

UNITED STATES PATENT OFFICE

2,250,410

CATALYTIC TREATMENT OF
HYDROCARBONS

Adrianus Johannes van Peski, Amsterdam, Netherlands, assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application April 28, 1939, Serial No. 270,655. In the Netherlands May 21, 1938

3 Claims. (Cl. 260—676)

This invention relates to the catalytic isomerization of saturated hydrocarbons.

A principal object of the invention is to provide a practical and economical process for the production of commercially valuable branched or more highly branched chain paraffin hydrocarbons from normal or only slightly branched chain paraffin hydrocarbons containing at least five carbon atoms per molecule and boiling at a temperature not substantially greater than about 160° C.

The process of the invention is of great commercial importance in that it provides a direct method for the production, via catalytic isomerization, of isoparaffin hydrocarbons from the more available and less valuable normal paraffin hydrocarbons such as normal pentane, normal hexane, normal heptane, normal octane, etc. The isoparaffins which contain at least five carbon atoms are useful as motor fuels and as components of anti-knock motor fuel compositions. In addition, the lower isoparaffins such as isopentane and the isohexanes are valuable starting materials in the production of tertiary olefines which in turn are valuable starting materials for the production of highly branched chain paraffin hydrocarbon motor fuels and motor fuel constituents via polymerization and hydrogenation or by direct coupling or alkylation with an isoparaffin. The process of the invention can be applied to the individual normal or slightly branched chain paraffin hydrocarbons to increase their anti-knock value or it may be applied directly to hydrocarbon fuel mixtures, such as straight-run gasolines, containing relatively high percentages of normal or only slightly branched chain paraffin hydrocarbons to isomerize said hydrocarbons and thus increase the total anti-knock value of the fuel mixture with a minimum of treatment and loss of the treated material.

The process of this invention comprises contacting the hydrocarbon to be treated, or a mixture of such hydrocarbons, with a catalyst consisting of or essentially comprising an acid-acting halide at a temperature not greater than about 150° C. under a pressure sufficiently high to ensure the presence of a liquid phase in the system and in the presence of such an amount of a hydrogen halide that the partial pressure of the hydrogen halide in the system is equal to at least three atmospheres.

The treatment of normally liquid paraffin hydrocarbons boiling up to about 160° C. in accordance with the process of the invention has the apparent effect of displacing the end groups of

the hydrocarbon molecule toward the center of the carbon chain; consequently, the process may be applied to the treatment of any such saturated hydrocarbon possessing a structure capable of modification in such a way as to result in a hydrocarbon molecule of a more condensed type. The process can be applied to the isomerization to isoparaffin hydrocarbons of any of the normal paraffin hydrocarbons higher than butane. Suitable normal paraffin hydrocarbons are normal pentane, normal hexane, normal heptane, normal octane, normal nonanes, etc. The hydrocarbons treated are preferably those which boil at a temperature not greater than about 160° C.

The process may be applied to the treatment of a suitable pure or substantially pure normal hydrocarbon or to a mixture consisting of or comprising one or a plurality of such hydrocarbons. For example, a suitable starting material may comprise, besides a substantial amount of a suitable normal or slightly branched chain paraffin hydrocarbon, one or a plurality of other hydrocarbons which may not be capable of isomerization under the conditions of operation, and/or one or more non-aqueous inert diluent materials.

If desired, relatively inert diluent gases such as hydrogen, nitrogen, carbon dioxide, methane, ethane, etc., may be introduced into the reaction zone to aid in establishing and/or maintaining the desired operating pressure.

The process is executed in the presence of a catalyst consisting of or essentially comprising an acid-acting halide. The term "acid-acting halide" is used herein and in the appended claims to designate those active metal or non-metal halides (other than the hydrogen halides) which will give an acid reaction in water. Representative acid-acting halides are the halides of aluminum, zinc, iron, arsenic, antimony, molybdenum, tungsten, cadmium, beryllium, tin, boron, and the like. The metal halides, particularly the chlorides of the above-listed metals, form a preferred group of catalysts. The catalysts may be used alone or in admixture with each other and/or other catalytic as well as non-catalytic materials. For example, one or more suitable halide catalysts may be mixed with or deposited on filler or supporting materials such as pumice, silica, alumina, charcoal, permutite, etc. The relative amount of the catalyst employed will depend upon the particular catalyst or catalyst mixture selected, upon the material to be treated and, to a certain extent, upon the conditions of operation, and may vary over a wide range. In general, the catalyst may be advantageously em-

ployed in an amount equal to from about 1% to about 15% by weight of the hydrocarbon material treated.

The process is preferably executed at temperatures not greater than about 150° C. At temperatures greater than about 150° C., losses of material due to cracking and other degradation reactions usually occur to an undesired extent. The lower limit of the practical operating range is set by the temperature at which the desired isomerization will take place at a practical rate and will depend upon the particular hydrocarbon material treated, the particular catalyst employed, the total pressure in the system, and the partial pressure of the hydrogen halide in the system. A favorable conversion of the treated hydrocarbon material is sometimes obtained at room temperature or only slightly elevated temperatures. For example, when normal pentane is treated, conversion to isopentane can be effected at a practical rate at temperatures below 50° C. and even as low as 20° C.

The process is executed under a superatmospheric pressure, the total pressure in the system being sufficiently high to ensure the presence of a liquid phase of hydrocarbon in the system, and the partial pressure of a hydrogen halide in the system being equal to at least three atmospheres. The total pressure in the system will in all cases be equal to at least three atmospheres and will depend upon the partial pressure of the hydrogen halide under which it is desired to operate, upon the temperature of operation, and upon the vapor pressure of the other components of the reaction system at the operating temperature. Total pressures as high as 20 atmospheres, and higher, may be conveniently employed. In general, total pressures of from about 3 to about 15 atmospheres are preferred.

The partial pressure of the hydrogen halide in the system should in all cases be equal to at least three atmospheres and it may, if desired, be as high as 20 atmospheres or higher. In general, the process is preferably operated with a partial pressure of a hydrogen halide in the system of from 3 to about 15 atmospheres. Since the actual partial pressure of hydrogen halide under the reaction conditions depends upon several factors such as the temperature, solubility, etc., and is difficult to determine accurately, the partial pressures of hydrogen halide herein referred to are those measured when the reaction mixture is first brought to a temperature of 20° C.

It is known that aluminum chloride in the presence of a small amount of hydrogen chloride is a catalyst for the isomerization of the normal paraffin hydrocarbons. However, this knowledge has failed to provide any technically feasible process for the conversion of the liquid normal paraffin hydrocarbons to isoparaffin hydrocarbons because of the fact that the isomerization reaction proceeds at a prohibitively low rate at the low temperatures necessary to avoid excessive cracking of the treated and resultant hydrocarbon. I have made the unexpected discovery that by operating under a total pressure in the reaction system sufficient to maintain a liquid phase therein and increasing the partial pressure of the hydrogen halide to at least three atmospheres results in materially increasing the rate of isomerization while permitting the use of temperatures at which undesired degradation reactions can be substantially obviated. About

1 atmosphere appears to be the minimum practical operating partial pressure of the hydrogen halide at which the high and selective conversions characteristic of the process are obtained.

As the partial pressure of the hydrogen halide in the system is increased from about 1 atmosphere to about 20 atmospheres, other conditions being the same, higher conversions of the desired isoparaffins are obtained per time unit of treatment. In general, I prefer to operate with a partial pressure of a hydrogen halide in the system of from about 3 to about 15 atmospheres.

The term "hydrogen halide" as used herein and in the appended claims embraces hydrogen chloride, hydrogen bromide, hydrogen iodide and hydrogen fluoride. In most cases hydrogen chloride is suitable, and, due to its availability and cheapness, its use is preferred. A hydrogen halide from any source is suitable. Since the process is preferably executed in the substantial absence of water, care should be taken to avoid introduction of water into the system with the constituents of the reaction mixture.

One of the practical advantages of the process of the invention is that the desired conversion of the treated hydrocarbon material to branched or more branched chain hydrocarbon material can be effected with the use of relatively shorter treatment times than are required by the known methods without the necessity of increasing the temperature and thereby increasing the extent of occurrence of undesired degradation reactions. The time of treatment will depend upon the particular hydrocarbon material treated, upon the particular catalyst employed, upon the partial pressure of the hydrogen halide in the system, and upon the temperature and other conditions of operation.

The process of the invention may be executed in a batch, intermittent or continuous manner. When separation of the isomerized hydrocarbon from the unreacted material is desired, such separation may be effected in any suitable manner as by fractional distillation, etc., and the unreacted material returned to the reaction zone for further treatment.

The following examples illustrate suitable modes of executing the process of the invention. The invention is not to be regarded as restricted to the particular catalyst, the particular modes of operation, the particular hydrocarbons treated, or the particular operating conditions specified in the examples.

Example I

A hydrocarbon mixture consisting of about 91.5% normal pentane and about 8.5% of isopentane was charged to an autoclave along with about 10% of its weight of anhydrous aluminum chloride. Hydrogen chloride gas was forced into the autoclave until the total pressure therein at about room temperature was about 5 atmospheres (gauge) and the partial pressure of the hydrogen chloride therein was about 4.5 atmospheres. The mixture in the autoclave was kept at about 20° C. for about 16 hours during which time it was agitated by revolution of the autoclave.

At the end of 16 hours, the mixture was discharged from the autoclave, the hydrogen chloride and the aluminum chloride removed, and the hydrocarbon material analyzed. It was found to consist of 38% by weight of isopentane, 11% by weight of isobutane, 44% by weight of n-pentane and about 7% of higher boiling constituents.

Example II

The same hydrocarbon material was treated with the same catalyst and under substantially the same conditions of temperature and reaction time. However, the operation was effected under a total gauge pressure of about 3.5 atmospheres, the partial pressure of the hydrogen chloride in the system being about 3.0 atmospheres.

The resulting hydrocarbon reaction product consisted of 21.7% by weight of isopentane, 1.4% of isobutane, and 76.9% by weight of normal pentane. The product was devoid of higher or lower boiling hydrocarbons.

Example III

A hydrocarbon mixture consisting of about 91.5% by weight of normal pentane and about 8.5% by weight of isopentane was treated with about 10% of its weight of aluminum chloride at about 20° C. for a period of about 17 hours under a hydrogen chloride partial pressure of about 0.5 atmosphere. The reaction product was found to consist of about 9.5% by weight of isopentane and about 90.5% by weight of normal pentane. Only about 1% of the treated normal pentane was converted to isopentane.

It was found that keeping other conditions substantially the same and increasing the partial pressure of hydrogen chloride resulted in a materially increased conversion of normal pentane to isoparaffin (principally isopentane) after a partial pressure of at least 1 atmosphere was reached.

When a partial pressure of hydrogen chloride of 1.5 atmospheres was used, the resulting hydrocarbon product contained about 19% by weight of isoparaffin hydrocarbons (isopentane and isobutane, with the latter present in only small amount), and about 81% of normal pentane. At a hydrogen chloride partial pressure of 5.5 atmospheres, about 53% of the treated normal pentane was converted to isoparaffin hydrocarbons (primarily isopentane) with the formation of no hydrocarbons lower than butane. At a hydrogen chloride partial pressure of about 7.5 atmospheres, about 66% of the treated normal pentane was converted to isoparaffin hydrocarbons (primarily isopentane) with the formation of no hydrocarbons lower than butane. At a partial hydrogen chloride pressure of about 10.5 atmospheres, about 92% of the treated normal pentane was converted to isopentane and isobutane, with the former materially predominating, and with the formation of no hydrocarbons containing less than four carbon atoms.

Example IV

About 100 parts of normal hexane were charged to a suitable pressure reaction vessel along with about 5% of its weight of aluminum chloride. Hydrogen chloride gas was added in an amount sufficient to provide a partial pressure of hydrogen chloride of about 10 atmospheres in the system. The reaction mixture was maintained at about 80° C. for about 16 hours. At the end of this time, the hydrogen chloride and aluminum chloride were separated from the hydrocarbon material and the hydrocarbon material analyzed. It consisted of 8% by weight isohexane, 5% by weight isopentane, 10% by weight isobutane, about 1% by weight propane, the remainder being unchanged normal hexane.

While I have described my invention in a detailed manner and provided specific examples illustrating suitable modes of executing the same, it is to be understood that modifications may be made and that no limitations other than those imposed by the scope of the appended claims are intended.

I claim as my invention:

1. A process for the conversion of normal hexane to isoparaffin hydrocarbons which comprises contacting normal hexane in the liquid phase with an aluminum chloride catalyst at a temperature of from 20° C. to 150° C. for a time not exceeding 17 hours under a pressure of hydrogen chloride equivalent to from three to twenty atmospheres when measured at 20° C.

2. A process for the conversion of normal pentane predominantly to isopentane which comprises contacting normal pentane in the liquid phase with an aluminum chloride catalyst at a temperature of from 20° C. to 150° C. for a time not exceeding 17 hours under a pressure of hydrogen chloride equivalent to from three to twenty atmospheres when measured at 20° C.

3. A process for the conversion of a normal paraffin hydrocarbon to an isoparaffin hydrocarbon which comprises contacting a normally liquid normal paraffin hydrocarbon which boils at a temperature not greater than about 160° C. with an acid-acting halide catalyst in the liquid phase at a conversion temperature of from 20° C. to 150° C. for a time not exceeding 17 hours under a pressure of a hydrogen halide equivalent to from three to twenty atmospheres when measured at 20° C.

ADRIANUS JOHANNES VAN PESKI.