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ISOMERIZATION OF PARAFFINS

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This application is a continuation-in-part of our co-pending application, Serial No. 282,083, filed June 30, 1939, which in turn is a continuation-in-part of our application, Serial No. 118,587, filed December 31, 1936.

This invention relates particularly to the isomerization of normally liquid straight chain paraffin hydrocarbons to produce more highly branched compounds.

In a more specific sense the invention is applicable not only to individual paraffin hydrocarbons of straight chain structure but also to hydrocarbon mixtures containing these compounds in substantial percentages such as straight run gasolines and their fractions, which contain in addition to paraffin hydrocarbons of highly knocking characteristics other hydrocarbons comprising some paraffins of branched chain structure and the usual run of naphthenes and aromatics.

The isomerization of individual normally liquid paraffin hydrocarbons such as normal pentane, and normal hexane is frequently desirable in the manufacture of derivatives since the isomeric compounds are more reactive and, in the case of gasoline or gasoline fractions containing various naphthenic hydrocarbons, the isomerization has the effect of increasing the antiknock value of the gasolines to a marked extent as will be shown in later examples.

There should be no need for extensively recounting the number of possible isomers of paraffin hydrocarbons since these are all predictable on the present theories of organic chemistry and are well known to those familiar with this subject. However, the following table is shown to indicate in a general way the change in structure and properties of normal paraffin hydrocarbons and their isomers, particularly since the pentanes constitute some of the lower-boiling constituents of ordinary gasolines.

Compound	Formula	Boiling point	Density	Octane No.
		°C.		
n-Pentane	$CH_3(CH_2)_3CH_3$	36.3	0.6475 @ 0° C.	63
i-Pentane	$CH_3CH(CH_3)CH_2CH_3$	28	0.6394 @ 0° C.	88
Neo-pentane	$C(CH_3)_4$	9.5	0.6251 @ 14.4° C.	

It will be observed from the above that, as the structure of the molecule becomes more compact, boiling point and specific gravity both decrease while the antiknock value as expressed by octane number generally increases although figures are not available for the neopentane. Similarly, the isomeric hexanes, heptanes, and octanes will show the same progressive relationships as their structure becomes more condensed. As the molecular weight of paraffin hydrocarbons increase, the number of possible and known isomers increases more than arithmetically so that in cases of isomerization involving mixtures of n-paraffins and particularly n-paraffins in admixture with other hydrocarbons in gasolines, the determination of the extent of isomerization is not possible by analytical methods but can be estimated from the observed change in antiknock value.

In one specific embodiment, the present invention comprises treatment of paraffin hydrocarbons or hydrocarbon mixtures containing substantial percentages thereof, such as straight run gasoline fractions with catalysts comprising metal halides of the Friedel-Crafts type and hydrogen halides to effect isomerization reactions. There are several alternative catalysts which may be employed in accomplishing the isomerization reaction among paraffin hydrocarbons and although they may be used more or less interchangeably, some are more effective than others and it is not intended to infer that they are definitely equivalent.

Among the compounds which may be used are such metallic halides of the Friedel-Crafts type as the halides of aluminum, zinc, iron and zirconium either alone or in admixture with one another. Extensive experiments have indicated that it is essential that a hydrogen halide be added in the reaction zone along with these compounds to obtain satisfactory results. These catalysts may be used alone or impregnated upon various types of adsorbent carriers to produce granular catalysts utilizable either in liquid, mixed or vapor phase operation. At temperatures above those boiling points where distillation

of the catalyst is to be avoided, superatmospheric pressures may be employed. There are also some variations in the relative amounts of metal halides and hydrogen halides used at optimum treating conditions but the determination of these ratios is somewhat a matter of experiment.

We have determined that by the use of the class of catalysts mentioned, and particularly by the concurrent use of considerable superatmospheric pressures, normally liquid paraffin hydrocarbons of straight chain structure, and particularly the normal compounds may be converted into hydrocarbons of more highly branched structure with yields of the order of 50–60%. Such yields are obtainable at temperatures within the approximate range of 50–250° C. and superatmospheric pressures. Evidently the use of superatmospheric pressures of the order of 1 to 200 atmospheres and preferably 10 to 200 atmospheres at temperatures of 150° C. and higher, besides depressing the volatilization of metal halide catalysts tends also to depress numerous undesirable side reactions which would result in the formation of hydrogen and low molecular weight hydrocarbons, so that the reaction proceeds more or less in one direction until an equilibrium is established.

While inert gases such as nitrogen may be employed in producing the necessary pressure, experiments have shown that it is preferable to employ hydrogen which seems to minimize undesirable side reactions involving decomposition rather than the desired isomerization. As is customary in hydrogenation processes, the hydrogenation reactions are fostered by increase in pressure and in some instances, pressures of 2000 pounds per square inch or higher produce beneficial effects when the hydrocarbon involved tends to undergo decomposition under the isomerizing conditions.

The process may be operated under batch or continuous conditions either in liquid, mixed, or vapor phase as may be desirable or expedient in view of the particular catalyst combination shown and the particular hydrocarbon mixture undergoing treatment. A simple method of operation consists in adding 5 to 10% of granular anhydrous aluminum chloride to a treating vessel containing hydrocarbons and provided with a mechanical agitating device. It is best to employ a treater which can be sealed from atmospheric contact and which can be operated under pressure if necessary. The solid catalyst is then kept in suspension by moderate agitation by introducing a slow stream of hydrogen chloride.

Vapor phase operations may be conducted by passing vapors of hydrocarbons mixed with a small amount of hydrogen chloride over solid granular catalysts comprising the preferred metal halides, an example of such catalyst being granular aluminum chloride or a composite produced by impregnating solid adsorbents with aluminum chloride. In the use of a readily vaporizable catalyst such as aluminum chloride, it may be sublimed directly into a stream of hydrocarbon vapors and hydrogen chloride followed by settling of the spent catalyst and fractionation of the products.

The following examples are introduced to indicate in a general way the nature of the results obtainable in the operation of the process, but they are not given with the intention of limiting the scope of the invention in exact correspondence with the numerical data at present.

Example I

The vapors of normal pentane mixed with about 1 percent by volume of hydrogen chloride were passed through a mass of granular catalyst comprising 10 to 20 mesh particles of activated carbon base supporting about an equal weight of anhydrous aluminum chloride. The temperature employed was 200° C. and a pressure of 450 pounds per square inch was maintained to depress the volatilization of the aluminum chloride. The vapors of 25 parts by weight of n-pentane were passed over 30 parts by weight of the composite catalyst per hour. Fractionation of the products indicated that the once-through yield of isopentane was about 27% by volume of the n-pentane charged. There was produced in addition 3.5% by volume of isobutane and 3.5% by volume of n-butane. By operating continuously and recycling the unconverted normal compound the final overall yield of isopentane was approximately 80%.

Example II

In this example a gasoline fraction boiling within the range of 50–90° C. and obtained from a highly paraffinic Michigan gasoline was treated. The fraction had an octane number of 54 and corresponded roughly to a mixture of hexanes, since n-hexane boils at about 70° C. This fraction was subjected to isomerization for the improvement of its antiknock value in the presence of aluminum chloride and hydrogen chloride at two temperatures to observe the effect at each. The gasoline fraction was placed in a pressure vessel, aluminum chloride was added and the heating was conducted over a period of six hours, after which the vessel was cooled and the gaseous and liquid products recovered and examined. The following table gives the principal results obtained in the two runs:

	Run #1	Run #2
Temperature, ° C.	150	200
Charge in treater "gasoline," parts by weight	200.0	200.0
$AlCl_3$, do	20.0	20.0
HCl, do [1]	5	5
Maximum pressure, atmospheres	16	45
PRODUCTS OF THE REACTION PER CENT BY WEIGHT OF ORIGINAL "GASOLINE"		
Propane	3.3	8.6
Butane (at least 85% iso)	6.0	12.2
Upper layer	78.5	63.5
Hydrocarbon in lower layer	8.7	11.8
Loss	3.5	3.9
Octane number of upper layer	65	72

[1] Approximate.

The foregoing runs show a considerable increase in antiknock value with only moderate losses. By a limited chemical treatment further quantities of the hydrocarbons recovered by the hydrolysis of the lower aluminum chloride sludge layer are rendered utilizable in the gasoline layer so that the overall yield is still higher than that shown. The butane can be further utilized by successive steps of dehydrogenation and polymerization to still further augment the yield of motor fuel fraction.

Example III

The vapors of normal pentane mixed with about 1 per cent by volume of hydrogen chloride were passed through a mass of granular catalyst comprising 10 to 20 mesh particles of activated

carbon base supporting about an equal weight of anhydrous aluminum chloride. The temperature employed was 200° C. and a pressure of 450 pounds per square inch was maintained to depress the volatilization of the aluminum chloride. The vapors of 25 parts by weight of normal pentane were passed over 30 parts by weight of the composite catalyst per hour. Fractionating of the products indicated that the once-through yield of isopentane was about 27% by volume of the normal pentane charged. There was produced in addition 3.5% by volume of isobutane and 3.5% by volume of normal butane. By operating continuously and recycling the unconverted normal compound the final overall yield of isopentane was approximately 80%.

Example IV

71 parts by weight of diatomaceous earth was mixed with 29 parts by weight of anhydrous aluminum chloride, and placed in a pressure vessel. 4% by weight of hydrogen chloride gas was introduced and the contents of the vessel were placed under a pressure of 25 atmospheres by the introduction of dry hydrogen. After heating the vessel for a period of three hours at a temperature of approximately 250° C. during agitation, it was found that the aluminum chloride was exactly adsorbed on the diatomaceous earth so that an apparently dry material was formed.

Normal pentane vapors containing about 2% by weight of hydrogen chloride was passed through the catalyst at a temperature of 190° C. and a pressure of 400 pounds per square inch. There was produced about 25% by volume of isopentane based on the volume of normal pentane charged as a once-through yield. Some side reactions occurred as indicated by the presence of about 5% by volume of lower and 5% by volume of higher boiling hydrocarbons. In recycle operation, the ultimate yield of iso-pentane was approximately 70%.

Example V

70 parts by weight of pumice was mixed with 32 parts of substantially anhydrous aluminum chloride and heated in a pressure vessel at 250° C. under 25 atmospheres of hydrogen pressure in the presence of 4–5% by weight of hydrogen chloride gas as in the two preceding examples.

The vapors of normal pentane containing approximately 2% by weight of hydrogen chloride were passed over the above catalyst at a temperature of 180° C. under a pressure of 400 pounds per square inch. In a once-through run, the yield of iso-pentane was approximately 20% and this was increased to an ultimate yield of 65% by recycling operations.

Example VI

The vapors of normal pentane containing approximately 4 mol per cent of hydrogen chloride were passed over a solid granular catalyst comprising zinc chloride on an adsorbent alumina (25% by weight of zinc chloride) at a temperature of 274° C. under a pressure of 1500 pounds per square inch. The charge rate was equivalent to a liquid hourly space velocity measured as volumes of charge per volume of catalyst space per hour of 0.27. The once through yield of isopentane was 21.4% and upon recycling was increased to an ultimate yield of approximately 63%.

Example VII

An acid washed commercial pentane-hexane fraction having an octane number of 57.7 was passed over the same type catalyst as used in Example VI at a temperature of 300° C. under a pressure of 1500 pounds. The charge rate measured as liquid volumes of hydrocarbon per volume of catalyst space per hour was about 0.5. An isomerized product having an octane number of 70 is produced.

Example VIII

Normal pentane containing approximately 4 mol per cent of hydrogen chloride was contacted with a catalyst comprising iron chloride on alumina (25% by weight iron chloride) at a temperature of 275° C. under a pressure of 1500 pounds. Liquid hourly charge rate measured as liquid volumes of charge per volume of catalyst space per hour was about 0.25. In a once through run the yield of isopentane was approximately 20% and this was increased to an ultimate yield of 62% by recycling.

The nature of the present invention and its practical aspects can be seen from the foregoing specification and examples although neither section is intended to impose undue limitations upon the proper scope of the invention.

We claim as our invention:

1. A process for increasing the antiknock properties of a normally liquid hydrocarbon fraction boiling in the gasoline range and containing paraffins of relatively low antiknock value which comprises subjecting the hydrocarbon fraction under isomerizing conditions of temperature, pressure and time to the action of an isomerizing catalyst of the Friedel-Crafts type in the presence of an added hydrogen halide and correlating the amount of hydrogen halide and said isomerizing conditions of temperature, pressure and time to convert a substantial portion of the paraffins contained in said fraction into isomers thereof having the same molecular weight as and of higher antiknock properties than said paraffins.

2. A process for increasing the antiknock properties of a normally liquid hydrocarbon fraction boiling in the gasoline range and containing normal paraffins of less than 7 carbon atoms to the molecule which comprises subjecting the hydrocarbon fraction under isomerizing conditions of temperature, pressure and time to the action of an isomerizing catalyst of the Friedel-Crafts type in the presence of an added hydrogen halide and correlating the amount of hydrogen halide and said isomerizing conditions of temperature, pressure and time to convert a substantial portion of the paraffins contained in said fraction into branched chain paraffins of the same molecular weight.

3. A process for isomerizing a normally liquid paraffin hydrocarbon boiling in the gasoline range which comprises subjecting said paraffin under isomerizing conditions of temperature, pressure and time to the action of an isomerizing catalyst of the Friedel-Crafts type in the presence of added hydrogen halide and correlating the amount of hydrogen halide and said isomerizing conditions of temperature, pressure and time to convert a substantial portion of said paraffin into an isomer or isomers thereof having the same molecular weight as said paraffin.

4. A process for isomerizing a normally liquid paraffin hydrocarbon boiling in the gasoline range which comprises subjecting said paraffin

under isomerizing conditions of temperature, pressure and time to the action of an aluminum halide in the presence of added hydrogen halide and correlating the amount of hydrogen halide and said isomerizing conditions of temperature, pressure and time to convert a substantial portion of said paraffin into an isomer or isomers thereof having the same molecular weight as said paraffin.

5. A process for isomerizing a normally liquid paraffin hydrocarbon boiling in the gasoline range which comprises subjecting said paraffin under isomerizing conditions of temperature, pressure and time to the action of an isomerizing catalyst of the Friedel-Crafts type in the presence of added hydrogen halide, said temperature being in the approximate range of 50° C. to 250° C., and correlating the amount of hydrogen halide and said isomerizing conditions of temperature, pressure and time to effect, as the principal reaction in the process, the conversion of a substantial portion of said paraffin into an isomer or isomers thereof having the same molecular weight as said paraffin.

6. A process for isomerizing a normally liquid paraffin hydrocarbon boiling in the gasoline range which comprises subjecting said paraffin under isomerizing conditions of temperature, pressure and time to the action of an isomerizing catalyst of the Friedel-Crafts type in the presence of added hydrogen halide, said temperature being in the approximate range of 50° C. to 250° C. and said catalyst being supported on a solid carrier material, and correlating the amount of hydrogen halide and said isomerizing conditions of temperature, pressure and time to convert a substantial portion of said paraffin into an isomer or isomers thereof having the same molecular weight as said paraffin.

7. The process as defined in claim 5 further characterized in that said catalyst comprises an aluminum halide.

8. The process as defined in claim 6 further characterized in that said catalyst comprises an aluminum halide.

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