

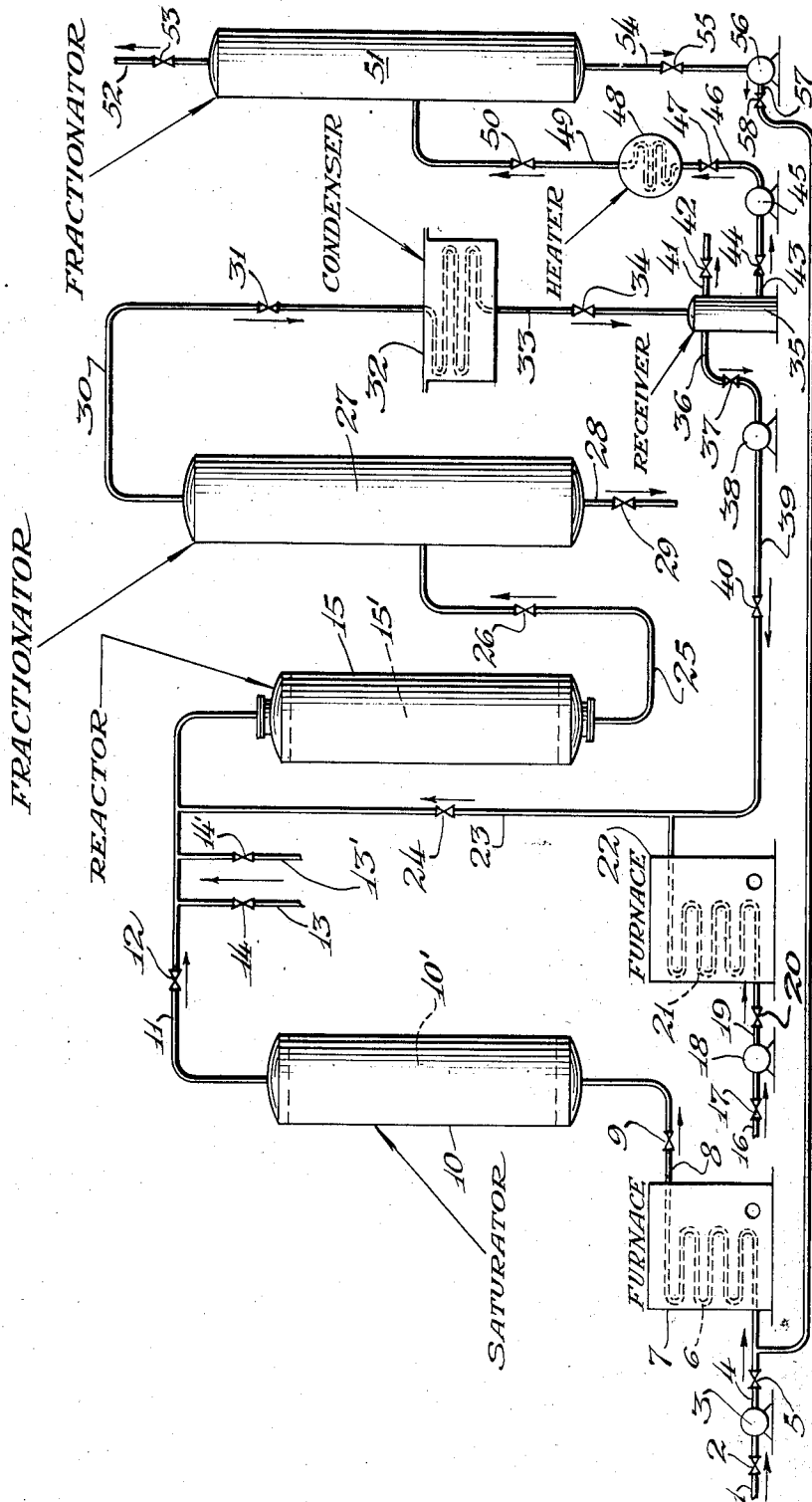
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J. D. DANFORTH

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CONVERSION OF HYDROCARBONS

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Inventor:
Joseph D. Danforth
By Speer Gary
Attorney

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CONVERSION OF HYDROCARBONS

Joseph D. Danforth, Chicago, Ill., assignor to
Universal Oil Products Company, Chicago, Ill.,
a corporation of Delaware

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This is a continuation-in-part of my co-pending application Serial No. 373,961, filed January 10, 1941.

This invention relates to a process for the isomerization of essentially saturated hydrocarbons including paraffins and cycloparaffins and is more specifically concerned with processes involving the use of metal halide-hydrogen halide catalysts.

The invention is still more specifically directed to a process flow which permits continuous operation over relatively long periods of time.

The isomerization of various hydrocarbons and hydrocarbon fractions produced in connection with the refining of petroleum is of considerable importance at the present time. In the case of normal butane, the first isomerizable hydrocarbon in the paraffin series, it is found that its isomer is considerably more reactive so that it is capable of direct alkylation by olefins and alternatively utilizable compounds in the presence of catalysts so that higher motor fuel boiling range hydrocarbons of high antiknock value are readily producible by these methods. Also, when isobutane is dehydrogenated to isobutene the latter compound may be catalytically polymerized and then hydrogenated to produce isooctanes of unusually high antiknock rating which are used as blending agents in aviation fuels.

In the case of normally liquid saturated hydrocarbons such as, for example, normal or mildly branched paraffins which occur in straight run gasolines, it is advantageous to isomerize these compounds in order to increase the antiknock value of the gasoline. Many methods have been tried for accomplishing this object. In the case of normal butane isomerization may be effected with metal halide-hydrogen halide catalysts without too great difficulty since normal butane has the least tendency of the normal paraffins to undergo undesirable decomposition reactions at temperatures at which isomerization proceeds at a practical rate. In the case of normal pentane and other normally liquid paraffin hydrocarbons, however, decomposition reactions tends to occur so that the yields of desired isomers are reduced and catalysts are contaminated and lose their catalytic effectiveness due to accumulations of metal halide-hydrocarbon complexes which coat the active surfaces of the primary catalyst. In the present process advantage is taken of the fact that normal butane does not undergo extensive decomposition reactions during isomerization in order to more effectively isomerize higher boil-

ing hydrocarbons and hydrocarbon fractions which have decomposition tendencies.

In one specific embodiment the present invention comprises a process for the isomerization of essentially saturated hydrocarbons by passing normal butane through a bed of granular aluminum chloride to dissolve a portion of the aluminum chloride, introducing the solution of aluminum chloride in normal butane along with higher boiling hydrocarbons and added hydrogen chloride into a reaction zone containing granular packing material, fractionating the products from the reaction zone to produce a light gas mixture comprising hydrogen chloride, isobutane, normal butane, and heavier hydrocarbons and recycling the gas mixture containing hydrogen chloride back to the packed reaction zone and the normal butane back to further contact with the aluminum chloride.

The essential features of the present process will be brought out in a description of the operation given in connection with the attached diagrammatic drawing which shows by the use of conventional figures in side elevation an arrangement of apparatus in which the process may be conducted.

Referring to the drawing normal butane is introduced to the plant arrangement by way of line 1 containing valve 2 to a pump or compressor 3 which discharges through line 4 containing valve 5 through a heating element 6 arranged to receive heat from a furnace 7. It is preferable that the normal butane pass through the granular aluminum chloride in liquid phase and that ordinarily it should be at an elevated temperature since its solvent capacity for the aluminum chloride increases with temperature. Thus, it has been found to be good operating practice to pass the liquid butane through the granular aluminum chloride at temperatures of from about 180 to about 200° F. under pressures of the order of 250 pounds per square inch, or higher temperatures at higher pressures as high as 500 pounds per square inch, the butane from the heating element in the drawing passing through line 8 containing valve 9 under these approximate conditions and then flowing upwardly through a bed of aluminum chloride 10 contained in a saturator 10.

The solution of aluminum chloride and normal butane passes through line 11 containing valve 12 through a reactor 15 which contains granular packing material 15'. This material may be of varying character and may include materials of a relatively non-absorbent or dense

character such as crushed silica, crushed fire-brick, "Porocel" particles, etc. or may be of a more absorbent character such as clays either raw or acid treated, prepared aluminas, activated carbon and other similar materials. Hydrogen chloride sufficient to make up for incidental losses is introduced through line 13 containing valve 14 and heavier essentially saturated hydrocarbon fractions such as, for example, a normal pentane fraction, a normal hexane fraction or a mixture of paraffin and naphthene hydrocarbons constituting the lower boiling fractions of a straight run gasoline or naphtha is also introduced into line 11. This heavier material is charged to pump 18 by way of line 16 containing valve 17 and discharged through line 19 containing valve 20 through a heating element 21 arranged to receive heat from a furnace setting 22, the heated material passing through line 23 containing valve 24 and then into reactor 15. The temperature to which the incoming heavier hydrocarbon charge is heated will depend upon its boiling range and chemical composition and in some instances it may not be introduced at a very high temperature. However, temperatures of from about 100 to about 400° F. may be employed at this point. Heavier fractions will usually require lower temperatures and lighter fractions may be subjected to higher temperatures without undue decomposition. If desired hydrogen may be introduced to the reactor 15 by way of line 13' containing valve 14' to diminish side reactions.

In reactor 15 aluminum chloride carried in solution in the normal butane is deposited upon the surfaces of the granular packing material and thence serves to continually introduce fresh catalyst which is distributed on the granules so as to expose a large amount of surface and thus catalyze isomerization reactions most effectively. As the catalyst surfaces become coated with deposits of aluminum chloride-hydrocarbon complexes, they are conveniently renewed by the aluminum chloride introduced by the normal butane so that the continuity of the process is only limited by complete saturation of the particles at which time the reactor will require dismantling and cleaning. Although only one reactor is shown in the drawing it is comprised within the scope of the invention to employ reactors in parallel so that the charge may be diverted through a fresh reactor while the spent reactor is being cleaned and refilled.

During passage through reactor 15 both the normal butane and the heavier materials will undergo isomerization reactions to a varying extent. The temperature to be employed, the amount of hydrogen chloride and the rate of passage of the granular material will vary with different proportions of normal butane and heavier hydrocarbons so that no narrow limits can be fixed for the conditions in the reactor. However, as previously stated the temperature will seldom exceed 400° F. and there is apparently little advantage to be gained by using more than 20 mole per cent of hydrogen chloride based on the average molecular weight of the hydrocarbon charge. The space velocity will again be dependent on such factors as temperatures, amount of hydrogen chloride used, the quality of the charge and the type of filling material.

The total products from reactor 15 are indicated in the drawing as passing through line 25 containing valve 26 to a primary fractionator 27 which may be employed for separating the prod-

ucts to obtain hydrogen chloride and normal butane for recycling, and isobutane and heavier isomerized hydrocarbons for recovery as products of the process. Any system of fractionation may be employed even though it may vary considerably from the one outlined in the drawing. As shown in the drawing the hydrocarbon fractions heavier than normal butane are recovered from fractionator 27 through a bottom line 28 containing valve 29. These bottoms may be further fractionated if desired to recover light blending material and reject heavier fractions if desired. The overhead from fractionator 27 consists of hydrogen chloride, hydrogen (if hydrogen has been introduced to the plant), light hydrocarbons in varying amounts consisting of methane, ethane and propane and both isobutane and normal butane and pass through line 30 containing valve 31 to condenser 32. During passage through condenser 32 conditions of temperature and pressure are employed so that the mixture of iso and normal butane is condensed and passes in liquid phase through line 33 containing valve 34 into receiver 35. As indicated in the drawing, the lighter gases and hydrogen chloride may be withdrawn from this receiver through either line 41 containing valve 42 or line 36 containing valve 37. However, this simple separation may be modified by the use of high pressure fractionation to effect a sharper separation although means for accomplishing this end are not shown in the drawing. A portion of the gases withdrawn from line 41 containing valve 42 may be further separated into hydrogen chloride, hydrogen and hydrocarbons. However, as indicated a portion or all of the gaseous phase in receiver 35 may pass through line 36 containing valve 37 to a recirculating pump or compressor 38 which discharges through line 39 containing valve 40 back to line 23 leading to isomerizing reactor 15.

The mixture of butanes in receiver 35 is withdrawn by pump 45 through line 43 containing valve 44 and discharged by way of line 46 containing valve 47 through a heater 48 wherein the mixture of butanes is brought to a temperature suitable for effecting separation of isobutane and normal butane. The heated material passes through line 49 containing valve 50 to a fractionator 51. This fractionator may be operated with an inlet temperature of about 150° F. under a pressure of the order of 100 to 110 pounds per square inch, and a top temperature of 120° F. and a bottom temperature of 150° F. Isobutane passes then through line 52 containing valve 53, along with any hydrogen chloride or light gases which may have been dissolved in the butane mixture in receiver 35.

Normal butane passes through line 54 containing valve 55 to a recycling pump 56 which discharges through line 57 containing valve 58 back to line 4 for use first as a carrying material for aluminum chloride and then for partial isomerization in reactor 15 as already described.

The following data are introduced to indicate the type of results obtainable when operating in accordance with the process of the present invention although it is not intended that the proper scope of the invention should be limited in exact accordance therewith.

Runs were made in apparatus similar to that described in connection with the drawing in which normal butane was used as a catalyst carrier and a commercial hexane was used as heavier isomerization charging stock.

EXAMPLE I

In the first continuous run the saturator containing granular aluminum chloride was maintained at a temperature of 240° F., the packed reactor was maintained at a temperature of 212° F. and a pressure of 500 pounds per square inch was maintained on both saturator and reactor. The mixture of equal parts by volume of butanes and hexane was charged to the reactor at such a rate that 0.23 volumes of the total charge per volume of reactor space was introduced per hour. Hydrogen chloride was introduced at the rate of 11 to 12 moles per 100 moles of total hydrocarbon charge. The following table shows the significant data obtained during the course of the run:

Table 1

Period No.	Hours on stream	Octane No. of hydrocarbon fraction containing no butanes
1.....	2-12	70.5
2.....	12-22	73.1
3.....	22-32	78.9
4.....	32-42	78.9
5.....	42-52	78.9
6.....	52-62	78.5
7.....	62-72	78.5
8.....	72-82	78.9
9.....	82-92	78.9

EXAMPLE II

In a second test 2 parts of commercial hexane to one part of normal butane by volume was used, giving the data shown in Table 2:

Table 2

Period No.	Hours on stream	Octane No. of fraction of products containing no butanes
1.....	92-102	77.0
2.....	102-112	76.1
3.....	112-122	77.3
4.....	122-132	75.9
5.....	132-142	75.9

In the above runs no difficulties were encountered in connection with the formation of aluminum chloride complexes in the saturator whereas it was found impossible to run for any length of time if the total charge was introduced into the saturator even in the absence of hydrogen chloride on account of the formation of viscous complexes which coated the granular aluminum chloride and soon reduced its activity to a low value.

As used in the above specification, the term "saturated hydrocarbon" is intended to include paraffinic and cycloparaffinic hydrocarbons.

I claim as my invention:

1. An isomerization process which comprises contacting normal butane, in liquid phase, with aluminum chloride under conditions such as to dissolve aluminum chloride in the liquid butane, commingling normally liquid saturated hydrocarbons with the butane-aluminum chloride solution, passing the resultant mixture through a reaction zone containing a solid packing material and depositing aluminum chloride from the solution onto said packing material, and subjecting the hydrocarbons to isomerizing conditions during their passage through the reaction zone.

2. The process as defined in claim 1 further characterized in that said normally liquid hydrocarbons comprise normal paraffins.

3. The process as defined in claim 1 further characterized in that said normally liquid hydrocarbons comprise a paraffinic gasoline fraction.

4. An isomerization process which comprises passing liquefied normal butane through a body of aluminum chloride under conditions such as to dissolve a portion of said body in the butane, commingling normally liquid isomerizable paraffins and hydrogen chloride with the solution of aluminum chloride in butane, passing the resultant mixture through a reaction zone containing a solid packing material and depositing aluminum chloride from the solution onto said packing material, maintaining the reaction zone under paraffin isomerizing conditions and therein isomerizing substantial portions of the normal butane and the normally liquid paraffins.

5. An isomerization process which comprises passing liquefied normal butane through a body of aluminum chloride under conditions such as to dissolve a portion of said body in the butane, commingling normally liquid isomerizable paraffins and hydrogen chloride with the solution of aluminum chloride in butane, passing the resultant mixture through a reaction zone containing a solid packing material and depositing aluminum chloride from the solution onto said packing material, maintaining the reaction zone under paraffin isomerizing conditions and therein isomerizing substantial portions of the normal butane and the normally liquid paraffins, fractionating the resultant products to separate therefrom a hydrogen chloride-containing gas and a liquid normal butane fraction, returning the latter to further contact with said body of aluminum chloride, and recycling at least a portion of the hydrogen chloride-containing gas to the reaction zone.

JOSEPH D. DANFORTH.