

UNITED STATES PATENT OFFICE

2,337,418

DESTRUCTIVE ISOMERIZATION

Robert F. Ruthruff, Chicago, Ill.

No Drawing. Application November 15, 1939,
Serial No. 304,601

8 Claims. (Cl. 260-676)

This invention relates to a process wherein hydrocarbon fractions are simultaneously cracked and isomerized. More particularly, this invention relates to a process wherein higher boiling hydrocarbons are simultaneously cracked and isomerized with the production of lower boiling isoparaffins. Still more particularly, this invention relates to a process wherein higher boiling hydrocarbons are simultaneously cracked and isomerized with the production of isobutane and low boiling liquid isoparaffins.

As is well known to those skilled in the art, certain isomeric octanes form the basis of modern high octane number aviation fuels. These isomeric octanes are usually made by the catalytic polymerization of isobutene or isobutene-normal butenes mixtures followed by hydrogenation of the polymer produced, or by the catalytic alkylation of isobutane with isobutene, normal butenes or mixtures thereof. The isomeric octanes formed by either of these two methods are quite suitable as components of high octane number aviation fuels. Their straight octane number is high, ranging from 92 to 98 depending upon the exact mode of their production. They have a high lead response and zero unsaturation. Unfortunately, these isooctanes are not sufficiently volatile to be used straight in modern aviation fuels and it is impossible to blend them with the highly volatile stocks usually available in a refinery without a great sacrifice in the high octane number originally achieved only after great effort.

Many attempts have been made to increase the volatility of isooctanes formed by the hydrogenation of catalytic polymer or directly by alkylation without at the same time sacrificing a large part of the high octane number of the straight isooctanes. Since isopentane is the only low boiling liquid isoparaffin readily available, isopentane-isooctane blends have been proposed as aviation fuels. As those skilled in the art are aware, aviation fuels meeting current specifications cannot be prepared in this way. If the blend meets the 10% off specification, the 50% off specification is not satisfied. Likewise, if the blend has the proper amount of isopentane to satisfy the 50% off specification, the minimum permissible temperature for 10% off is far exceeded. To correct for these deficiencies, light naphtha has been added to the isopentane-isooctane blend. When this is done the octane number is very much below that shown by the straight isooctane. Very recently, 2,2, dimethyl butane has been suggested as a blending agent

for isooctanes, with or without isopentane. While the use of this compound as a blending agent results in considerable improvement the fact remains that this hexane is very difficult to obtain. At present this material is made by the thermal alkylation of isobutane with ethene at extremely high pressures. To reduce ethene polymerization, the concentration of this olefine must be kept at an extremely low level. This means that the yield per pass of the desired compound is very low, which in turn necessitates an extremely high recycle ratio and the separation of the small amount of the isomeric hexane from a large amount of unreacted material.

It is evident that a simple, convenient and economic method for the production of a low boiling naphtha having a high content of isoparaffinic hydrocarbons would be of high utility. Such a light, highly isoparaffinic naphtha can be employed to increase the volatility of isooctanes and thus produce a blend meeting current aviation specifications and at the same time exhibiting high octane number. Such a light, highly isoparaffinic naphtha can also be employed as a blending agent for ordinary automobile fuel and for other purposes if desired.

In addition, as those skilled in the art are aware, generally in the manufacture of isooctanes by either catalytic polymerization-hydrogenation or by catalytic alkylation the production of isooctanes is conditioned entirely by the amount of isobutane and/or isobutene available. In catalytic polymerization, if a mixture comprising isobutene and normal butenes is charged to the reactor, it is advisable to polymerize not more than one volume of normal butenes per volume of isobutene present, if a hydrogenated polymer of high octane number is to be produced. Refinery gas streams consisting of hydrocarbons containing four carbon atoms to the molecule and olefine containing gas mixtures made by the dehydrogenation of the butane cut from natural gas usually contain two to four volumes of normal butenes per volume of isobutene present. In catalytic alkylation, isobutane must be employed as the paraffinic component of the reacting pair. Again, in refinery butane cuts the volume of olefines present far exceeds the volume of isobutane. The same is true of gases produced by the dehydrogenation of a natural gas butane cut. Accordingly, it is evident that a simple, convenient and economic method for the production of isobutane would be of high utility.

The term destructive isomerization has been applied to the process wherein paraffins of higher boiling point and exhibiting no branching or a low degree of branching are converted into hydrocarbons of lower boiling point and exhibiting a high degree of branching.

One object of this invention is to provide an improved process for the destructive isomerization of hydrocarbons. A further object of this invention is to provide an improved process for the destructive isomerization of hydrocarbons wherein the relative proportions of gaseous destructively isomerized products and liquid destructively isomerized products may be controlled. Other objects of this invention will be evident from a perusal of the instant specification.

For a description of the process of destructive isomerization reference may be made to my United States application, Serial Number 32,379, filed July 20, 1935, and which has since matured into United States Patent 2,172,146, issued September 5, 1939. In this, it is shown that when a hydrocarbon fraction, for example, a straight run heavy naphtha, is treated at low temperatures, for example 205° F. to 210° F., with a suitable catalyst, for example, aluminum chloride promoted with hydrogen chloride, carbon tetrachloride, water or the like, a large part of the hydrocarbon fraction charged is converted into gaseous products and these consist almost exclusively of isobutane.

To this process the term destructive isomerization is applied. Isomerization is used to designate reactions wherein a compound is converted into a second compound having the same chemical composition and molecular weight but different structure than that of the first. The classical synthesis of urea from ammonium cyanate and the conversion of normal butane into isobutane are examples of isomerization. In the present instance however, in addition to forming a compound of different structure than that of the charge, the new compound also has a different molecular weight. In the example cited, a considerable amount of the heavy naphtha charge, having an average molecular weight of say 142, is converted into isobutane having a molecular weight of 58. In other words, in this reaction, the charge was first decomposed and the resulting fragments were then isomerized—hence the term destructive isomerization.

It might be argued that the above reaction was entirely one of destruction without any isomerization. For example, it might be argued with no little merit that the isobutane resulted from the preferential decomposition of 2-methyl paraffins between carbon atoms 3 and 4. In this way isobutane could be formed without any isomerization. A mass of experimental data shows that this stand is not tenable. For example, in the example cited, Mount Pleasant heavy naphtha was used as charge. As is well known to those skilled in the art, this material consists largely of straight chain paraffins. In addition, this stock was heavily acid treated before use so as to remove aromatics and similar compounds, so as charged it consisted essentially of a mixture of straight chain paraffins.

Supplementary experiments have also confirmed the fact that straight chain paraffins are destructively isomerized with the production of isobutane. For example, a heavily acid treated Mount Pleasant heavy naphtha was exhaustively

treated with chlorosulfonic acid. This last named reagent removes hydrocarbons having tertiary carbon atoms. Upon subjecting the thus treated material to destructive isomerization as before, large amounts of isobutane formed. Furthermore, synthetic normal heptane and synthetic normal heptane after exhaustive treatment with chlorosulfonic acid as previously described, when subjected to destructive isomerization gave isobutane in greater yields and with greater ease than the Mount Pleasant heavy naphtha.

A further study of the products of destructive isomerization has revealed a most important but hitherto unnoticed fact. On fractionating the products obtained by the destructive isomerization of a heavy naphtha for example, one cut may be obtained representing the isobutane produced and a second containing a material boiling from above isobutane up to the endpoint of the heavy naphtha charge. The octane number of this second cut has been found to be materially higher than that of the heavy naphtha charge. As is well known by those skilled in the art, octane number increases as volatility increases. To evaluate the effect of volatility on the octane number increase observed, this second cut was again distilled, taking overhead a fraction boiling from above isobutane up to the initial of the heavy naphtha charge and leaving as bottoms a material having approximately the same boiling range as the heavy naphtha charge. On determining the octane numbers of the two fractions thus made it was found that the bottoms had an octane number not greatly different than that of the original heavy naphtha charge, while the light naphtha overhead had an extremely high octane number. It is apparent that the reaction is predominantly one of destructive isomerization only, any parts of the original charge escaping destructive isomerization are not affected to any great extent. In a large number of experiments the light naphtha overhead had octane numbers averaging 80 motor, some 15 to 20 units higher than that of an East Texas light naphtha of the same boiling range. Investigation showed that the light naphtha formed during the destructive isomerization of hydrocarbon fractions consisted largely of isoparaffins, these accounting for the unusually high octane numbers observed.

To summarize, in the destructive isomerization of heavy naphtha the following major products are obtained:

- A. Isobutane.
- B. Light naphtha of very high octane number and consisting largely of isoparaffins.
- C. Heavy naphtha of the same boiling range and approximately the same octane number as the charge.
- D. Material having a higher boiling point than that of the charge.

It will be evident to those skilled in the art that the process of destructive isomerization differs materially from both thermal reforming and catalytic reforming. In thermal reforming, the gas formed contains all gaseous paraffins and olefines together with hydrogen. In destructive isomerization the gas consists essentially of isobutane. In thermal reforming, the light naphtha produced is highly unsaturated. The light naphtha obtained in destructive isomerization is completely saturated or nearly so. The product from thermal reforming having the same boiling range as that of the charge is highly olefinic

and has a much higher octane number than that of the charge. The same fraction from destructive isomerization contains no olefines or practically none and has an octane number differing little from that of the original charge. In catalytic reforming, the gas produced consists largely of hydrogen, very little light naphtha is produced and the material having the same boiling range as that of the charge consists largely of aromatic hydrocarbons.

While from the previous discussion it is obvious that both isobutane and a highly isoparaflinic light naphtha are highly desirable products, it should be equally obvious that under varying circumstances these two products are required in varying proportions. For example, in some refineries, a large amount of isobutane and a small amount of highly isoparaflinic light naphtha may be required, in other refineries the converse will be true. The great disadvantage of the process for destructive isomerization discussed fully in the previously mentioned United States Patent 2,172,146 and reviewed briefly herein, is the fact that the proportion in which these two products are produced is not subject to control on the part of the operator.

The instant invention provides a process of destructive isomerization wherein the proportions of isobutane and highly isoparaflinic light naphtha in the product may be controlled within wide limits. Briefly, the instant invention provides a process of destructive isomerization wherein the proportions of isobutane and isoparaflinic light naphtha may be controlled within wide limits through the employment of a series of contact agents, said contact agents comprising a suitable destructive isomerization catalyst diluted with more or less of certain finely divided metals or activated finely divided metals. It has been found that when suitable destructive isomerization catalysts are mixed with relatively large amounts of certain finely divided metals, or activated finely divided metals, such as aluminum, magnesium and zinc, the destructively isomerized product contains little or no isobutane and consists essentially of highly isoparaflinic light naphtha. By varying the catalyst-metal ratio employed it is possible to vary the isobutane-highly isoparaflinic light naphtha ratio over wide limits so that it is possible, by a suitable choice of catalyst-metal ratio to produce isobutane and highly isoparaflinic light naphtha in the proportions required to satisfy practically any refinery economy.

A wide variety of hydrocarbon fractions may be used as charging stocks in destructive isomerization. A particularly suitable charging stock for the purpose comprises a virgin heavy naphtha having a boiling range from about 250° F. to 400° F., more or less. Such naphthas as those from East Texas crudes, Midcontinent crudes and similar average crudes are well suited to the process as are naphthas having an abnormally high amount of normal paraffins such as Michigan naphthas, Pennsylvania naphthas, liquid hydrocarbons produced by the interaction of carbon monoxide and hydrogen (kogasins), paraffinic fractions from the solvent extraction of kerosenes and the like. Preferably a light naphtha or a straight run gasoline of normal boiling range is not used as a charge for in such cases the high octane number light naphtha formed by destructive isomerization would be diluted with unconverted virgin light

naphtha. Also when aluminum halide type catalysts are employed it is preferable to use an olefine free charge in order to reduce polymer formation to a minimum.

A number of catalysts may be employed to promote the uncontrolled destructive isomerization reaction. Among these may be mentioned aluminum halides, silica and clays, both natural clays, treated natural clays and synthetic clays. The operating conditions to be employed when operating at atmospheric pressure and when using aluminum chloride as a catalyst have already been outlined and further details may be obtained by consulting the previously mentioned United States Patent 2,172,146. It has been found that aluminum bromide is much more effective in this reaction than aluminum chloride due to the greater solubility of the former in hydrocarbons.

As has been mentioned previously, the crux of the instant invention resides in the incorporation of suitable finely divided metals or suitable activated finely divided metals into the usual catalysts employed in the uncontrolled destructive isomerization reaction in order to control the ratios of isobutane and light highly isoparaflinic naphtha produced. Among suitable finely divided metals for the purpose may be mentioned aluminum, magnesium and zinc; these may be employed as the straight metals or after activation if desired. Suitable processes for activation will be described in detail hereinafter.

Destructive isomerization may be conducted batchwise or preferably in a continuous system wherein the charge is passed over any of the various catalysts mentioned or other suitable contacts which may be mounted on supports if desired. Temperature of operation is usually rather low, varying from say 100° F. to 800° F., usually from 200° F. to 700° F. The exact temperature to be employed depends largely on the catalyst selected. When highly active contacts are used temperatures of from 200° F. to 400° F. may be employed while less active catalysts require higher temperatures, for example, in the range 400° F. to 700° F. When catalysts are employed containing finely divided metals or activated finely divided metals in accord with the teachings of this invention, it is usually advisable to operate at temperatures slightly higher than those employed when the straight catalysts are being used. This will be considered in greater detail subsequently herein.

If desired, the reaction may be conducted under superatmospheric pressure. Actually, because of the rather low velocity of this destructive isomerization reaction, for economy in reactor size and the like it may be desirable to run under high superatmospheric pressure, especially when the less active catalysts are employed.

For the better understanding of this invention several specific examples thereof are included but it is to be understood that these examples are illustrative only and in no way limit the scope of the instant invention. The examples included herein are divided into two classes. Those bearing the designation A cover the preparation of representative contact agents in accord with the teachings of this invention while examples bearing the designation B describe the employment of representative contact agents prepared in accord with this invention in the destructive isomerization of hydrocarbons.

Example 1A

One hundred and thirty-three and a half pounds of anhydrous aluminum chloride were ground to a fine powder in a ball mill, care being taken to exclude moisture. Twenty-seven pounds of aluminum powder were then added and the whole was made into a uniform mixture. For convenience in later operations the mixture was run through a pill machine thereby being formed into cylindrical pellets approximately $\frac{1}{4}$ inch in diameter and $\frac{1}{4}$ inch high. The minimum isobutane-light highly isoparaffinic ratio in the products is observed when this catalyst is employed in destructive isomerization. Even if the content of finely divided metal is greatly increased, the isobutane-light highly isoparaffinic naphtha ratio remains unchanged or practically so. As the finely divided aluminum powder obtained commercially was coated with a thin layer of stearic acid, prior to adding to the aluminum chloride the finely divided aluminum powder was extracted with ether to remove this organic coating.

Example 2A

The catalyst was prepared exactly as described in Example 1A except that finely divided activated aluminum powder was employed. As is well known to those skilled in the art, metallic aluminum may be activated by treating it with a solution of a salt of a metal which is less electropositive than aluminum and which is consequently deposited thereon. In the activation of the aluminum powder, the material was first washed with ether to remove the previously mentioned organic coating and was then, preferably after a superficial etch with very dilute caustic, added to an alcoholic solution of mercuric chloride following which the material was washed with alcohol and dried.

Finely divided aluminum metal or finely divided magnesium metal may also be activated by treatment with an aqueous or alcoholic solution of a salt of mercury, copper, cadmium, nickel, iron, zinc and the like. Also, both finely divided aluminum metal and finely divided magnesium metal may be activated by treating superficially with halogen. For example, the finely divided metal may be mixed with a small amount, say 1% by weight, of a halogen such as iodine and the mixture may be heated with agitation. Or, the finely divided metal may be suspended in a boiling solution of iodine or other halogen in a suitable organic medium, for example, a mixture of ether and benzene. Prior to any activation process it is advisable to remove any organic coating that may be upon the surfaces of the individual metal particles and with aluminum, the speed of activation is greatly increased if the clean metal particles are first superficially etched by a very dilute caustic solution.

Example 3A

Some 63 pounds of zinc dust are allowed to fall downward through an excess of a 1% solution of copper sulfate. The resulting zinc-copper couple is washed and dried and is intimately mixed with 133.5 pounds of finely pulverized aluminum chloride. Solely for convenience in subsequent operations the resulting mixture is formed into pellets as described in Example 1A.

Having described the preparation of several representative catalysts in accord with the teachings of this invention, attention will now

be devoted to the use of these catalysts in destructive isomerization.)

Example 1B

The paraffinic fraction obtained by the solvent extraction of a kerosene and the catalyst prepared as described in Example 2A were added continuously to an agitated liquid phase reactor. The weight of the catalyst was equivalent to 12% by weight of the hydrocarbon fraction, which had a boiling range of approximately 300° F. to 500° F. The reaction was conducted at 400° F. and the reaction vessel and an efficient fractionating column connected thereto were operated at the pressures necessary to give an overhead from the fractionating column having a maximum boiling point of 300° F. Sludge was drawn continuously from the reaction vessel to prevent the accumulation of heavy ends, exhausted catalyst, etcetera, therein. Overhead from the fractionator consisted almost exclusively of light, highly isoparaffinic naphtha, the amount of isobutane and other gaseous hydrocarbons being practically zero. In other words, the isobutane-light highly isoparaffinic naphtha ratio was practically zero. In a parallel experiment in which straight aluminum chloride was used, this ratio was found to be 0.5. It was observed that the rate of reaction was two to three times as fast in the experiment using straight aluminum chloride as that in the reaction employing aluminum chloride mixed with activated aluminum powder. It is evident that the presence of the activated aluminum powder not only changes the course of the reaction but also reduces the activity of the aluminum chloride. This lower reaction rate may be compensated, if desired, by increasing the operating temperature slightly, for example, 25° F. to 50° F. A number of experiments which need not be considered in detail showed that on increasing the activated aluminum content of the aluminum chloride from zero up to that specified in Example 2A, the isobutane-light, highly isoparaffinic naphtha ratio decreased from 0.5 to practically zero.

Example 2B

A sample of acid treated Mount Pleasant heavy naphtha having a boiling range of approximately 250° F. to 400° F. was processed in the presence of a catalyst made in accord with Example 2A, an apparatus similar to that described in Example 1B being employed. Operating temperature was 210° F. and atmospheric pressure was used. The total overhead from the reactor was easily condensed and had an isobutane-light highly isoparaffinic naphtha ratio of practically zero. When operating in a similar manner with the exception that no activated aluminum powder was used in the catalyst the ratio was one.

Example 3B

A liquid phase reactor was practically filled with an East Texas heavy naphtha having a boiling range of approximately 250° F. to 400° F. and containing 1% aluminum bromide dissolved therein. The agitator with which the reactor was provided was started and additional East Texas heavy naphtha containing 1% aluminum bromide dissolved therein and 0.1% magnesium powder suspended therein was added continuously to the reactor. The overhead obtained at atmospheric pressure contained no gaseous hydrocarbons. Sludge was withdrawn continuously from the reactor.

Example 4B

A high pressure reactor was filled with a catalyst made in accord with Example 1A. East Texas heavy naphtha having a boiling range of approximately 250° F. to 400° F. was passed over this catalyst at a pressure of 5000 pounds per square inch and a temperature of 450° F. After almost complete pressure reduction the reaction products were fractionated to give a light highly isoparaflinic naphtha, a fraction having approximately the same boiling range as the charge and higher boiling bottoms. Very little gas was formed. If desired, the fraction having the same boiling range as that of the charge may be recycled to the reactor.

The foregoing description and examples serve to outline the scope and spirit of the present invention and manifest its advantages to those skilled in the art to which it pertains but it is not intended that these shall be regarded as limitations upon the scope of the invention except insofar as included in the appended claims.

I claim:

1. A method of converting heavy naphtha which comprises subjecting said heavy naphtha, in the presence of a mixture consisting of an aluminum halide in intimate association with a metal selected from the group consisting of aluminum, magnesium and zinc, to a temperature in the approximate range 100° F. to 800° F. for a time sufficient to convert a substantial portion of said heavy naphtha into isobutane and isoparaflinic light naphtha.

2. The method in accordance with claim 1 wherein said selected metal is activated by being in intimate association with a minor quantity of an element having an electrode potential below that exhibited by said selected metal.

3. A method of converting heavy naphtha which comprises subjecting said heavy naphtha,

in the presence of a mixture consisting of aluminum chloride in intimate association with metallic aluminum, to a temperature in the approximate range 100° F. to 800° F. for a time sufficient to convert a substantial portion of said heavy naphtha into isobutane and isoparaflinic light naphtha.

4. The method in accordance with claim 2 wherein said metallic aluminum is activated by being in intimate association with a minor quantity of an element having an electrode potential below that exhibited by metallic aluminum.

5. A method of converting heavy naphtha which comprises subjecting said heavy naphtha, in the presence of a mixture consisting of aluminum chloride in intimate association with metallic magnesium, to a conversion temperature under destructive isomerization conditions for a time adequate to convert a substantial portion of said heavy naphtha into isobutane and isoparaflinic light naphtha.

6. The method in accordance with claim 5 wherein said metallic magnesium is activated by being in intimate association with a minor quantity of an element having an electrode potential below that exhibited by metallic magnesium.

7. A method of converting heavy naphtha which comprises subjecting said heavy naphtha, in the presence of a mixture consisting of aluminum chloride in intimate association with metallic zinc, to a conversion temperature under destructive isomerization conditions for a time adequate to convert a substantial portion of said heavy naphtha into isobutane and isoparaflinic light naphtha.

8. The method in accordance with claim 7 wherein said metallic zinc is activated by being in intimate association with a minor quantity of an element having an electrode potential below that exhibited by metallic zinc.

ROBERT F. RUTHRUFF.