons which are originally absent or present only in small proportions. Thus, by separating out the desired products and recycling the others, very high ultimate yields of the desired products can be obtained. In one specific embodiment, the present invention is directed particularly to the production of iobutane and/or motor-fuel hydrocarbons from normal paraffins having four to five carbon atoms per molecule.

As the catalyst, hydrogen fluoride may be used in the following ways: alone; with relatively small proportions of modifiers such as water, basic organic nitrogen compounds, and/or salts; and/or in conjunction with solid contact masses or surfaces, preferably those which comprise iron and/or alumina, such as steel shavings, alumina gel, bauxite, and the like.

Conversion stocks for the process should be composed of saturated hydrocarbons containing preferably little or no unsaturated hydrocarbons; they may comprise normal butane, normal pentane, and/or higher paraffins, provided that they are not so high-boiling as to make gas-phase conversion not feasible. Petroleum distillate fractions of undesirably low ostane number or of volatility other than that desired for some particular purpose may be used; such fractions may comprise either distillates as they ordinarily occur in the industry or fractions of inferior octane number obtained upon removing constituents of superior octane number from existing stocks. The conversion stock may also comprise residues from the application of selective solvent treating, azeotropic distillation, or the like to separate hydrocarbons having relatively enhanced value when separated from each other.

An understanding of some aspects of my invention may be aided by the accompanying drawings, wherein Figure 1 and Figure 2 are flow-diagrams showing diagrammatically two specific arrangements for practicing my invention. Corresponding parts in each figure are designated by the same numerals.

In the embodiment of Figure 1, a hydrocarbon material, which for the sake of simplicity may be taken to be chiefly or substantially entirely normal butane, is admitted through inlet 11, valve 12 and charge pump 13 to conduit 14, wherein it is mixed with concentrated hydrofluoric acid, which is admitted through inlet 15, valve 16, and charge pump 17. The proportion of acid may be from about 0.1 to 4 times or more by weight of the hydrocarbon material; preferably, it is in the range of 0.2 to 2 times by weight of the hydrocarbon material. The use of very small proportions results in slow or incomplete conversion, and the use of very large proportions causes a decrease in the production capacity of the equipment.

The resulting hydrocarbon-hydrofluoric acid mixture in conduit 14 is passed to heating coil 18, in which it is heated to the desired reaction temperature. The temperature should be so high that the reaction mixture is in the gaseous condition; it usually may be within the range of about 250° F. or less to 1000° F. or more. Usually the optimum temperature is in the range of 400 to 800° F.; at lower temperatures, the conversion is relatively slow, and at higher temperatures excessive cracking and/or dehydrogenation occurs. The pressure may be within the range of about atmospheric to 5000 pounds per square inch or more; usually the optimum pressure is in the range of 250 to 2500 pounds per square inch. At low pressures, since the volume of reactants is relatively large, a reaction chamber of comparatively large size is required; at high pressures, relatively expensive high-pressure equipment is required. In any particular instance, the most economical operating pressure may be determined by a study of the various factors involved in the various possible alternatives.

From heating coil 18, the mixture is passed through valve 19 and conduit 20 to reactor 21, wherein it is maintained at the reaction temperature for a time sufficient to effect the desired degree of reaction. The reaction time may be within the range of less than 1 minute to more than 300 minutes, depending chiefly upon the temperature; for example, at 750° F., satisfactory conversions of normal butane are usually obtained in 2 to 15 minutes, and at 650° F., in 15 to 90 minutes. When the time is short, for example, less than about 10 minutes, heating coil 18 may be of such length that the reaction is virtually completed therein, and reactor 21 may then be by-passed or removed from the system.

There is a tendency for small proportions of relatively nonvolatile hydrocarbons, which are formed incidentally in the reaction zone, to accumulate and to carbonize or form coke on the walls of reactor 21. This action may be advantageously minimized by scrubbing the reaction zone with a high-boiling oil, such as mineral seal oil, to absorb and remove the nonvolatile material substantially as soon as it is formed. The scrubbing oil is admitted through inlet 22 having valve 23 to distributing means 24 near the top of reactor 21. The proportion of scrubbing oil is preferably from about 0.1 to about 1.0 times by weight of the hydrocarbon reactants. Smaller proportions are sometimes insufficient to effect the desired absorption, and larger proportions sometimes tend to interfere by the oil undergoing reaction itself. The reactor is so designed that the time of residence of the scrubbing oil therein is relatively short, preferably of the order of a tenth to a hundredth of the reaction time, in order to minimize reconstruction or cracking of the oil itself.

Reactor 21 usually need not contain any packing, or the like, so that the scrubbing oil simply falls from top to bottom as a spray; in some cases, however, especially those in which the reaction time is relatively long, it preferably is loosely packed with a suitable contact material resistant to corrosion by concentrated hydrofluoric acid. Among contact materials may be mentioned metals, such as various steels, Monel metal, alloys of chromium, nickel, magnesium, and/or aluminum and the like, and granular substances, such as alumina, bauxite, carbon, and the like.

The effluent from reactor 21 comprises the re-

action mixture, chiefly of hydrogen fluoride and low-boiling hydrocarbons, which are partly or wholly in the gaseous condition; when scrubbing with an oil is practiced, it also comprises this oil, which is in the liquid condition. This effluent passes from the bottom of reactor 21 through conduit 25 and valve 26 to separator 27, in which it is separated into a liquid scrubbing-oil phase and a gaseous hydrofluoric acid-and-hydrocarbon phase, as by gravitational or centrifugal means.

The scrubbing-oil phase may be recycled through valve 28, conduit 29, and pump 30 to the top of reactor 21. Preferably, however, at least part of it is passed through valve 31 and conduit 32 to fractionator 33, wherein it is purified, for example by separation into the following three fractions: (1) a minor fraction comprising hydrocarbons boiling below the temperature in reactor 21, which may be withdrawn through outlet 34 having valve 35 but which is usually preferably passed through valve 71 to conduit 40; (2) a large fraction of relatively unchanged absorbing oil, which is recycled through valve 36 and pump 30 to the top of reactor 21; and (3) a minor fraction comprising very high-boiling or semi-solid material, which is withdrawn through outlet 37 having valve 38.

The gaseous phase from separator 27 is passed through valve 39 and conduit 40, preferably together with the lowest-boiling fraction from fractionator 33, to partial condenser 41, wherein relatively high-boiling materials, for example those boiling higher than the hexanes, are condensed. Suitable conditions may be such as, for example, a temperature of 450° F. and a pressure of 450 pounds per square inch. If it is desired to use a lower pressure, a correspondingly lower temperature is used; for example, at 100 pounds per square inch the condenser temperature may be about 300° F. The resulting mixed phases are passed through valve 42 and conduit 43 to separator 44, wherein they are separated by gravity. The resulting liquid phase, which comprises cyclics, acid-solubles, and other material, for example hydrocarbons boiling in the hexane range and higher, is withdrawn through outlet 45 having valve 46. The gas phase which comprises chiefly hydrofluoric acid, and hydrocarbons of up to about six carbon atoms per molecule, is passed through conduit 47 and valve 48 to second partial condenser 49.

In partial condenser 49, pentanes, hexanes, and most of the hydrofluoric acid are condensed. Suitable conditions may be such as, for example, a temperature of 325° F. and a pressure of 400 pounds per square inch, or a temperature of 225° F. and a pressure of 100 pounds per square inch. The exact optimum conditions for any particular case may be readily determined by trial. The resulting mixed phases are passed through valve 50 and conduit 51 to separator 52, wherein they are separated by gravity. The resulting mixture of liquid phases passes through valve 53 to separator 72, from which the heavier or hydrogen fluoride phase is recycled through valve 73 and conduit 54 to heating coil 18, and from which the lighter or hydrocarbon phase passes through valve 74 to conduit 60; separators 52 and 72 are preferably so elevated in position that the recycling of the acid phase is advantageously effected by gravity, without the use of a pump.

The gaseous phase from separator 52 is passed through valve 55 and conduit 56 to separator 57.



In separator 57, the gas phase from separator 52 is separated into two liquid phases, as by cooling and gravitational means. The heavier or hydrofluoric acid phase is recycled through valve 58 and conduit 54 to heating coil 18. The lighter or hydrocarbon phase is passed through valve 59 and conduit 60 to fractionating means 61, together with the hydrocarbon phase from separator 72.

In fractionating means 61, these hydrocarbon materials are fractionally distilled to yield an isobutane fraction and any other desired products. Light gases, such as methane, ethane, and the like, are preferably withdrawn from the system, as through outlet 62 having valve 63. Propane and hydrofluoric acid pass, at least partly as an azeotropic mixture, through valve 64, and are recycled to coil 18 by conduit 65; if desired, excess propane may be withdrawn, as through outlet 62 and valve 63. Isobutane is withdrawn through outlet 66 having valve 67. Normal butane is recycled through valve 68 and conduit 65. Hydrocarbons heavier than butane may be recycled with the normal butane, especially if the highest possible yield of isobutane is desired; but if desired, selected or especially valuable fractions may be advantageously withdrawn; for example, isopentane may be withdrawn through valved outlet 69, and/or material boiling above normal butane or above isopentane may be withdrawn through valved outlet 70.

It is understood that fractionating means 61 may comprise whatever distilling columns and auxiliary equipment appear necessary or convenient for effecting the separations indicated. If desired, any of the fractions withdrawn may be subjected to one or more purification steps not shown, such as, for example, defluorination by contacting with bauxite at a suitable temperature.

In the embodiment of Figure 2, a hydrocarbon material, which for the sake of simplicity may be taken to be chiefly or substantially entirely normal pentane, is admitted through inlet 11, valve 12, and charge pump 13 to conduit 14, wherein it is mixed with concentrated hydrofluoric acid, which is admitted through inlet 15, valve 16, and charge pump 17. The resulting hydrocarbon-hydrofluoric acid mixture is passed to heating coil 18, in which it is heated to the desired reaction temperature. The preferred proportions of hydrofluoric acid and the preferred reaction conditions for this embodiment of my invention are substantially the same as for the embodiment shown in Figure 1, and previously discussed. The heated reaction mixture from coil 18 is passed to reactor 21, wherein it is subjected to the desired reaction conditions of temperature and pressure for a time sufficient to effect the desired extent of reaction. If desired, reactor 21 may be packed with steel turnings or other solid material suitable for aiding in the catalysis of the reaction.

The effluent mixture from reactor 21 is passed 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 may be recycled through valve 75 and conduit 76 to pump 17. Preferably, however, at least part of it is passed through valve 77 and conduit 78 to fractionator 79, wherein it is separated into the following two fractions: (1) an overhead fraction comprising substantially anhydrous hydrofluoric acid with small proportions of light hydrocarbons,

such as propane and butane, which is recycled through valve 80 and conduit 76 to pump 17, and (2) a minor bottom fraction comprising acid-soluble material, water, and hydrogen fluoride, which is withdrawn through outlet 81 having valve 82.

The lighter or hydrocarbon phase from separator 27 is passed through valve 83 and conduit 84 to fractionating means 85, wherein it is fractionally distilled to yield an isobutane fraction and any other desired products. Light gases, such as methane, ethane, and the like, are preferably withdrawn from the system, as through outlet 86 having valve 87. Propane and hydrofluoric acid pass, at least partly as an azeotropic mixture, through valve 88, and are recycled to coil 18 by conduit 89; if desired, any excess propane may be withdrawn, as through outlet 86 and valve 87. Isobutane is withdrawn through outlet 90 having valve 91. Any normal butane is usually preferably recycled through valve 92 and conduit 89. Hydrocarbons heavier than butane may be recycled with the normal butane, especially if the highest possible yield of isobutane is desired; but if desired, selected or especially valuable fractions may be advantageously withdrawn. For example, isopentane may be withdrawn through outlet 93 having valve 94; normal pentane is preferably recycled through valve 95 and conduit 89; and material boiling above normal pentane may be withdrawn through outlet 96 having valve 97. Fractionating means 85 may comprise whatever distilling columns and auxiliary equipment are necessary or convenient for effecting the separations indicated.

If desired, any of the fractions withdrawn from fractionating means 85 may be passed through one or more purification steps. For example, the fraction boiling above normal pentane may pass through valve 98 and conduit 99 to fluorine remover 100, which contains 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 400° 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 in accordance with the results of a trial for the particular case organically combined fluorine is substantially completely removed from the hydrocarbon material, which then is passed through valve 101 and conduit 102 to fractionator 103 for separation into any desired final fractions. A substantial fraction comprising motor-fuel hydrocarbons may be withdrawn through outlet 104 having valve 105, and a minor fraction comprising hydrocarbons boiling above the motor-fuel range may be withdrawn through outlet 106 having valve 107.

The volatility of the motor-fuel product is advantageously controlled by adjusting the proportion of relatively light constituents, any excess of which is recycled from fractionating means 85. For example, if a relatively volatile motor fuel is desired, less of these light constituents is recycled, and more is left in the motor-fuel fraction. Some adjustment is also possible by controlling the proportion of relatively high-boiling constituents which is withdrawn from the bottom of fractionator 103. If desired, part or all of the above-mentioned high-boiling constituents may be recycled, by means not shown, to pump 13; usually, however, it is preferable to remove this material from the system, because it tends to carbonize in the heater and/or reactor.

Although the isobutane product from fractionating means 85 may be subjected to one or more purification steps, such as defluorination or the like, it usually need not be purified, especially if it is to be used as feed to an alkylation process catalyzed by a hydrofluoric acid catalyst.

Some aspects of my invention are illustrated in the following examples, which are illustrative, but not necessarily limitative, of the invention.

*Example I*

A hydrocarbon stream consisting of substantially pure normal butane is subjected to the action of 50 per cent of its weight of concentrated hydrofluoric acid in a process similar to that described in connection with Figure 1. The reaction temperature is about 650° F., the pressure is about 750 pounds per square inch, and the reaction time is about 30 minutes. Reactor 21 is packed with steel turnings, and about 5 per cent, by weight of hydrocarbon treated, of a high-boiling absorber oil is passed continuously through the reaction zone to prevent coking up of the reactor. Under these conditions the ultimate yield of isobutane is about 75 per cent by weight of the normal butane feed. Of the other 25 per cent, about 10 per cent is converted to propane; and about 15 per cent, to heavier hydrocarbons.

*Example II*

A hydrocarbon stream consisting mainly of normal pentane is subjected to the action of about 70 per cent of its weight of substantially anhydrous hydrofluoric acid in a process similar to that described in connection with Figure 2. The reaction temperature is about 700° F., the pressure is about 1000 pounds per square inch, and the reaction time is about 20 minutes. Pentanes in the product are recycled. Under these conditions, the yield of motor-fuel hydrocarbons having 6 or more carbon atoms per molecule is about 25 per cent by weight of the material charged, and the yield of isobutane is about 60 per cent; the remainder is converted to propane and to material boiling above the motor-fuel range.

*Example III*

In a batch process, normal butane was treated in a steel reactor with 3 times its weight of anhydrous hydrofluoric acid. The maximum temperature was about 515° F., the maximum pressure was about 230 atmospheres, and the time at these conditions was about 40 minutes. About two hours was required to heat the reactor to its maximum temperature. The reactor was cooled, and the contents were withdrawn for analysis. By fractional analysis the recovered hydrocarbon material was found to have approximately the following composition:

| Product: | Weight percent |
|---|---|
| Propane | 10 |
| Isobutane | 26 |
| Normal butane | 51 |
| Isopentane | 8 |
| Normal pentane | 2 |
| Hexanes and higher | 3 |
| | 100 |

In a corresponding continuous process, in which reaction conditions are comparable but in which recycling is practiced, the major product withdrawn is isobutane; isopentane and/or higher-

boiling hydrocarbons may be also withdrawn, but if desired, they may be recycled to increase the ultimate yield of isobutane.

*Example IV*

In a batch process, normal pentane was treated in a steel reactor with twice its weight of concentrated hydrofluoric acid. The maximum temperature, reached in about one hour after starting the heating, was 572° F. This temperature was maintained for 30 minutes; then the reactor was cooled rapidly, and the products were withdrawn for examination. On a normal pentane-free basis, the proportions of the various products were as follows:

| Product: | Weight percent |
|---|---|
| Propane | 12.4 |
| Isobutane | 29.8 |
| Normal butane | 18.6 |
| Isopentane | 26.4 |
| Hexanes | 8.2 |
| Higher-boiling | 4.6 |
| | 100.0 |

It is apparent from these data that, in a corresponding continuous process, by recycling undesired products, especially propane and/or normal butane, normal pentane can be converted in high yield to isobutane and/or isopentane and/or motor-fuel hydrocarbons.

*Example V*

In a steel bomb, normal butane was subjected to the action of twice its weight of concentrated hydrofluoric acid at a maximum temperature of 356° F. and a pressure of 3700 pounds per square inch for a period of three hours. The bomb was cooled, and the products were withdrawn. The hydrocarbon material recovered had the following composition.

| Product: | Weight percent |
|---|---|
| Propane | 3.2 |
| Isobutane | 4.3 |
| Normal butane | 90.0 |
| Isopentane | 2.5 |
| | 100.0 |

Although, in this example, the reaction conditions were obviously very unfavorable, an appreciable reaction did occur; the conditions used are therefore considered to be within the broadest scope of this invention.

*Example VI*

Isopentane and about 60 per cent of its weight of concentrated hydrofluoric acid were allowed to stand in a steel bomb for four weeks at a temperature of 175° F. Then the products were withdrawn, and the resulting hydrocarbon material was found to have approximately the following composition:

| Product: | Mol percent |
|---|---|
| Butanes (mostly isobutane) | 8.6 |
| Isopentane | 69.6 |
| n-Pentane | 10.3 |
| Hexanes and heavier | 11.5 |
| | 100.0 |

Although, in this example, the isopentane was mostly in the liquid phase because of the relatively low temperature, the results show that isopentane can be treated and/or recycled to give appreciable yields of isobutane; also, they indicate that isopentane can be converted to any desired extent into relatively heavy motor-fuel hydrocarbons, whereby control of the volatility of relatively heavy products may be advantageously obtained in the manner generally described herein.

My invention provides a new process for converting normal butane and/or pentane to isobutane. It is applicable also to the production of isopentane, for example by the conversion of normal pentane and/or heavier paraffins to isopentane. It would also be possible to convert isobutane and/or isopentane to normal butane and/or normal pentane, respectively, by this invention, if a need for such a conversion should arise. Motor fuel of controlled volatility can be produced in substantial proportions as a product of my process. My invention comprises also a novel means for preventing coking up of reaction chambers used in the process. Furthermore, it provides a simple method of separating heavy acid-soluble material from hydrofluoric acid which is to be recycled.

There are many modifications of my process, of which only a few are described in this specification. Hence, it is not intended that mention herein of specific apparatus, materials, conditions, purposes, or the like should unduly limit the scope of my invention. In the specific embodiments described, it is understood that additional equipment such as pumps, valves, coolers, fractionators, or the like, such as are well-known to those skilled in the art, may be used wherever needed or convenient.

I claim:

1. A process for isomerizing low-boiling paraffin hydrocarbons of at least four carbon atoms per molecule in a straight chain to form low-boiling isoparaffins, which comprises subjecting in a reaction zone such a paraffin to the action of hydrofluoric acid as the sole effective isomerization catalyst, in an amount from about 0.1 to 4 times by weight of the hydrocarbon material, under an elevated temperature and pressure such that said paraffin and hydrofluoric acid are in gas phase, passing a minor amount of a heavy oil through said reaction zone as a liquid to absorb reaction products of high molecular weight and minimize carbon and tar formation, passing effluents of said reaction zone to a first separator and removing as a liquid said heavy oil and absorbed constituents, removing also from said first separator as a gas a mixture of low-boiling hydrocarbons and hydrofluoric acid, subjecting said gas to partial cooling and condensation to liquify hexane and heavier hydrocarbons and removing the resultant liquid from the process, subjecting the remaining gas to further partial cooling and condensation to liquify the major portion of hydrofluoric acid, and separating same from uncondensed gas, cooling and condensing said uncondensed gas to form a liquid hydrofluoric acid phase and a liquid hydrocarbon phase, passing said liquid hydrocarbon phase to a fractional distillation and recovering therefrom low-boiling isoparaffins.

2. The process of claim 1, in which said elevated temperature is in the range of 250 to 1000° F.

3. The process of claim 1, in which said elevated temperature is in the ranges of 400–800° F.

4. The process of claim 1, wherein the reaction zone contains a solid contact mass.

5. The process of claim 1, in which said paraffin is normal pentane and in which said isoparaffin so produced is isobutane.

6. A process for converting low-boiling paraffin hydrocarbons of at least four carbon atoms per molecule in a straight chain to form low-boiling isoparaffins, which comprises passing such a paraffin in admixture with hydrofluoric acid as the sole effective conversion catalyst, in an amount from about 0.1 to 4 times by weight of the hydrocarbon material, through a large vertical reaction zone, maintaining the mixture in said reaction zone in gas phase under an elevated temperature and pressure for a time to effect a substantial conversion of said paraffin to form low-boiling isoparaffins including at least one isomer of said paraffin, introducing at the top of said vertical reaction zone a heavy hydrocarbon oil which remains in liquid phase under said conversion conditions to absorb reaction products of high molecular weight and minimize carbon and tar formation, passing effluents of said reaction zone to a first separator and removing as a liquid said heavy oil and absorbed constituents, passing said liquid to a fractionating means and removing low-boiling hydrocarbons absorbed therein, removing a gas from said first separator and admixing said low-boiling hydrocarbons with said gas, subjecting the resultant mixture to partial cooling and condensation to liquify hexane and heavier hydrocarbons and removing the resultant liquid from the process, subjecting the remaining gas to further partial cooling and condensation to liquify the major portion of hydrofluoric acid together with some pentanes and hexanes, and separating same from uncondensed gas, separating the resulting liquid into a hydrofluoric acid phase and a hydrocarbon phase and returning said hydrofluoric acid phase to said reaction zone, cooling and condensing the last said uncondensed gas to form a hydrofluoric acid phase and a hydrocarbon phase and returning said hydrofluoric acid phase to said reaction zone, combining the two last said liquid hydrocarbon phases and passing same to fractionating means, and recovering from said fractionating means low-boiling isoparaffins so produced.

7. The process of claim 6, wherein the proportion of absorbing fluid is in the range 0.1 to 1 times by weight of the hydrocarbon material treated and its residence in the reaction zone is not greater than one-tenth that of the paraffin undergoing conversion.

8. A process for converting a low-boiling paraffin having at least four carbon atoms per molecule to form other low-boiling paraffins, which comprises passing a gaseous mixture comprising such a low-boiling paraffin and hydrogen fluoride as the sole conversion catalyst downwardly through a reaction zone while at a conversion temperature in the range of about 250 to 800° F., maintaining said mixture in said reaction zone for a time sufficient to convert a substantial amount of said paraffin forming other low-boiling paraffins including at least one isomer of said paraffin, concomitantly passing downwardly through said reaction zone in liquid phase a heavy oil to absorb reaction products of high molecular weight and minimize tar and carbon formation, said oil being passed through said zone at a rate such that it undergoes substantially no conversion, and separating from effluents of said reaction zone low-boiling hydrocarbons produced therein.

9. A process for isomerizing a low-boiling paraffin having at least four carbon atoms per molecule to form other low-boiling paraffins, which comprises passing a gaseous mixture comprising such a low-boiling paraffin and hydrogen fluoride as the sole isomerization catalyst through a reaction zone while at an isomerization temperature in the range of about 250 to 800° F., maintaining said mixture in said reaction zone for a time sufficient to isomerize a substantial amount of said paraffin forming an isomer thereof, cooling and effecting a partial condensation of effluents of said reaction zone to condense and remove as a liquid heavy oils, subjecting remaining vapors to further cooling and effecting a partial condensation thereof to condense a major part of the hydrogen fluoride and of remaining hydrocarbons heavier than butane, separating from the last said partially condensed mixture liquids so formed and uncondensed vapors, separating from said liquids liquid hydrogen fluoride and liquid hydrocarbon as separate materials, subjecting said uncondensed vapors to additional cooling and condensing to form a second liquid hydrogen fluoride phase and a second hydrocarbon phase, combining said liquid hydrogen fluoride phases and passing same to said reaction zone, combining the last two said hydrocarbon phases and subjecting same to fractional distillation, recovering from said fractional distillation normally gaseous-paraffin hydrocarbons and a minor amount of hydrogen fluoride and passing same to said reaction zone, and recovering also from said fractional distillation low-boiling isoparaffins as products of the process.

10. A process for converting a low-boiling paraffin hydrocarbon having at least four carbon atoms per molecule to other low-boiling paraffins, which comprises passing to the top of an elongated vertical reaction zone in vapor phase a paraffinic hydrocarbon material comprising such a low-boiling paraffin and hydrogen fluoride as the sole effective catalyst in an amount between about 0.2 and about 4 times by weight of the hydrocarbon material, maintaining the resulting gaseous mixture of hydrogen fluoride and paraffinic hydrocarbon material in said reaction zone at a conversion temperature between about 250 and about 800° F. and under a superatmospheric pressure for a reaction time sufficient to form other low-boiling paraffin hydrocarbons including at least one isomer of said low-boiling paraffin, injecting into the top of said reaction zone a liquid hydrocarbon material in a manner such as to scrub the inner surfaces of said reaction zone and maintain the same free of carbonaceous deposits, said liquid hydrocarbon material being relatively nonvolatile at said reaction temperature and passed through said reaction zone at a rate such that its residence time therein is not greater than 0.1 times said reaction time, and recovering from the bottom of said reaction zone hydrogen fluoride, reaction products, and said liquid hydrocarbon material.

11. The process of claim 10 in which said materials effluent from said reaction zone are passed as a single effluent mixture to a separator, separating therefrom a liquid phase comprising said liquid hydrocarbon material and a gas phase comprising hydrogen fluoride and paraffinic reaction products, returning a portion of said liquid phase to the top of said reaction zone, subjecting a further portion of said liquid phase to purification to remove volatile material and liquid impurities, recovering a purified liquid hydrocarbon material and passing same to the top of said reaction zone, combining said volatile material with said gas phase and recovering therefrom a hydrocarbon fraction comprising an isoparaffin

produced in said reaction zone as a product of the process.

12. The process of claim 10 in which the reaction zone is packed with granular alumina.

13. A process for converting a low-boiling paraffin having at least four carbon atoms per molecule to form other low-boiling paraffins, which comprises passing a gaseous mixture comprising such a low-boiling paraffin and hydrogen fluoride as the sole effective conversion catalyst, in an amount from about 0.1 to 4 times by weight of the hydrocarbon material, downwardly through a reaction zone while at a conversion temperature in the range of about 250 to 800° F., maintaining



said mixture in said reaction zone for a time sufficient to convert a substantial amount of said paraffin forming other low-boiling paraffins, including at least one isomer of said paraffin, concomitantly passing downwardly through said reaction zone in liquid phase a heavy oil to absorb reaction products of high molecular weight and minimize tar and carbon formation, said oil being passed through said zone at a rate such that it undergoes substantially no conversion, and separating from effluents of said reaction zone low-boiling hydrocarbons produced therein.

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