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PRODUCTION OF ISOBUTANE

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This invention or discovery relates to the production of iso-butane; and it comprises a catalytic method for the production of iso-butane from normal butane without cracking, in which normal butane substantially free of unsaturated hydrocarbons is maintained in contact with a small amount of a metal halide such as aluminum bromide at a temperature below the critical temperature of the normal butane; all as more fully hereinafter set forth and as claimed.

The paraffin hydrocarbons having one or more side chains or having an iso-structure have higher anti-knock value as fuels for internal combustion engines than the corresponding normal or straight-chain paraffins. Furthermore, the paraffins having an iso-structure are recognized as being more reactive than the normal paraffins and for many purposes such as chemical synthesis these more highly branched paraffins are preferred. The normal hydrocarbons containing 4 to 6 or more carbons are available from various sources such as various types of gasoline from which they may be recovered in substantially pure form. It is often desirable in view of the greater utility of the paraffins having the iso-structure to convert these normal paraffins to iso-paraffins, particularly to convert normal butane, pentane or hexane to iso-butane, iso-pentane or iso-hexane.

Various catalytic processes have heretofore been proposed for converting normal hydrocarbons into iso-hydrocarbons but the conditions under which these processes are carried out are such that substantial portions of the normal hydrocarbons are cracked to produce compounds having a lower and higher carbon content, as well as unsaturated compounds which tend to react with the catalyst to form a tar-like residue. Thus, in these processes, a substantial amount of the raw material is wasted and the catalyst is used up and is not recoverable.

I have discovered that if normal butane substantially free from unsaturated hydrocarbon compounds is maintained in contact with a metal halide catalyst, particularly an aluminum halide, at a temperature below the critical temperature of the n-butane and preferably under pressure sufficient to maintain the n-butane in a liquid state, the n-butane will undergo an internal rearrangement to produce iso-butane, without substantial cracking or the production of compounds of lower carbon content, and the aluminum halide catalyst may be recovered for reuse. The process is truly catalytic, as the aluminum halide does not form the typical tarry residue and undergoes no apparent change, so that it may be separated from the hydrocarbons and reused indefinitely.

The conversion of the n-butane to iso-butane according to the method of my invention is an

equilibrium reaction and a relatively long period of time is required to carry the reaction to equilibrium. Periods up to about 2000 hours have been required to reach equilibrium under certain conditions. The time required for equilibrium will vary with the particular catalyst used, the concentration of the catalyst and the temperature at which the reaction is carried out. However, in normal operation I do not generally carry the reaction to equilibrium. As in all equilibrium reactions, the rate of reaction from n-butane to iso-butane is considerably higher in the early stages than after a relatively large amount of iso-butane has been formed. I find it more convenient and economical therefore to carry out the reaction in such manner that the iso-butane formed is recovered from the reaction mixture before equilibrium is reached. This can be done conveniently either in a batch or continuous type of process. In most cases I have found it more practical to conduct the conversion of the n-butane to iso-butane in such manner that the iso-butane is removed as it is formed, for example by refluxing liquid n-butane in contact with the aluminum halide catalyst and fractionally distilling the lower boiling iso-butane out of the system as it is formed. Because of the fact that no cracking takes place to form volatile lower hydrocarbons a substantially pure iso-butane can thus be produced directly. Furthermore, no undesirable tarry residue is formed with the catalyst and the catalyst retains its activity indefinitely so that continuous operation may be carried on merely with the addition of fresh amounts of n-butane to replace that converted to iso-butane and fractionated out.

The compounds which I have found to be effective as catalysts in the method of my invention are the metal halides, and I have found that the aluminum halides such as aluminum chloride and aluminum bromide in substantially anhydrous form are particularly suitable. Aluminum bromide, while it is more costly than aluminum chloride, has certain technical advantages, and since the catalyst is not used up in the process but retains its activity for an indefinitely long period, aluminum bromide is preferred for use. The amount of the catalyst used may vary over a relatively wide range. With concentrations as low as 0.5 mol per cent I have effected conversion of substantial amounts of n-butane to iso-butane and I have used concentrations up to 10 mol per cent with increases in the isomerization rate with increasing amounts of catalyst. However, with the higher concentrations the increase in reaction rate is relatively small and it is not generally desirable to use concentrations greater than about 5 mol per cent.

I have also found that the anhydrous hydrogen

halides such as hydrogen bromide act as promoters to increase the catalytic activity of the metal halide catalysts. I have found it desirable, therefore, in many cases to use an anhydrous hydrogen halide in conjunction with the metal halide catalyst. For example, I have found that when about 1.0 mol per cent of anhydrous hydrogen bromide is used in conjunction with about 3.0 mol per cent of aluminum bromide, as the catalyst, the initial rate of reaction is increased approximately 100 per cent over that obtained with aluminum bromide alone.

The temperature at which the reaction is carried out is an important factor in the method of my invention. It is essential, in order to avoid cracking of the n-butane, that the reaction be carried out at a temperature below the critical temperature of the n-butane; that is, below about 153° C. I have found that substantial cracking takes place in a relatively short time if the conversion of the n-butane to iso-butane is carried out above this temperature. The method of my invention is therefore carried out at a temperature below the critical temperature and preferably at a pressure sufficient to maintain the n-butane in a liquid state. Ordinarily it is desirable that the reaction be carried out at a temperature materially below the critical temperature, particularly when a batch method is used. The equilibrium constant of the reaction favors the production of greater percentages of iso-butane when lower temperatures of reaction are used. For example, when the reaction is carried out at a temperature of 25° C. the maximum yield of iso-butane is about 80 per cent, whereas at temperatures of about 75° C. the maximum yield is 70 per cent iso-butane. Thus, operation at lower temperatures produces a higher equilibrium conversion to iso-butane. In continuous operation the use of lower temperatures is of less importance, as iso-butane is continuously fractionated out and the initial rate of reaction is preserved. However, in both batch and continuous operation, I have found it most practical to use a temperature of about 20° to 40° C. and preferably about 25° C.

In batch operation the method of my invention may be carried out by merely placing liquid n-butane in a closed vessel with a small amount of catalyst such as aluminum bromide at a temperature of about 25° C. and a pressure corresponding to the vapor pressure of the n-butane and agitating the mixture for a suitable length of time. Agitation is generally required to obtain satisfactory contact between the n-butane and the catalyst throughout the reaction period or until solution of the catalyst is effected. In general a compromise between time and yield should be made. In the normal course of the reaction at about 25° C. using 5 mol per cent of aluminum bromide as the catalyst, approximately the following yields may be expected:

Time	Iso-butane
Hours	Mol %
100	35
200	50
300	58
500	67
1,000	73
2,000	78

After a suitable time period the iso-butane may be recovered from the reaction mixture by fractional distillation and the catalyst may be sep-

arated out. The catalyst may be reused indefinitely.

In continuous operation, the n-butane mixed with the catalyst is gently heated in a vessel provided with a suitable condensing column and usually under pressure sufficient to maintain the n-butane in the liquid state. The condensing column should be such as to permit the iso-butane, which has a lower boiling point than the n-butane, to be fractionally distilled out of the system. I have found that a column having about twenty theoretical plates may be used under a pressure of about 60 pounds per square inch, corresponding to an operating temperature of about 30°-40° C. The heat supplied to the reaction chamber should be just sufficient to maintain a constant reflux.

The following example is an illustration of the results which may be obtained by the operation of the method of my invention in a batch type process. To 100 parts of liquefied n-butane contained in a suitable steel pressure vessel and maintained at a sufficiently low temperature to prevent evaporation, there was added 14 parts of anhydrous aluminum bromide. The pressure vessel was closed and the contents allowed to warm up to room temperature. The pressure vessel and its contents were then shaken vigorously for 10-15 minutes to effect solution of the catalyst. It was then placed in a suitable thermostat held at 25° C. At the end of 168 hours the bomb was placed in a dry ice-acetone bath and, after allowing time for precipitation of the catalyst, the bomb head was removed, the contents decanted and fractionated. A yield of 40 parts iso-butane was obtained together with 60 parts unconverted n-butane.

In one example of the operation of the process of my invention in a continuous manner the following results were obtained. The apparatus used comprised a steel reaction vessel equipped with an auxiliary line for supplying liquid n-butane and a suitable fractionating column having about 20 theoretical plates together with a cooling jacket and a column head cooled to maintain a head temperature below about 26° C. One hundred parts of n-butane were charged containing 23 parts of aluminum bromide dissolved therein. Heat was supplied to the reaction vessel, the temperature being maintained at about 40° C., the pressure in the system at about 60 pounds per square inch absolute. After 2-3 hours, it was found possible to withdraw essentially pure vaporous iso-butane from the top of the column at a rate of about 2-3 parts per hour, n-butane being supplied at a corresponding rate to the reaction vessel.

The method of my invention, I have found, is also applicable in principle to the conversion of other normal hydrocarbons than butane to iso-hydrocarbons. That is, by the treatment of a normal hydrocarbon such as n-pentane and n-hexane with an aluminum halide catalyst at a temperature below the critical temperature of the hydrocarbon, a substantial amount of iso-pentane or iso-hexane may be produced without cracking and without using up the catalyst. I do not intend, therefore, that the method of my invention shall be specifically limited to the production of iso-butane except as hereinafter defined in the appended claims.

What I claim is:

1. A method of producing isobutane from normal butane without cracking, comprising contacting liquid normal butane with about 0.5 to

10 mol per cent of an aluminum halide catalyst at a temperature below the critical temperature of normal butane.

2. A method of producing isobutane from normal butane without cracking, comprising contacting liquid normal butane with about 0.5 to 10 mol per cent of aluminum chloride at a temperature below the critical temperature of normal butane.

3. A method of producing isobutane from normal butane without cracking, comprising contacting liquid normal butane with about 0.5 to 10 mol per cent of aluminum bromide at a temperature below the critical temperature of normal butane.

4. A method of producing isobutane from normal butane without cracking, comprising contacting liquid normal butane with about 0.5 to 10 mol per cent of an aluminum halide catalyst in the presence of a hydrogen halide at a temperature below the critical temperature of normal butane.

5. A method of producing isobutane from normal butane without cracking, comprising con-

tacting normal butane with an aluminum halide catalyst entirely dissolved in liquid normal butane at a temperature below the critical temperature of normal butane.

6. A continuous method of producing isobutane from normal butane without cracking, comprising contacting liquid normal butane with about 0.5 to 10 mol per cent of an aluminum halide catalyst in a contacting zone at a temperature below the critical temperature of normal butane, continuously withdrawing isobutane from the contacting zone, and continuously supplying normal butane to said zone.

7. A continuous method of producing isobutane from normal butane without cracking, comprising contacting normal butane with an aluminum halide catalyst entirely dissolved in liquid normal butane in a contacting zone at a temperature below the critical temperature of normal butane, continuously withdrawing isobutane from the contacting zone, and continuously supplying normal butane to said zone.

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