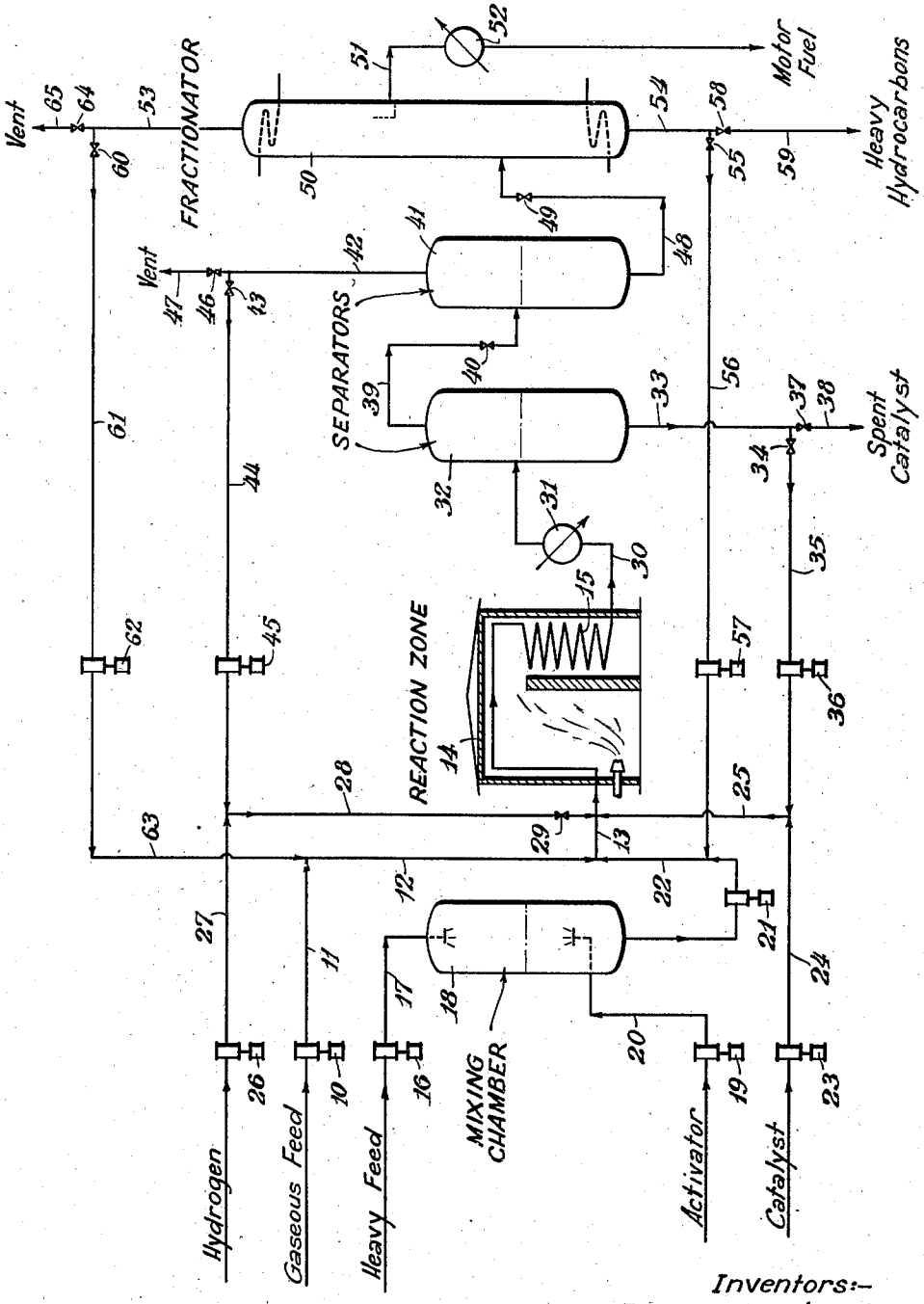
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CONVERSION OF BUTANES INTO HIGH ANTIKNOCK MOTOR FUEL

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Inventors:-
Edmond L. d'Ouville
Bernard L. Evering

By Clarence H. Seeley
Attorney

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CONVERSION OF BUTANES INTO HIGH ANTIKNOCK MOTOR FUEL

Edmond L. d'Ouville and Bernard L. Evering, Chicago, Ill., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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This invention relates to the production of high antiknock motor fuels rich in branched-chain paraffin hydrocarbons, and more particularly to a process for converting paraffin hydrocarbons having four carbon atoms per molecule into such motor fuels in a single step. Still more specifically, it relates to a conversion process wherein at least one of the butanes is treated with an active aluminum halide catalyst in the presence of paraffin hydrocarbons having at least 16 carbon atoms per molecule, such as paraffin wax and materials containing large amounts of paraffin wax, whereby an intermediate fraction boiling in the motor fuel range is formed consisting almost entirely of branched-chain paraffin hydrocarbons.

In the operation of most petroleum refineries and particularly in natural gasoline and distillate recovery plants large quantities of the butanes are available. These hydrocarbons have a number of uses, including their use as fuel either alone or blended in limited quantities in gasoline and the like. Also, a number of methods are available for converting them into motor fuels, but most of these require a number of separate operations and the others either do not produce motor fuels of the highest quality or require another valuable material such as one or more hydrocarbons of the olefin series. For example, a fraction rich in butanes can be polymerized thermally but the product is unsaturated and therefore not well suited for use as aviation gasoline. By dehydrogenating the butanes, olefins are produced which can be polymerized either thermally or catalytically into motor fuels which are likewise unsaturated. In a special process of this type isobutane can be converted into iso-octene which, upon hydrogenation, yields iso-octane. This is, of course, an excellent aviation fuel constituent but the process involved is relatively expensive because of the number of operations necessary to produce iso-octane in this manner. Recently, processes have been developed in which isobutane is combined with a gaseous olefin to produce isoparaffins boiling in the motor fuel range, but in many cases the necessary olefins are not available for this purpose.

One of the major problems confronting the petroleum industry at the present time is the production of sufficient quantities of premium aviation fuels at a reasonable cost and much effort has been directed to the manufacture of aviation fuels consisting largely of branched-chain paraffin hydrocarbons, which are particularly adapted to such service due to their high antiknock values, freedom from gum-forming tendencies and relatively high heat content per unit weight of fuel. The principal methods hitherto proposed for accomplishing this have been outlined above and some of their disadvantages stated.

We have found that branched-chain paraffin hydrocarbons having from about five to about ten carbon atoms per molecule can be easily and economically produced by the reaction of either or both of the butanes and a substantially saturated heavy hydrocarbon fraction rich in paraffin hydrocarbons having at least 16 carbon atoms per molecule in the presence of an active aluminum halide. An ideal heavy feed stock is paraffin wax but others which are substantially as effective in causing the butanes to react and which are available at relatively low cost are slack wax, i. e. an unsweated paraffin wax, and foots oil, which is produced by the sweating operation and contains large quantities of low melting paraffin waxes. By means of our process premium antiknock motor fuels are produced from two materials having low values in themselves in a single economical step.

It is an object of our invention to provide a process for the production of branched-chain paraffin hydrocarbons from the butanes. Another object is to provide a process whereby high antiknock motor fuel constituents can be economically produced from the butanes and heavy materials rich in paraffin wax or analogous substances. Other objects, advantages and uses of our invention will appear from the following detailed description read in conjunction with the drawing which forms a part of this specification and shows in a schematic manner an apparatus suitable for carrying out our invention.

In one of its broad aspects our invention comprises the reaction of one or both of the butanes and a substantially saturated heavy hydrocarbon fraction consisting predominantly of paraffin hydrocarbons having at least 16 carbon atoms per molecule in the presence of an active aluminum halide catalyst and in the presence of an activator affording a hydrogen halide under the reaction conditions at a temperature in the range from about 100° F. to about 400° F. and under a pressure sufficient to maintain the butanes largely in the liquid phase, e. g., about 200 to about 3000 pounds per square inch. Preferably the reaction is carried out in the presence of free hydrogen under a partial pressure in the range from about 300 to about 3000 pounds per

square inch, since the hydrogen greatly retards the rate of deactivation of the catalyst.

The butane-containing feed stock of our process can be any substantially completely saturated normally gaseous fraction rich in at least one of the butanes. Preferably the butane content is in excess of 50% by volume and includes a considerable proportion, for example, at least 25% of isobutane. Such fractions are available in those refineries carrying out processes in which the olefinic content of a gaseous fraction such as "plant butane" from cracking still gas is caused to react, thus leaving the butane relatively free from olefins. Catalytic polymerization and alkylation are examples of such processes. As mentioned above, butane fractions are plentiful in natural gasoline and distillate recovery plants and these are excellent source of gaseous feed for our process.

The heavy feed stock is, as already set forth, a substantially saturated fraction consisting predominantly of paraffin hydrocarbons having at least 16 carbon atoms per molecule. Suitable materials are paraffin wax, slack wax, foots oil, petrolatum, ozocerite, etc. Other very waxy petroleum fractions may also be used, and in general they should contain at least 50% by weight of paraffin hydrocarbons having melting points above about 60° F. Another feed stock which can be employed advantageously is the heavy fraction produced as a by-product in the manufacture of iso-octane in the usual way containing the hydrogenated tetramers and heavier polymers of isobutylene.

The butanes and the heavy paraffin hydrocarbons should be present in the reaction zone in a mol ratio of at least 1:1, and preferably this ratio is in the range from about 2:1 to about 4:1, depending upon the nature of the heavy paraffins and the degree of conversion desired per pass. Higher yields are obtainable when the heavy paraffins contain relatively large numbers of carbon atoms per molecule so that it is desirable to use waxy materials having 20 to 30 carbon atoms per molecule if such materials are available. It is also advantageous to use a material practically free from light ends so that the intermediate boiling product can be separated readily from the unreacted heavy feed stock by fractional distillation. For example, materials having an initial boiling point in the range from 500° F. to 550° F. are suitable.

The active aluminum halide catalyst used in carrying out our invention is preferably an aluminum chloride catalyst, but anhydrous aluminum bromide, for example, is also effective. In a continuous type of process such as will be described it is preferred to introduce the catalyst into the reaction zone in the form of a slurry or solution, for instance in a portion of the feed stock or as a liquid aluminum halide-hydrocarbon complex. As will be brought out below, the catalyst complex formed during the reaction retains its activity for a considerable period of time and it is therefore advantageously separated from the reaction products and recycled.

The concentration of catalyst present in the reaction zone can vary within wide limits, depending primarily upon the temperature, reaction time and catalyst activity or "freshness." Generally, the catalyst concentration will be within the range from about 5% to about 30% by weight of the hydrocarbons present, although it will be understood that the actual catalyst consumption will be considerably smaller and generally within the range from about 0.1% to about 5.0% by weight. Furthermore, it is not necessary that our process be operated by concurrent contacting of the catalyst and reactants, as herein described, but the reaction can be carried out batchwise or by causing the reacting hydrocarbons to flow through a bed of aluminum chloride, for example, mounted on a support such as active carbon, various types of clays, etc.

Under most conditions we employ an activator with the aluminum halide catalyst. When our preferred catalyst, aluminum chloride, is used, the presence of an activator is necessary in order that a reasonable reaction rate may be obtained, but in the case of aluminum bromide the activator can be dispensed with under some circumstances.

As activator we use a substance affording a hydrogen halide under the reaction conditions, which can be either a hydrogen halide itself, such as hydrogen chloride or hydrogen bromide, or it can be carbon tetrachloride or one of the alkyl halides such as methyl chloride or bromide, ethyl chloride or bromide, etc. In general the chlorinated and brominated hydrocarbons, particularly the more volatile ones, are suitable, and even water can be used since hydrogen halide will be generated therefrom by reaction with the catalyst, but this is not preferred since the catalyst is thus deactivated more rapidly than would otherwise be the case. Preferably the amount of activator used is sufficient to supply a concentration in the reaction zone of about 1 to 2 mols of hydrogen halide per mol of aluminum halide, which will usually be in the range from about 0.1% to 5.0% by weight, based on the reacting hydrocarbons present.

Another important variable which influences the course of the reaction is temperature. In general temperatures ranging from about 100° F. to about 400° F. are suitable, although different reaction times and amounts of catalyst are almost imperative in order that economically practicable results may be obtained at various temperatures. Usually it is preferred to carry out the reaction in the range from about 150° F. to about 300° F. in order that it may proceed rapidly and without danger of over-treatment.

The reaction pressure should be sufficient to keep the butanes largely in the liquid phase and when hydrogen is used the pressure should be in the range from about 300 to about 3000 pounds per square inch. Preferably, however, the hydrogen partial pressure is in the range from about 500 to about 1500 pounds per square inch. The hydrogen employed can be relatively pure or it may contain impurities such as methane as long as the hydrogen content is above about 50 mol per cent.

By carrying out our invention as above described, we are able to convert large amounts of the butanes into branched-chain paraffin hydrocarbons suitable for use in aviation fuel. Simultaneously additional amounts of these materials are produced from the heavy feed stock, and all of the desirable hydrocarbon products can be separated from unconverted material by fractional distillation.

While we do not wish to be limited thereto we believe that the condensation of the butanes with each other proceeds because of the hydrogen deficiency produced when the heavy paraffinic feed stock is converted into a material having a smaller number of carbon atoms. Since there is a very strong tendency for all of the products of the

reaction in the presence of the aluminum halide catalyst to be saturated, these fragments take up hydrogen from the butane and the resulting hydrogen deficiency causes the butanes to condense and form normally liquid branched-chain hydrocarbons. While one might expect that free hydrogen introduced into the reaction zone would impede this process by saturating the fragments of the heavy feed, this does not occur and the hydrogen acts only on the aluminum halide-hydrocarbon complex and helps maintain its activity by preventing the hydrocarbons associated therewith from becoming highly unsaturated. It is also believed that the mechanism whereby the normal butane is made to enter into the reaction includes the simultaneous isomerization of normal butane to isobutane, which is, of course, relatively more active. Regardless of the theory of the reactions involved, we have found that excellent yields of isoparaffinic hydrocarbons boiling in the motor fuel range can be obtained according to our invention.

It is apparent that the process of our invention can be carried out either batchwise or continuously, although we prefer a continuous operation, and that certain portions of the apparatus must be constructed of corrosion-resistant materials to prevent rapid deterioration thereof from the active halogen compounds present. Many types of apparatus can be constructed readily by one skilled in the art for carrying out our invention, but we will describe our invention in detail in connection with only one of these as illustrated in the drawing, to which reference is now made.

The normally gaseous feed as set forth above is introduced into the system by means of pump 10 and lines 11, 12 and 13 and thence into a reaction zone 14, which, as shown, is a heated elongated coil 15 maintained at the desired reaction temperature. A pressure vessel, including stirring equipment, may be substituted for reaction zone 14, but the form shown is preferred for continuous operation. In order to maintain the necessary agitation between the catalyst and the other reactants it is necessary that the velocity through the coil 15 shall be great enough to insure turbulent flow. Knot-hole mixers or other baffle arrangements may be inserted in coil 15 at several places to aid in achieving this result. The heavy feed stock is passed by means of pump 16 and line 17 into a chamber 18 in which it is mixed with activator supplied by pump 19 in line 20. In the arrangement shown, which is particularly suitable when the activator is a gas such as hydrogen chloride, only that portion of the activator which dissolves in the heavy feed is allowed to escape from chamber 18 and for most purposes this is sufficient. However, activator can be mixed directly with either the normally gaseous feed or the heavy feed or both as long as it enters reaction zone 14. When very high pressures are used in reaction coil 15, the pressure in chamber 18 is preferably maintained in an intermediate range, for instance, 200 to 300 pounds per square inch. The heavy feed now containing dissolved activator enters line 13 by means of pump 21 and line 22, and the catalyst is likewise supplied to line 13 by means of pump 23 and lines 24 and 25. When hydrogen is employed this is also introduced into line 13 through compressor 26, lines 27 and 28 and valve 29, and it will be assumed hereinafter that the reaction is carried out in the presence of hydrogen.

The entire reaction mixture from coil 15 passes through line 30 and preferably through a cooler 31 to separator 32. The products consist of an aluminum halide-hydrocarbon complex which settles out in the lower portion of separator 32 and an upper layer consisting essentially of unreacted gaseous and heavy feed stocks, branched-chain paraffin hydrocarbons intermediate in boiling range and excess hydrogen. The catalyst complex is continuously withdrawn from separator 32 through line 33 and either recycled to line 13 through valve 34, line 35, pump 36 and line 25 or withdrawn from the system through valve 37 and line 38. Under some conditions a portion of the complex may be continuously withdrawn from the system and the remainder recycled, and the substantially spent complex can of course be regenerated or the aluminum halide recovered therefrom and reintroduced into the system through pump 23. Furthermore, at least a portion of the spent complex can be treated with water or otherwise to furnish hydrogen halide for use as activator in the process.

The remainder of the products from coil 15 are removed from the upper portion of separator 32 through line 39 and valve 40 and introduced into a separator 41 in which a major portion of the hydrogen is separated due to the reduction in pressure across valve 40. This hydrogen-containing gas which may also contain considerable quantities of hydrogen halide and some normally gaseous paraffins is withdrawn from separator 41 through line 42, and can be recycled through valve 43, line 44 and compressor 45 to line 28 or all or a portion of it can be vented from the system through valve 46 and line 47.

The lower layer, consisting essentially of hydrocarbons, is removed from separator 41 through line 48 and valve 49 and introduced into fractionating tower 50. Valve 49 is preferably of the pressure-reducing type adjusted to the desired fractionating pressure. Fractionating tower 50 is of a conventional type provided with a side stream outlet 51 and is operated so that the bottoms therefrom contain the unreacted heavy feed stock. The normally liquid hydrocarbons falling within the desired motor fuel boiling range are withdrawn through line 51 and cooler 52 to storage or for other treatment, and gases having less than 5 carbon atoms per molecule are withdrawn overhead through line 53. The heavy liquids collecting in the bottom of fractionator 50 are withdrawn through line 54 and are preferably recycled to line 13 for further treatment through valve 55, line 56, pump 57 and line 22. Under some conditions it may be desirable to withdraw a portion of these heavy materials from the system and this can be done through valve 58 and line 59.

The overhead passing through line 53 is rich in butanes and particularly in isobutane and may contain such other materials as are included in the gaseous feeds, and also some hydrogen halide. This overhead is preferably recycled to line 13 through valve 60, line 61, pump 62 and lines 63 and 12 so that the butanes present may be further converted to normally liquid branched-chain paraffin hydrocarbons. In order that inert gases may be prevented from accumulating in the system, a portion of the material in line 53 may be vented from the system either intermittently or continuously through valve 64 and line 65. Free hydrogen and/or hydrogen halide can be recovered from the gases vented through line 65, and those vented through line 47 as well, and these materials returned to the system.

It is apparent that we have described a novel

and useful method of producing branched-chain paraffin hydrocarbons from normally gaseous paraffin hydrocarbons containing four carbon atoms per molecule and heavy paraffinic materials having at least 16 carbon atoms per molecule.

Many modifications of our invention and of the apparatus shown herein for carrying out the same will be apparent to those skilled in the art and they will be able to supply numerous details not illustrated in the drawing, such as heat exchangers, provisions for fractionating tower control, etc. We do not desire, therefore, to be limited to the specific modifications used in illustrating our invention but only by the scope of the following claims.

We claim:

1. The process of producing a high anti-knock motor fuel rich in branched-chain paraffin hydrocarbons which comprises contacting a substantially completely saturated normally gaseous fraction containing at least 50 per cent by volume of at least one of the butanes, a substantially saturated heavy hydrocarbon fraction containing at least 50 per cent by weight of paraffin hydrocarbons having melting points above about 60° F., about 5 to 30 per cent of an aluminum chloride catalyst and about 0.1 to 5.0 per cent of hydrogen chloride based on the weight of hydrocarbons present, and free hydrogen, in a reaction zone maintained at a temperature in the range from about 100° F. to about 400° F. and under a pressure in the range from about 300 to about 3000 pounds per square inch, the butanes in said gaseous fraction and the paraffin hydrocarbons in said heavy fraction being present in said reaction zone in a mol ratio in the range from about 2 to 1 to about 4 to 1, removing the products from said reatcion zone, and separating said high anti-knock motor fuel from said products.

2. A process for the production of branched-chain paraffin hydrocarbons having between about five and about ten carbon atoms per molecule which comprises the steps of reacting paraffins having four carbon atoms per molecule in the presence of a heavy hydrocarbon fraction consisting predominantly of paraffin hydrocarbons having at least sixteen carbon atoms per molecule under the catalytic influence of an active aluminum halide catalyst, conducting the reaction at a temperature in the range of between about 100 and 400° F. and under a pressure sufficient to maintain the butanes at least largely in the liquid phase whereby there is a net disappearance of paraffins having four carbon atoms per molecule.

3. The process of claim 2 wherein the mol ratio of C_4 paraffin and heavy paraffin hydrocarbons within the reaction zone is in the range of between about 2:1 and 4:1.

4. A process for the production of high octane number branched-chain hydrocarbons including those having between about five and about ten carbon atoms per molecule which comprises the steps of subjecting isobutane to the catalytic action of an active aluminum halide in the presence of a substantially saturated heavy hydrocarbon fraction consisting predominantly of paraffin hydrocarbons having at least sixteen carbon atoms per molecule and under a pressure sufficient to maintain the isobutane largely in the liquid phase.

5. A process for the production of high octane number branched-chain hydrocarbons including those having between about five and about ten carbon atoms per molecule which comprises the steps of subjecting to the catalytic action of an active aluminum halide an admixture of butanes consisting of at least 25 volume per cent isobutane and a substantially saturated heavy hydrocarbon fraction consisting predominantly of paraffin hydrocarbons having at least sixteen carbon atoms per molecule, the mol ratios of butanes and heavy paraffin hydrocarbons within the reaction zone being in the range of between about 2:1 and about 4:1.

6. The method of producing large yields of branched-chain paraffinic hydrocarbons of the gasoline boiling range from lighter and heavier hydrocarbons which method comprises contacting a charging stock consisting essentially of butane and paraffin wax with an aluminum chloride catalyst promoted by hydrogen chloride at a temperature within the approximate range of 100° to 400° F. and under a pressure sufficient to maintain liquid phase conversion conditions whereby there is a net disappearance of butane and a production of branched-chain hydrocarbons of the gasoline boiling range.

7. The method of claim 6 wherein at least about 25% by volume of the butane in the charging stock is isobutane.

EDMOND L. D'OUVILLE.
BERNARD L. EVERING.