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## TREATMENT OF BUTANE

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This invention relates particularly to the treatment of butane of normal or straight-chain structure.

In a more specific sense, the invention is concerned with a process whereby normal butane is converted into iso-butane, the process involving the use of special catalysts and particular conditions of operation which favor the isomerization reactions so that relatively high yields of the iso-compound are produced.

Since the invention is concerned principally with the two 4-carbon atom paraffin hydrocarbons and their transformation, one into the other, the following table is introduced to indicate the structure and the principal physical characteristics of these two compounds:

*Properties of butanes*

| Name | Structure | B. P., °C. | Critical temperature, °C. | Critical pressure, atmospheres |
|---|---|---|---|---|
| n-Butane | $CH_3CH_2CH_2CH_3$ | +0.5 | 151 | 36 |
| i-Butane | $CH_3-CH(CH_3)-CH_3$ | −10.5 | 134.5 | 37 |

Butanes are produced in considerable quantities in the oil refining industry. They occur in substantial amounts in natural gases (in which the normal compound usually predominates), in refinery gases which are evolved from crude petroleum storage tanks, and in the primary distillation of crudes, and they are also present in considerable percentages in the gases produced incidental to cracking heavy petroleum fractions for the production of gasoline. In the case of cracked gas mixtures the relative proportions of iso and normal butanes vary, but the ratio of the iso to the normal compound is as a rule considerably higher than in natural gas.

Butanes may be considered as more or less marginal compounds in respect to their desirability in ordinary gasoline, that is, a certain percentage of them is essential for sufficient vapor pressure to insure ease in starting, while an excess tends to produce vapor lock. For these reasons the total percentage of 4-carbon atom hydrocarbons is commonly adjusted in conjunction with the boiling range and vapor pressure of the other gasoline components to produce a gasoline of desirable starting characteristics according to seasonal demands.

The butanes at the present time bear a further important relationship to oil refining in that their excess production is being utilized as a source of gasoline either by ordinary thermal cracking or by special catalytic dehydrogenation processes followed by polymerization in which catalysts may or may not be used. Investigations have shown that iso-butane is considerably more amenable to cracking and dehydrogenation, both with and without catalysts, than the normal compound. Considering the corresponding mono-olefins, the normal butenes are considerably more difficult to polymerize, either thermally or catalytically, than iso-butene, and it is found also that the octenes representing the dimers of the iso-butene are of higher antiknock value than those from n-butenes, which holds also for the octanes produced by hydrogenation. It is, therefore, of considerable importance at the present time to convert as much as possible of the normal butane production into iso-butane, and the present invention is especially concerned with a process for accomplishing this object.

In one specific embodiment, the present invention comprises treatment of normal butane for the isomerization thereof into iso-butane, with a catalyst comprising essentially anhydrous aluminum chloride supported on activated carbon.

In effecting various reactions among organic compounds, utilizing aluminum chloride as a catalyst, difficulty is frequently encountered in that intermediate addition compounds are formed which are more or less of a sticky and viscous character, so that the original granules of anhydrous chloride become coated and the effective catalytic surface is lost. This tendency may be overcome to some extent by employing vigorous agitation during the course of the catalytic reactions, but it can never be entirely obviated, so that in general the full effectiveness of aluminum chloride is never attained. These phenomena are particularly noticeable in hydrocarbon reactions such as those with which the present invention is concerned.

Another property of anhydrous aluminum chloride which must be taken into account is its tendency to sublime at a temperature of approximately 180° C., so that if it is employed at temperatures above this point it must be injected or sublimed into the reaction zone. In the process of the present invention, in which the aluminum chloride employed is strongly absorbed by activated carbons, both of the disadvantages enumerated are to a large extent overcome since the tendency of the aluminum chloride to volatilize is partially counteracted by the absorbent action

of the carbons or chars employed, and these supports further act to absorb and retain some of the viscous addition compounds and prevent the composite catalyst granules from adhering to form large agglomerates.

The method of preparation of the type of catalyst used for the isomerization of normal butane is to mix a properly activated and adsorbent carbon with anhydrous aluminum chloride and then heat the mass under elevated temperatures and pressures until the chloride has been adsorbed into the pores of the carbon. The proportions of adsorbent carrier and aluminum chloride may be varied as desired to make catalyst composites of varying activity. It has been found possible and practical to make stable granular catalysts resistant to disintegrating influences by using approximately equal parts by weight of absorbent carbon and anhydrous aluminum chloride. Such proportions, after thorough mechanical mixing, are placed in a pressure vessel, which is preferably lined with glass, a small amount of hydrogen chloride is added, the vessel is brought up to a pressure of approximately 25 atmospheres by the introduction of hydrogen and heated at a temperature of approximately 250° C. for several hours. After such a treatment of the original mix the product obtained is dry and granular, the aluminum chloride apparently having disappeared, though it is actually present in the pores and on the surface of the carbon as evidenced by the violent reaction of the granules with water and their catalytic activity in organic reactions.

Owing to the adsorptive properties of the activated carbon, catalysts of the above character may be employed in isomerizing normal butane with substantially no tendency for the original particles to run together due to the formation of intermediate sludge-like products, so that much larger quantities of material may be treated before the catalyst has lost its activity. Another advantage resides in the fact that the adsorbed aluminum chloride will remain in place without volatilization at considerably higher temperatures than its normal sublimation point, when normal butane is passed over a stationary granular bed of catalyst.

The term "activated carbon" as used in the present specification is intended to include any type of prepared carbon or carbonaceous material which is more or less granular and possessed of good porosity and structural strength and which has been prepared by general steps involving the leaching of adsorbed materials from granular residual carbonaceous materials such as wood char and various varieties of coke by mineral acids and by the controlled heating, preferably under vacuum, to expel adsorbed liquids and gases. It is recognized that various forms of active granular chars will vary considerably in adsorptive capacity so that therefore the properties of catalysts prepared in accordance with the present invention will vary both in respect to the amount of aluminum chloride which they are able to absorb and in respect to the periods of service in which they are able to maintain a practical activity in different organic reactions.

We have determined that by the use of the class of catalysts mentioned, and particularly by the concurrent use of considerable superatmospheric pressure, normal butane may be converted into isobutane with a yield of as high as 60% to 65%. Evidently the use of superatmospheric pressures of the order of 10–50 atmospheres at temperatures of 150° C. and higher, besides depressing the volatilization of the aluminum chloride, 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.

The following example is introduced as characteristic of the practical operations of the present process, though it is not introduced with the intention of limiting the scope of the invention in exact correspondence with the numerical data since some latitude is possible in the proportions of activated carbon and aluminum chloride, and temperature and pressure may also be varied within the limits already specified. These variations may be considerable in the case of gas mixtures, in which normal butane occurs as a constituent in varying percentages.

In the manufacture of the catalyst for the isomerization reaction, 100 parts by weight of an activated carbon and 100 parts by weight of anhydrous aluminum chloride were thoroughly mixed in a dry atmosphere and then placed in a pressure vessel lined with glass to avoid corrosion. An amount of hydrogen chloride gas was introduced equal to 5% by weight of the total mix and the pressure was then raised to a total of 25 atmospheres by the introduction of substantially dry hydrogen. The vessel was heated to a temperature of 250° C. and the contents mechanically agitated for a period of three hours. The product had the general appearance of granular carbon but was somewhat more gray than black. The particles were entirely homogeneous in appearance and gave a vigorous evolution of heat when contacted with water.

Normal butane containing about 2% by weight of hydrogen chloride was passed through a granular mass of the catalyst at a temperature of about 200° C., a pressure of 650 lbs. per sq. in. and a moderate space velocity. It was found that the exit gases contained 53% of isobutane, 3% of propane, 8% of hydrocarbons of more than 4 carbon atoms to the molecule and the balance unchanged n-butane. Compared with an equivalent weight of ordinary granular anhydrous aluminum chloride, the prepared catalyst could be used approximately four times as long before the gradual deposition of carbonaceous residues and by-products rendered the action of the adsorbed aluminum chloride ineffective.

The herein disclosed method of preparing the catalyst is not claimed per se in the present application inasmuch as this subject matter is claimed in our companion application, Serial No. 103,391. The use of metallic halides broadly, including aluminum chloride, in the isomerization of n-butane is claimed in our companion application, Serial No. 103,383.

We claim as our invention:

1. A process for producing isobutane which comprises subjecting normal butane, in the substantial absence of polymerizable olefins, to the action of activated carbon impregnated with anhydrous aluminum chloride under conditions such that isomerization of normal butane constitutes the principle reaction in the process, whereby to convert a major portion of the normal butane into isobutane.

2. A process for producing isobutane which comprises subjecting normal butane, in the substantial absence of polymerizable olefins, to the action of activated carbon impregnated with anhydrous aluminum chloride at temperatures of

the order of about 150 to 250° C., and under pressures of the order of about 10 to 50 atmospheres, whereby to effect isomerization of normal butane into isobutane as the principal reaction in the process.

3. A process for producing isobutane which comprises subjecting normal butane, in the substantial absence of polymerizable olefins and in the presence of a relatively small amount of hydrogen chloride, to the action of activated carbon impregnated with anhydrous aluminm chloride under conditions such that isomerization of normal butane constitutes the principal reaction in the process, whereby to convert a major portion of the normal butane into isobutane.

4. A process for producing isobutane which comprises subjecting normal butane, in the substantial absence of polymerizable olefins and in the presence of a relatively small amount of hydrogen chloride, to the action of activated carbon impregnated with anhydrous aluminum chloride at temperatures of the order of about 150 to 250° C. and under pressures of the order of about 10 to 50 atmospheres, whereby to effect isomerization of normal butane into isobutane as the principal reaction in the process.

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