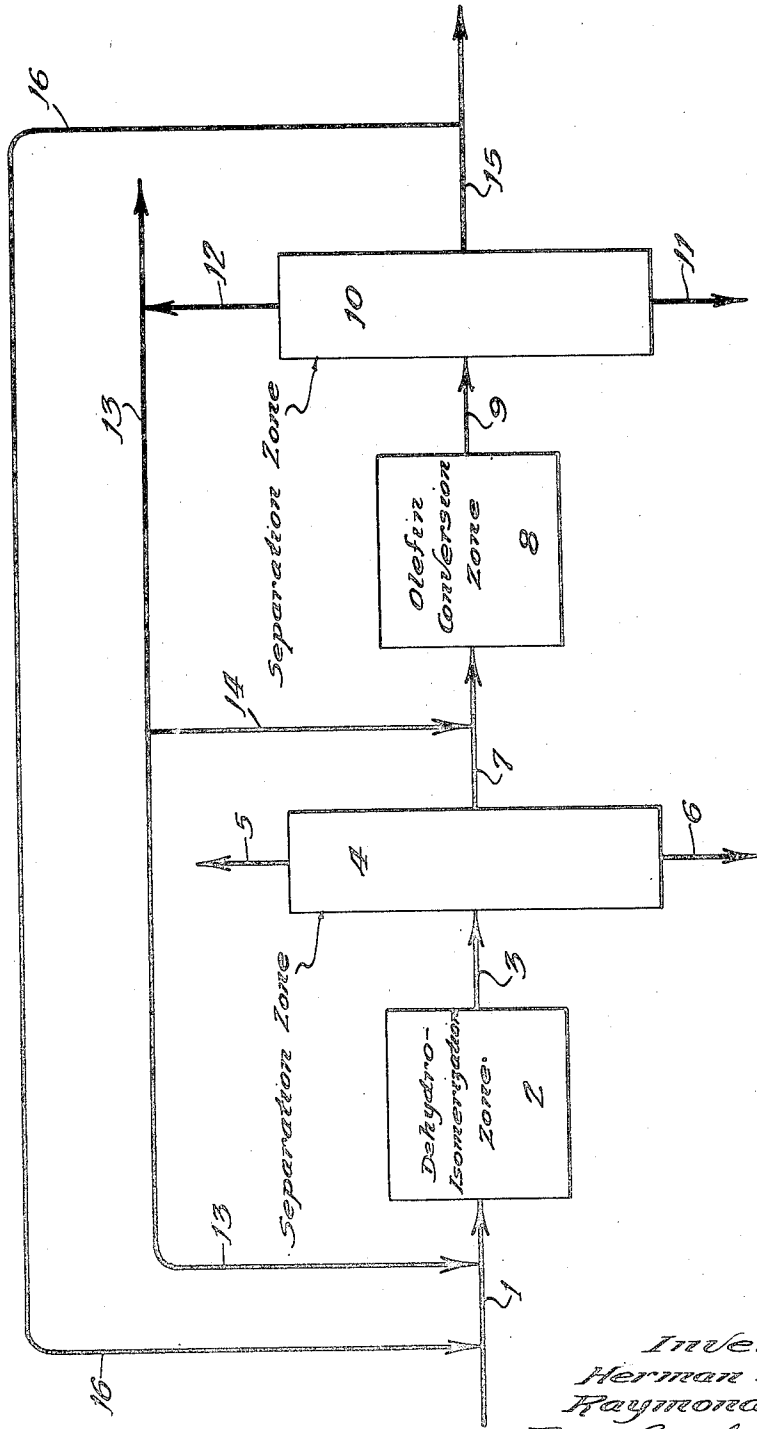
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CONVERSION OF HYDROCARBONS

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CONVERSION OF HYDROCARBONS

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This application is a continuation-in-part of our co-pending application Serial No. 518,996, filed January 20, 1944, now U. S. Patent 2,389,406, which in turn is a continuation-in-part of our application Serial No. 256,760, filed February 16, 1939, now U. S. Patent 2,346,657, and relates to a combination of interdependent and cooperative steps for the conversion of an isomerizable paraffinic hydrocarbon into branched-chain hydrocarbons of high anti-knock characteristics.

In a broad aspect the present invention relates to a process for converting a paraffinic hydrocarbon containing at least 4 carbon atoms to the molecule into a higher boiling branched chain hydrocarbon, which comprises subjecting said paraffinic hydrocarbon to contact with dehydrogenating and isomerizing catalysts under conditions to form branched-chain olefinic hydrocarbons, and subjecting said olefinic hydrocarbons to conversion in the presence of a condensation catalyst under conditions to form said higher boiling branched-chain hydrocarbons.

One specific embodiment of the present invention relates to a process for converting normal butane, which comprises subjecting normal butane to simultaneous dehydrogenation and isomerization to form a mixture of iso- and normal butylenes, polymerizing said butylenes, separating an unconverted butane fraction from the polymerization effluent products, and recycling the separated butane fraction to said simultaneous dehydrogenation and isomerization.

Another specific embodiment of the present invention relates to a process for converting normal butane, which comprises subjecting normal butane to simultaneous dehydrogenation and isomerization to form a mixture of iso- and normal butylenes, separating said mixture and commingling isobutane therewith, alkylating said isobutane with said butylenes, separating an unconverted normal butane fraction and an unconverted isobutane fraction from the alkylation effluent products, recycling the normal butane fraction to said simultaneous dehydrogenation and isomerization, and recycling the isobutane fraction to said alkylation.

In the first step of the present process a paraffin containing at least 4 carbon atoms to the molecule, such as normal butane, is subjected to dehydrogenation and isomerization. The effluent products from this operation comprise a mixture of iso- and normal olefins, such as iso- and normal butylenes, which mixture is particularly suitable for conversion into higher boiling branched-chain hydrocarbons. Thus, for example, it has

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been found that when a mixture of iso- and normal butylenes are utilized to alkylate with isobutane, a product having a higher anti-knock rating is obtained than when a fraction consisting of normal butylenes is utilized in the alkylation reaction. These advantages are further illustrated in the following table which shows results obtained in alkylating isobutane by (1) butylene-1, (2) butylene-2, and (3) isobutylene at 60° F. in the presence of hydrogen fluoride of 98% concentration.

The results shown below were obtained by the separate analysis of two different samples of the products from each test, in one case the alkylate was subjected to depentanization to remove hydrocarbons containing 5 carbon atoms and less to the molecule, while in the second case the alkylate was subjected to debutanization to remove hydrocarbons containing 4 carbon atoms and less to the molecule.

Olefin	Butylene-1	Butylene-2	Isobutylene
Isobutane to butylene ratio	9.7	8.5	8.4
I-C Octane No. for Depentanized Alkylate with 4.6 cc. of Tetraethyl Lead	104.7	109.2	111
I-C Octane No. for Debutanized Alkylate—Clear	90.2	96.1	95.5
+4cc. of Tetraethyl lead		108.7	109.7
+4.6cc. of Tetraethyl lead	105.5		

It will be noted from the above table that products having higher leaded octane numbers are obtained by the alkylation of isobutane with isobutylene as compared to alkylation with normal butylenes and particularly butylene-1.

The effluent products of the first step of the present process may have a butylene content comprising 25 mol percent or more of isobutylene, approximately 50 mol percent of butylene-2 and the remainder of butylene-1, and thus will produce alkylates of higher octane number than would be obtained when utilizing the effluent products of conventional normal butane dehydrogenation processes when effected under substantially the same conditions. The conventional dehydrogenation process does not employ an isomerization catalyst in admixture with the dehydrogenation catalyst.

A major difficulty and expense in connection with the first step of the process is the separation of the olefin products from unconverted paraffinic hydrocarbons. These paraffins and olefins are of close boiling range and in many cases their boiling points overlap so that separation thereof cannot be effected by purely fractional distilla-

tion means and other expensive methods must be resorted to. However, in the present combination process, the second step of the process functions not only to produce the branched-chain hydrocarbon but also to separate the unconverted normal paraffins from the olefins by converting the olefins into a higher boiling product which may readily be separated by fractionation. For example, the mixture of butylenes and butanes separated in the first step of the process may be subjected to an alkylation reaction with isobutane, in which alkylation reaction the butylenes are reacted with isobutane to form higher boiling products and the higher boiling products then may be readily separated by fractionation from the unconverted butanes. Usually an excess of isobutane is used in the alkylation reaction and the separated butanes may be further separated by fractionation into a normal butane fraction, which may be recycled to the first step of the process for further conversion therein, and an isobutane fraction which may be recycled to the second step of the process for further use therein.

It is thus seen that the present invention provides a unitary process for the conversion of a normal paraffin into a mixture of olefins particularly suitable for use in the second step of the process and that the second step of the process converts said mixture and also serves to separate the unconverted hydrocarbons for recycling to the first step of the process. The operation of the first step of the process determines the final products obtained from the second step of the process, while the second step of the process serves to segregate the products for recycling back to the first step of the process.

The paraffinic hydrocarbon utilized as charging stock to the first step of the process may comprise any suitable paraffin containing at least 4 carbon atoms to the molecule, but preferably comprises normal butane, normal pentane or mixtures thereof. These paraffins may readily be converted into the desired olefinic hydrocarbons in the manner to be hereinafter set forth in detail. When charging paraffins containing 6 or more carbon atoms to the molecule, the paraffinic hydrocarbons may undergo some cyclization so that the effluent products may contain aromatic hydrocarbons. However, the aromatic hydrocarbons may be alkylated in the second step of the process to produce alkyl aromatics which, if of a satisfactory boiling range, are desirable in motor fuel.

When the process is being operated to produce gasoline, the paraffinic hydrocarbon charging stock should not be of too high molecular weight as otherwise the final product of the process may boil outside the range of motor fuel. In general, the paraffinic hydrocarbon should not contain more than 8 carbon atoms to the molecule when the process is operated to produce gasoline. However, with certain alkylation catalysts, decomposition of higher boiling olefinic hydrocarbons occur during the alkylation reaction. This decomposition is termed depolyalkylation and may comprise, for example, the splitting of an olefinic hydrocarbon containing 8 carbon atoms to the molecule to fragments containing 4 carbon atoms to the molecule, which subsequently undergo alkylation as 4-carbon atom fragments. In such cases the use of higher boiling paraffinic hydrocarbons in the first step of the process would be permissible since the final product of the process will boil within the desired motor fuel range.

Similarly, when the second step of the process comprises alkylation, the alkylatable hydrocarbon used therein should not be of such high boiling point that the final product of the process boils above the motor fuel range. The preferred alkylatable hydrocarbons comprise isobutane, isopentane or mixtures thereof. Isohexane, isoheptane, iso-octane, etc., may also be used within the scope of the invention, particularly when the paraffinic hydrocarbon charged to the first step of the process is of low molecular weight. In some cases the alkylatable hydrocarbon utilized in the second step of the process may comprise an aromatic hydrocarbon and the final product of the process then will comprise alkyl aromatics which may be used for motor fuel if of satisfactory boiling range or which may be used for any other purpose desired.

In the first step of the process the paraffinic hydrocarbon is subjected to conversion in the presence of mixed dehydrogenation and isomerization catalysts. The mixed catalyst may comprise separate layers of dehydrogenation and isomerization catalysts, or intimate mixtures of separately precipitated dehydrogenation and separately precipitated isomerization catalyst or coprecipitated or successively precipitated dehydrogenation and isomerization catalysts. A preferred arrangement comprises separate layers of these catalysts, the dehydrogenation catalyst being disposed above the isomerization catalyst when employing down flow of the normal paraffin charge and the dehydrogenation catalyst further being considerably larger in quantity as compared to the isomerization catalyst.

In some cases, a relatively thin layer of isomerization catalyst may be sufficient to obtain the advantages of the present invention. Complete details of suitable dehydrogenation and isomerization catalysts and of various methods of manufacturing them are given in our Patent 2,346,657, which patent is to be considered as a part of the present specification. The preferred dehydrogenation catalyst comprises alumina composited with an oxide of a metal in the left-hand column of group VI of the periodic table, particularly chromia and molybdena, while the preferred isomerization catalyst comprises silica composited with alumina, zirconia and/or thoria.

The catalyst may be used in the shape of granules, powder or shaped particles and the process may be either of the fixed bed type, the fluidized type, slurry type, or any other suitable type. Conversion may be effected at temperatures of from about 900° to about 1100° F. under subatmospheric, atmospheric, or moderate superatmospheric pressures which may range up to 100 pounds per square inch.

In the second step of the process the olefinic hydrocarbons produced in the first step of the process are converted to produce higher boiling branched-chain hydrocarbons. The preferred olefin conversion step comprises alkylation of an alkylatable hydrocarbon with said olefins and this may be effected in the presence of any suitable alkylation catalyst including hydrogen fluoride, sulfuric acid, aluminum chloride and/or its organic complexes, etc. These catalysts are usually utilized at moderate temperatures which generally are below 200° F. and usually below a pressure of 500 pounds per square inch.

When the alkylatable hydrocarbon comprises an aromatic, phosphoric acid catalyst and particularly solid phosphoric acid catalyst as described in Patent 2,346,657, may be used. It is

understood that the present invention is not limited to any alkylation catalyst and that any suitable catalyst may be employed within the scope of the invention.

In another embodiment of the invention the olefin conversion step of the process may comprise polymerization of the olefins and here again any suitable catalyst may be used. The preferred catalyst comprises the solid phosphoric acid catalyst, and polymerization of the olefins is preferably effected at a temperature of about 225° to about 325° F. at a pressure of about 500 to about 700 pounds per square inch. Sulfuric acid is also a particularly suitable polymerization catalyst and may be employed in either of the conventional hot acid or cold acid polymerization processes.

The invention will be further illustrated in connection with the accompanying diagrammatic flow drawing which, in the interest of simplicity, will be described in connection with the conversion of normal butane.

Referring to the drawing, normal butane is introduced through line 1 into dehydroisomerization zone 2. In zone 2 the normal butane is contacted with the dehydrogenation and isomerization catalyst in the manner hereinbefore set forth, and the effluent products are directed through line 3 to separation zone 4. Zone 4 may comprise one or a plurality of fractionating, distilling, absorbing and stripping zones, etc., in order to separate products which are higher boiling and those which are lower boiling than the desired hydrocarbons containing 4 carbon atoms per molecule. The light products, which normally will comprise hydrogen, methane, ethane, ethylene, propane and propylene, are withdrawn from zone 4 through line 5. Higher boiling products which may comprise pentane originally present in the charging stock or formed during the operation, as well as a minor amount of higher boiling hydrocarbons, may be withdrawn from zone 4 through line 6.

The fraction comprising 4 carbon atom hydrocarbons is withdrawn from zone 4 through line 7 and is directed to olefin conversion zone 8. As heretofore set forth zone 8 preferably comprises either an alkylation or a polymerization zone and the effluent products therefrom are directed through line 9 to separation zone 10 which may comprise one or a plurality of fractionating zones. Normally liquid products are withdrawn from zone 10 through line 11 and may be subjected to any desired rerun fractionation in order to separate the desired fraction, or the liquid products may be subjected to any desired further treatment prior to said rerun fractionation. Thus, in the case of olefin polymers, the liquid product withdrawn through line 11 may be subjected to hydrogenation prior to or after rerunning.

When zone 8 comprises an alkylation process, zone 10 preferably comprises a plurality of fractionating zones so that the products may be separated into an isobutane fraction, a normal butane fraction, and an alkylate fraction. The isobutane fraction may be directed through lines 12 and 13 and may be withdrawn from the process, but preferably at least a portion of the isobutane is directed through line 14 and returned through line 7 to zone 8 for further use therein. Normal butane separated in zone 10 may be removed from the process through line 15 but preferably is recycled by way of lines 16 and 1 to zone 2 for further conversion therein.

When zone 8 comprises a polymerization operation, unconverted butanes may be separated in

zone 10 and recycled by way of lines 12, 13 and 1 to zone 2 for further conversion therein. In the polymerization operation lines 15 and 16 may be omitted.

The following example is introduced to further illustrate the novelty and utility of the present invention but not with the intention of unduly limiting the same.

When a normal butane fraction is subjected to contact with a mixture of alumina-chromia dehydrogenation catalyst and silica-alumina isomerization catalyst at a temperature of 1000° F. and atmospheric pressure, a mixture of butylenes is formed comprising approximately 25 mol percent isobutylene, 50 mol percent butylene-2 and 25 mol percent of butylene-1. The mixture of butylenes and unconverted butanes from the first step of the process is commingled with isobutane and the mixture subjected to alkylation at a temperature of 100° F. and a pressure of 100 pounds per square inch in the presence of a hydrogen fluoride catalyst. The effluent hydrocarbon products are separated into an isobutane fraction, normal butane fraction and an alkylate fraction. The isobutane fraction is recycled to the alkylation step and the normal butane fraction is recycled to the dehydrogenation-isomerization process. The alkylate may be rerun to separate a 300° F. end point fraction suitable for use as aviation fuel which fraction is substantially saturated and of high anti-knock value.

We claim as our invention:

1. A process for converting a normal paraffin having at least 4 carbon atoms to the molecule which comprises subjecting the normal paraffin to simultaneous dehydrogenation and isomerization in the presence of a physical mixture of a dehydrogenating catalyst and an isomerizing catalyst to form a mixture of iso- and normal olefins and unconverted normal paraffin, commingling an isoparaffin with said mixture, catalytically alkylating said isoparaffin with said olefins in the presence of said normal paraffin, separating from the effluent products of said alkylation an unconverted normal paraffin fraction and an unconverted isoparaffin fraction, recycling the normal paraffin fraction to said simultaneous dehydrogenation and isomerization, and recycling the isoparaffin fraction to said alkylation.

2. A process for converting normal butane which comprises subjecting the normal butane to simultaneous dehydrogenation and isomerization in the presence of a physical mixture of a dehydrogenating catalyst and an isomerizing catalyst to form a mixture of iso- and normal butylenes and unconverted normal butane, commingling isobutane with said mixture, catalytically alkylating said isobutane with said butylenes in the presence of said normal butane, separating from the effluent products of said alkylation an unconverted normal butane fraction and an unconverted isobutane fraction, recycling the normal butane fraction to said simultaneous dehydrogenation and isomerization, and recycling the isobutane fraction to said alkylation.

3. A process for the production of branched chain hydrocarbons which comprises simultaneously dehydrogenating and isomerizing a paraffinic hydrocarbon containing at least four carbon atoms per molecule by the action of a dehydrogenating catalyst in physical admixture with a minor proportion of an isomerizing catalyst, reacting the resultant branched chain olefinic product with an alkylatable hydrocarbon at alkylating

conditions to form a higher boiling branched chain hydrocarbon and recovering the same, and recycling unconverted paraffinic hydrocarbons to the dehydrogenation-isomerization step.

4. The process of claim 3 wherein said alkylatable hydrocarbon comprises an aromatic hydrocarbon.

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