July 9, 1968 E. L. D'OUVILLE 3,392,212

PROCESS FOR PRODUCING DIMETHYLBUTANE FROM PENTANE

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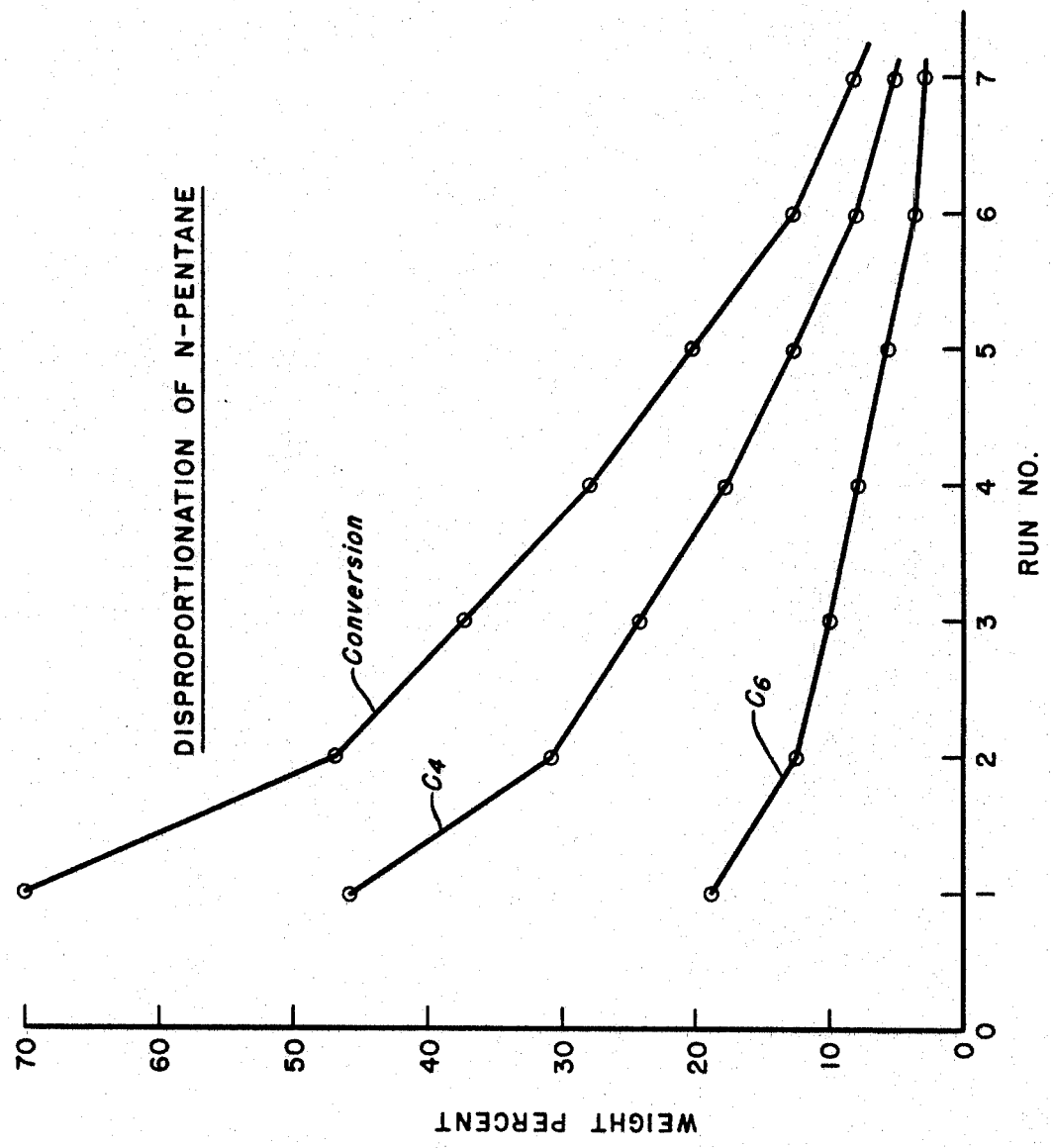


Fig. 1

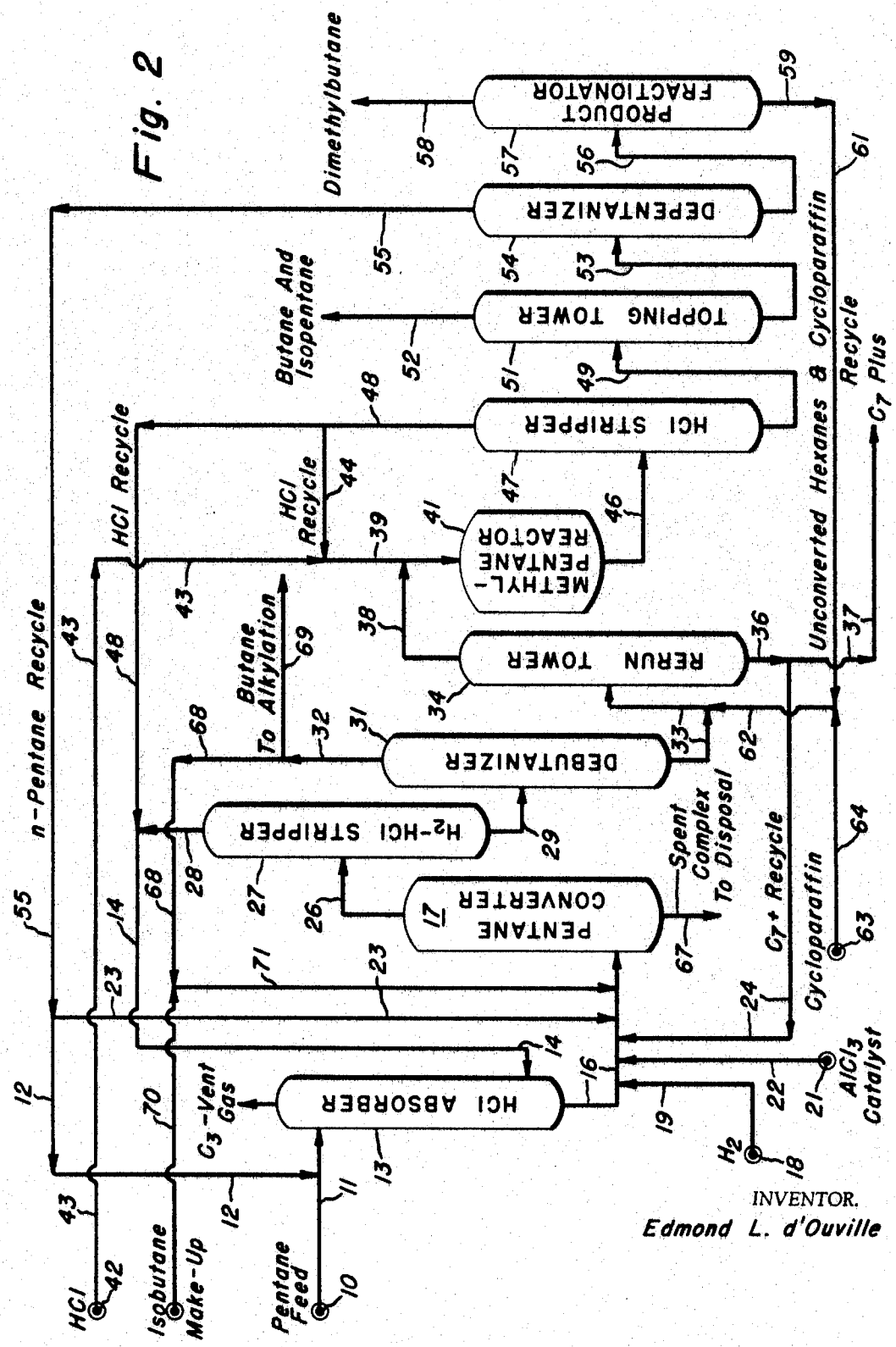
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Fig. 2



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3,392,212

PROCESS FOR PRODUCING DIMETHYLBUTANE FROM PENTANE

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Continuation-in-part of application Ser. No. 419,998, Dec. 21, 1964. This application Mar. 1, 1967, Ser. No. 619,856

5 Claims. (Cl. 260—683.73)

ABSTRACT OF THE DISCLOSURE

A combination process for producing dimethylbutanes from pentane in which process the pentane is first disproportionated to a synthetic benzene-free hexane fraction and isobutane, and the hexane fraction is then further converted to a dimethylbutane rich product in a relatively low temperature fixed-bed isomerization convertor. Provisions are made so that isobutane can be maintained in the disproportionation reactor to act as a buffer and control the ratio of synthetic hexane to isobutane produced. The present process solves the problem of obtaining a benzene free hexane charge which is needed for proper and economic operation of the low temperature fixed-bed isomerization process.

Cross-reference to related applications

This is a continuation-in-part of application Ser. No. 419,998, filed Dec. 21, 1964, and now abandoned.

Background of the invention

This invention relates to the catalytic conversion of hydrocarbons and more particularly to a process for the conversion of hydrocarbons involving the use of active aluminum halide catalysts. Still more specifically, it relates to a conversion process of this type in which one catalyst is an active liquid aluminum halide-hydrocarbon complex and the other is a solid aluminum halide-alumina catalyst.

Modern automobile engines require high octane gasoline, and this need has been met in the past by producing high octane blending stocks by catalytic reforming to produce aromatic rich fractions boiling above about 170° F. and by isobutane-butylene and/or propylene alkylation to produce branched-chain C_7 and C_8 isoparaffins also boiling above about 170° F. These processes have satisfied the need for higher boiling, high octane blending components. As the compression ratio of internal combustion engines is increased, thus increasing the octane requirement, the need for lower-boiling high octane blending components becomes more pressing. As the demand for unleaded gasoline increases, the need for such components becomes even more urgent. It is an object of this invention to provide an improved process for obtaining these components.

The low temperature isomerization process, using a solid aluminum chloride catalyst in the presence of hydrogen chloride gives excellent yields of dimethylbutane. Dimethylbutane (neohexane and diisopropyl) is an excellent blending material in that it has a high blending octane number and excellent volatility characteristics. At the low temperatures of this process, equilibrium favors the production of dimethylbutane. A serious disadvantage to the low temperature hexane isomerization process is that the catalyst is very susceptible to deactivation by certain impurities which may be present in the feed. It has been found that small quantities of aromatics (benzene, in particular), sulphur, or olefins, have an adverse effect on the catalyst. Therefore, it is necessary that the feed to the process be essentially free from such contaminants.

The feed should not contain more than about 10 p.p.m. aromatics (and preferably not more than 2–3 p.p.m.), 1–2 p.p.m. sulphur, and 50 p.p.m. olefins. Various methods of pretreating the feed to obtain acceptable levels of these impurities have been proposed. One of the most effective involves hydrofining and hydrogenation. This treatment is quite expensive and alternative means are desirous.

The feed to the low temperature hexane isomerization process usually consists essentially of hexanes without the above described impurities. The presence of pentanes in the feed does not have a significantly adverse effect on the reaction. Suitable feeds may be obtained from other refinery process units such as a toluene unit, cracking unit, or pipe still. This material, although available, is valuable in itself and less expensive feed would be economically advantageous.

Normal pentane is generally available in large quantities in the refinery. It has a low octane number (unleaded *MON*=61.9, *MON*+3 cc. *TEL*=83.6) and in many instances can be considered a distress material. An economical process for converting inexpensive normal pentane to valuable dimethylbutane would be a significant contribution to the petroleum processing art.

Summary of the invention

Basically, this invention consists of a combination of two process steps, one of which is well known in the art and the other which is disclosed in U.S. Patent No. 3,280,213, and U.S. Patent No. 3,285,990. The inventive concept disclosed herein is the novel preparation of a benzene-free, olefin-free synthetic hexane charge stock which may be isomerized without further treatment to dimethylbutanes by means of the low temperature fixed bed isomerization process. Step one of this invention consists of the disproportionation of pentane to the major components of butanes and hexanes. Step 2 consists of the isomerization of hexanes to dimethylbutane. The butanes from Step 1 may be recycled to act as a buffer in order to enhance the conversion of normal pentane to hexane, or alternatively, the butane may be transported to an alkylation unit for subsequent processing. A controlled quantity of the butane can be recycled in order to ultimately produce the desired product mix of isomerizate and alkylate.

This invention provides a process for the production of dimethylbutane from pentane which process comprises contacting pentane with aluminum chloride catalyst in the presence of hydrogen chloride to produce methylpentanes, and converting said methylpentanes to dimethylbutanes by contacting the methylpentanes with a solid aluminum chloride-absorbent catalyst in presence of hydrogen chloride. The preferred catalyst for disproportionating the pentane feed to produce methylpentane (2-methylpentane and/or 3-methylpentane) comprises a liquid aluminum chloride-hydrocarbon complex containing free aluminum chloride. A preferred solid aluminum chloride-adsorbent catalyst consists essentially of aluminum chloride, alumina and hydrogen chloride.

The invention further provides a process for producing dimethylbutane from pentane which comprises contacting pentane with liquid aluminum chloride-hydrocarbon complex containing hydrogen chloride and uncomplexed aluminum chloride to convert at least a portion of said pentane to monomethylpentanes, contacting monomethylpentanes with a solid catalyst consisting essentially of aluminum chloride, hydrogen chloride, and an adsorbent solid selected from the class consisting of alumina, and recovering dimethylbutane.

Brief description of the drawings

Reference to the attached drawings will be of assistance in understanding the invention and related data.

FIGURE 1 presents a summary of the results obtained in Example 2. Briefly it shows the disproportionation of normal pentane as a function of catalyst activity. The line labled "conversion" shows the percent normal pentane converted to non C_5 product. The other two lines show the percent of C_4 and C_6 in the product.

FIGURE 2 is a schematic flow diagram of a preferred embodiment of the invention.

Description of a preferred embodiment

A suitable active liquid aluminum halide-hydrocarbon complex for utilization in accordance with the invention is prepared by the action of aluminum chloride and hydrogen chloride on a substantially saturated hydrocarbon fraction containing an isoparaffin hydrocarbon at a temperature in the range of from about 50° F. to 175° F. Preferably this liquid catalyst complex is prepared from aluminum chloride and a substantially saturated fraction containing paraffin hydrocarbons having at least six carbon atoms and two side chains per molecule. Suitable saturated fractions are, for example, the hydrogenated polymers and co-polymers of olefins having less than six carbon atoms per molecule, normally, ethylene, propylene and the butylenes and amylenes, and the products of alkylation of isobutane and of isopentane of olefins of the class described. These fractions are very rich in highly branched paraffin hydrocarbons, the hydrogenated polymers of isobutylene, for example, being rich in so-called iso-octane (2,2,4-trimethylpentane). While certain alkylation products also contain these and other similar hydrocarbons, it is preferred to prepare the complex from a fraction rich in iso-octane although less volatile fractions rich in hydrogenated trimers and even heavier polymers of isobutylene are also effective in producing the desired complex. Usually, separate preparation of complex is necessary only to provide catalyst for start-up. Make-up complex can be formed in situ by adding aluminum chloride to the reactor where it complexes with hydrocarbons present therein.

The preferred aluminum halide-absorbent solid catalyst utilized in the process, broadly considered, is an aluminum halide positioned on surface-hydroxyl-containing adsorbent solid and associated with hydrogen halide. It is preferred that the hydrogen halide correspond to the particular aluminum halide used. Aluminum chloride is the preferred aluminum halide. More specifically, the preferred catalyst is the reaction product of aluminum chloride with surface hydroxyl groups of surface-hydroxyl-containing adsorbent solid associated with hydrogen chloride.

The term "surface-hydroxyl-containing adsorbent solid" includes the various forms of silica gel and the various alumina materials, natural and synthetic, which have a substantial portion of the surface existing in the hydroxyl form, as opposed to the "dehydrated" oxide form. No adsorbed water, as such, should be present. Aluminas which can be treated to produce the required surface hydroxyl groups are gamma, eta, and chi forms of alumina. The surface-hydroxyl-containing adsorbent solids are not significantly active for hydrocarbon isomerization, under the other conditions of the process, nor is the aluminum chloride reaction product alone significantly active; yet, the reaction product, when conjoined with HCl produces more hydrocarbon conversion than do the same amounts of aluminum chloride and HCl alone, or surface-hydroxyl-containing adsorbent solid either alone or with HCl, under the other conditions of the process.

Aluminum chloride can exist on the surface of alumina in three forms: reacted with surface hydroxyl groups to form —O—$AlCl_2$ groups, chemisorbed $AlCl_3$ monomer, and as physically adsorbed aluminum chloride. The reacted and chemisorbed forms associate HCl and thus form an active catalyst species; however, the chemisorbed monomer form is unstable and the aluminum chloride in this form tends to be desorbed by process and/or regeneration fluids, thus destroying this catalyst species. This species can be maintained or replaced, however, by replacing the aluminum chloride, e.g. in solution in the process stream. On the other hand, the reacted form is quite stable and, for example, the —O—$AlCl_2$ groups are not destroyed by atmospheric pressure inert gas purge at temperatures as high as 700° F., far above the sublimation temperature of aluminum chloride. The physically adsorbed form is even more unstable than the chemisorbed monomer form and is not a practical catalyst component.

The surface-hydroxyl-containing adsorbent solid should have a substantial amount of surface area. Only those pores in the adsorbent solid having diameters greater than about 35 Angstrom units (35 A.) are utilized in forming the catalyst, therefore it is the surface area of the pores larger than about 35 A. which is important. The surface of adsorbent solid pores having diameters greater than about 35 A. is termed herein "effective surface" and the term "effective surface area" is used herein to mean the total surface area of an adsorbent solid minus the surface area attributable to surface within pores having diameters less than about 35 A. The surface areas and pore diameters herein are those which are determined by nitrogen adsorption techniques. It is desirable that the surface-hydroxyl-containing adsorbent solid have an effective surface area in the range of about 25–700 square meters per gram (sq. m./gm.), preferably 50–500 sq. m./gm.

The bauxitic materials which are naturally occurring impure alumina hydrates, such as bauxite and laterite, are a suitable source of surface-hydroxyl-containing adsorbent solids. The aluminous materials which contain substantial amounts, or even large amounts, of oxides other than aluminum oxide are suitable for use in preparing surface-hydroxyl-containing adsorbent to be conjoined with aluminum chloride and HCl. The synthetic material known as silica-alumina, which is used as a hydrocarbon cracking catalyst, is such a suitable aluminous material.

It is preferred to use alumina materials, synthetic or naturally-occurring, such as bauxite, as the surface-hydroxyl-containing adsorbent solid for preparation of the catalyst. Any adsorbed molecular water should be removed from the solid prior to contacting it with aluminum halide, lest the effectiveness of some of the aluminum chloride to form a catalyst be destroyed by reaction or hydration with the water. Adsorbed water can be removed by drying or calcining the solid; however, if calcination is used it should not be carried out under conditions of temperature and time so severe as to destroy the surface hydroxyl groups.

A convenient method of ascertaining whether adsorbed water is absent and an effective amount of surface hydroxyl groups is present in a particular adsorbent solid to be used in preparing catalyst is to determine the weight loss of the defined solid upon heating to about 1832° F. This weight loss is termed "loss on ignition" (LOI). It has been found that satisfactory surface-hydroxyl-containing adsorbent solids are those which contain little or no adsorbed molecular water and which lose about 2–10 weight percent, preferably about 4–8 weight percent in the case of the aluminas, of their original weight upon being heated to about 1832° F. The weight loss in these ranges is due, almost entirely, to the destruction of surface hydroxyl groups with the consequent liberation of water.

The surface-hydroxyl-containing adsorbent solid for use in forming the catalyst is prepared in any manner providing a substantial portion of the effective surface in the hydroxyl form so that there are available hydroxyl groups for reaction with aluminum chloride. It is preferred that at least about 50 percent of the effective surface be in the hydroxyl form. Optimally, nearly all of the effective surface is in the hydroxyl form with no molecular water present.

A suitable method of producing a surface-hydroxyl-containing adsorbent solid is to calcine an alumina containing material to produce an adsorbent solid containing at least one of the following adsorbent solid forms: chi alumina, eta alumina, gamma alumina, or mixtures thereof. Suitable calcination conditions of time and temperature, e.g. a temperature in the range of about 300 to 1100° F. for a time in the range of about 1–24 hours, will produce an adsorbent solid having the required surface area and pore size properties and a LOI less than about 2–4 percent. Water, as liquid or vapor, is then added to the calcined adsorbent solid in the amount of about 1–5 weight percent or more. The added water is permitted to react with the surface of the adsorbent solid to produce surface hydroxyl groups. This hydrated adsorbent solid is then dried under carefully controlled conditions so that molecular water is removed without destroying an appreciable number of the surface hydroxyl groups. Suitable drying conditions are a temperature in the range of about 200–300° F. for a time of about 10–100 hours. Of course, if the adsorbent solid, such as bauxite for example, as received contains 8–10 percent or more of water, as determined by loss on ignition, the hydration step may be omitted.

The catalyst is formed by contacting aluminum chloride with the defined surface-hydroxyl-containing adsorbent solid and causing the aluminum chloride to react with the surface hydroxyl groups on the surface of the defined adsorbent solid, thus forming $-O-AlCl_2$ groups on the surface. During this reaction one mole of HCl is liberated for each mole of $AlCl_3$ reacted. HCl is caused to associate, mole for mole with the $-O-AlCl_2$ groups to form the active catalyst. It is postulated that an $-O-AlCl_2$ site, when associated with HCl, forms a proton and a negatively charged species, $(-O-AlCl_3)-$, which constitutes the actual catalyst.

The aluminum chloride content corresponding to maximum catalyst activity is that amount of aluminum chloride required to provide a monolayer of reacted aluminum chloride molecules, i.e., reacted with hydroxyl groups to form $-O-AlCl_2$ groups, over the effective surface area of the defined adsorbent solid. One gram of aluminum chloride will provide a monolayer of aluminum chloride molecules (or $-O-AlCl_2$ groups) over about 534 square meters of effective surface area.

The preferred method of preparing the catalyst is to form a dry physical mixture of aluminum chloride and surface-hydroxyl-containing adsorbent solid and react the mixture at a temperature in the range of about 0–500° F., preferably about 200–350° F. Normally sufficient pressure is utilized to minimize sublimation of aluminum chloride from the reaction mixture to reduce aluminum chloride loss. A flowing stream of gas may be used as the heat transfer medium for heating the reaction mixture and cooling the reaction products. Hydrogen is a preferred gas, however, other relatively unreactive gases such as nitrogen, helium, methane, ethane, propane, butane, etc. may also be used. The reaction time required decreases as the reaction temperature is increased. At the preferred reaction temperature of 200–350° F., a time of about 0.1 to 10 hours is normally sufficient to complete the reaction; however, longer reaction time is not detrimental. HCl is then caused to associate with the reaction product of aluminum chloride and surface-hydroxyl-containing adsorbent solid. This association is carried out at a temperature below about 180–200° F. since at higher temperature the association does not take place. In fact, a fully formed catalyst will liberate HCl if heated to a temperature of 180–200° F., or higher, even under pressures of 500 p.s.i.or more. The association with HCl is conveniently carried out by contacting the reaction product with anhydrous HCl at a pressure of about 10–500 p.s.i.a. and a temperature in the range of about 60–200° F. One mole of HCl associates for each mole of $AlCl_3$ which has reacted with the surface-hydroxyl-containing adsorbent solid. A time of about 1–100 hours is normally sufficient to complete the HCl association.

The most desirable ratio of aluminum chloride to the defined adsorbent solid depends upon the surface-hydroxyl content of the particular adsorbent solid used. For example, with surface-hydroxyl-containing adsorbent solid particles of about 20–60 mesh size and having an effective surface area of about 230 sq. m./gm., the proportions will normally be about 25–35 weight percent aluminum chloride and about 65–75 weight percent adsorbent solid. Most catalyst forming reaction mixtures comprise 10–50 weight percent aluminum chloride and 50–90 weight percent of the defined adsorbent solid. The catalyst can be prepared in a great number of particle sizes. The final catalyst configuration is determined by the configuration of the surface-hydroxyl-containing adsorbent solid used. The catalyst is hygroscopic, therefore care should be taken to avoid contacting the catalyst with moisture.

Example I

An aluminum chloride-hydrocarbon complex is prepared by stirring together at atmospheric pressure a quantity of anhydrous aluminum chloride with an excess of commercial iso-octane at 120° F. to 140° F. until a liquid complex results. During the complex formation, large amounts of isobutane are produced and the remaining hydrocarbon liquid contains 50% of material boiling higher than the end point of the original iso-octane. This heavy material is suitable for safety fuel while the isobutane can be utilized readily in an alkylation process for example. The complex itself is decanted from the unreacted aluminum chloride, which can be ultimately converted in its entirety to the complex by further treatment with adidtional quantities of iso-octane. The viscosity of the complex catalyst produced is less than that of S.A.E. 50 lubricating oil and it can be easily pumped through pipes, towers or any form of contacting equipment. This complex is active for the disproportionation of pentane. A complex catalyst prepared by the action of anhydrous aluminum chloride on a light naphtha fraction rich in straight-chain paraffin hydrocarbons at a temperature above 200° F., which is necessary in order that the complex may be formed in a reasonable time, is less fluid, but is also active for pentane conversion.

Example II

In order to demonstrate the effect of catalyst activity on the disproportionation of pentane, an aluminum chloride-hydrocarbon catalyst was prepared by reacting 100 grams of aluminum chloride with 100 cc. of iso-octane in a three neck flask that had been fitted with a water condenser and a stirrer. While stirring the reactants, gaseous HCl was added and the temperature was raised to 125–130° F. As the iso-octane was consumed in forming the complex, three additional 100 cc. increments were added. The purpose of using iso-octane was to deactivate the catalyst in order to reduce side reactions. At the end of about two hours, a sample of the freshly formed but partially deactivated complex catalyst was tested and proved to be satisfactory for use in the disproportionation experiment.

The experiment was conducted in a one liter stirred autoclave. 101.8 grams of the aluminum chloride complex catalyst (containing 67.4 grams of $AlCl_3$) was placed in the reactor which was quickly closed and sealed. About 400 grams of normal pentane (99 mole percent pure) was pressured into the reactor. HCl was added to give an equilibrium pressure of 30 p.s.i. and an HCl concentration of about 2.5 weight percent based on pentanes. Heat was applied so as to maintain the temperature at 212° F. for a period of two hours. After the reactor was cooled to room temperature, a sample of the liquid product was removed. A gas chromatography analysis was made of the stabilized liquid product. The remaining reaction products were removed from the reactor and catalyst was flushed

with 500 cc. of normal pentane. A charge of 650 cc. of fresh normal pentane was pressured into the reactor with an additional HCl charge. The above described procedure was repeated until a total of seven runs were made. All runs were for a period of 2 hours except the final one which was for 5.5 hours. The analysis of the final run is reported as of the end of 2 hours.

A summary of the experiment is presented in Table I. These results have been plotted in FIGURE I. Inspection of FIGURE I shows that as the $AlCl_3$—hydrocarbon complex becomes less active, the amount of normal pentane converted decreases. It also shows that the ratio of hexanes to butanes is essentially independent of catalyst activity and is substantially less than the theoretical ratio of 1:5.

TABLE I.—DISPROPORTIONATION EXPERIMENT

Run No.	1	2	3	4	5	6	7
Product Weight, grams	187.0	138.8	144.8	151.3	122.5	162.6	167.4
Temperature	212	212	212	212	212	212	212
Run Time, hours	2	2	2	2	2	2	5.5
Pressure	237	174	172	164	163	133	162
Product Analysis: [1]							[2]
Isobutane / n-Butane	46.0	30.8	24.2	17.8	12.7	8.0	5.3
Isopentane	22.4	21.7	18.2	14.9	11.9	8.2	91.7
n-Pentane	7.3	31.4	44.5	57.2	67.8	79.1	
2,2-DMB	6.7	1.3	0.7	0.4	0.2	0.2	0.1
2-MP+2,3-DMB	7.5	7.2	6.1	4.8	3.7	2.4	1.5
3-MP	3.0	2.7	2.4	1.8	1.4	0.9	0.5
n-Hexane	1.8	1.4	1.0	0.7	0.6	0.2	0.1
C_{7+}	5.3	3.5	2.9	2.4	1.7	1.0	0.8
	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Wt. percent Conversion to Other than Pentanes	70.3	46.9	37.3	27.9	20.3	12.7	8.3

[1] Determined by gas chromatography.
[2] Analysis at end of 2-hour period.
$AlCl_3$-iso C_8 complex 101.8 gms.
HCl, 2.5 wt. percent of pentane.

Example III

In order to show that the ratio of hexanes to butanes can be significantly increased by buffering the reaction, another experiment was performed in a manner similar to the previous one. 72 grams of $AlCl_3$ and 20.5 grams of HCl were used in preparing the catalyst. The hydrocarbon feed was composed of 52.6 weight percent normal pentane and 47.4 weight percent isobutane. The reaction was carried out at 212° F. for a period of three hours. Analysis of the product gave the following weight percent composition based on the pentanes converted:

Butanes	14.8
Hexanes	55.0
C_{7+}	30.2
	100.0

The ratio of hexanes to butanes is about 3.7 which is well above the theoretical value. From the results of Examples II and III, it can be seen that the ratio of hexanes to butanes produced in the disproportionation reaction may be controlled by means of buffering from a minimum of about 0.40 to at least 3.7.

Example IV

In this example, the results of pilot plant studies are used to illustrate the isomerization of deisobutanized and rerun effluent from the pentane converter to produce isopentane and dimethylbutane. The feed stream to the methylpentane converter has the following composition:

	Wt. percent
Normal butane	8.3
Isopentane	25.5
Normal pentane	35.7
Hexanes (incl. methylpentanes)	30.5
	100.0

Methylpentane isomerization reactor operating conditions employing $AlCl_3$-alumina catalyst prepared from 25–28% $AlCl_3$ and the remainder eta alumina are as follows:

Space velocity, $W_o/Hr./W_c$	0.15
Reactor temperaure, °F.	100–115
Reactor pressure, p.s.i.g.	200
Hydrogen chloride, wt. percent on feed	5–7
Naphthene inhibitor, wt. percent on feed	10–13

The naphthene inhibitor is used to prevent cracking. Only small increases in conversion result from higher reactor temperature. Higher temperatures decrease catalyst life and equilibrium neohexane concentration. Therefore, the reactor temperature is maintained as low as practical using cooling water at about the temperature employed commercially. The pressure is maintained high enough to keep the reactants in the liquid state. Under these conditions the product pentane fraction contains about 81% isopentane which is about 95% of equilibrium.

The effluent from the methylpentane converter has the following composition after HCl and propane and lighter having been removed in the HCl stripper.

Component:	Weight percent
Isobutane	4.6
n-Butane	4.2
Isopentane	52.0
n-Pentane	9.2
2,2-dimethylbutane	11.0
2,3-dimethylbutane	2.6
2-methylpentane	7.0
3-methylpentane	3.4
n-Hexane	1.7
Methylcyclopentane	0.6
Cyclohexane	3.7
	100.0

After distillation in a product recovery system similar to that shown in FIGURE 2, the dimethylbutane overhead from a tower corresponding to product fractionator **57** in FIGURE 2 and having 55 theoretical plates operating at a reflux ratio of 25 has the following composition.

Component:	Mole percent
2,2-dimethylbutane	99.5
2,3-dimethylbutane	0.2
2-methylpentane	0.3
	100.0

Turning now to FIGURE 2, pentane feed from source **10** is passed via line **11**, combined with n-pentane recycled from line **12**, and fed near the top of HCl absorber tower **13**. In this tower HCl is absorbed from an HCl-containing gas stream which enters the tower from line **14** and which is described below. Make-up isobutane may also be added to the absorber tower **13** via line **70** and **71**. The HCl-containing feed stream is passed from the bottom of the absorber tower via line **16** into pentane converter **17**. A hydrogen-containing stream from source **18** is passed via line **19** into line **16** where it is admixed with the converter feed stream. The hydrogen is introduced in an amount sufficient to supply the hydrogen deficiency created by side reactions in the disproportionation reaction of pentane to produce isobutane and methylpentane, but excess hydrogen should not be employed to the extent that the disproportionation reaction is inhibited. Ordinarily, a hydrogen partial pressure of about 100 p.s.i. is sufficient to supply the hydrogen deficiency without unduly inhibiting disproportionation.

Aluminum chloride catalyst from source **21** is passed via line **22** into converter feed line **16** to make up catalyst losses and withdrawals from the converter **17**. Spent complex is withdrawn from converter **17** via line **67** and sent to waste disposal. Two hydrocarbon recycle streams

are also combined with the converter feed in line **16**, these are n-pentane recycle from line **23** and C_7^+ recycle from line **24**.

Pentane converter **17** contains a pool of the liquid aluminum chloride-hydrocarbon complex containing dissolved free aluminum chloride. The feed from line **16** is dispersed into this pool of catalyst, with which the hydrocarbons are immiscible, the conversion of pentane to produce isobutane and methylpentane taking place as the hydrocarbon droplets rise to the surface of the pool. Suitable pentane converter operating conditions include a temperature in the range of 50 to 250° F., preferably 100–200° F., a pressure sufficient to maintain the liquid phase, a hydrogen partial pressure in the range of about 20 to 200 p.s.i., and HCl concentration of about 1 to 15 wt. percent based on feed, and a weight hourly space velocity in the range of about 0.01 to 2.0 $W_o/Hr./W_c$. Aluminum chloride make-up is fed to the converter and complex catalyst is spent at a rate required to maintain the hydrocarbon content of the complex below about 50%. This is easy to do because with a complex containing the preferred hydrocarbon content of about 20–40% the activity is such that only a small amount of additional complex is formed, while the disproportionation activity remains high. Conversion products are withdrawn from the hydrocarbon phase above the catalyst phase and are passed via line **26** into H_2–HCl stripper **27** wherein hydrogen, hydrogen chloride and light hydrocarbons are stripped from converter product and passed via line **28** and **14** into the HCl absorber **13** for recovery and recycle of the HCl. Stripper bottoms is passed via line **29** into debutanizer **21** from which relatively pure butane is distilled and passed via line **32** either into line **68** for recycle via line **71** into pentane converter **17**, or into line **69** for use in another process such as in alkylation. Debutanizer bottoms is passed via line **33** into rerun tower **34** from which a C_7^+ stream is withdrawn via line **36**. A portion of this stream is recycled via line **24** and **16** into converter **17** and, if desired, another portion is withdrawn from the process as product via line **37**. The n–C_4 to C_6 stream distilled overhead from the rerun tower **34** is withdrawn via line **38** and passed via feed line **39** into methylpentane reactor **41**. This stream is completely free from aromatics and is rich is methylpentane, thus it is a nearly ideal feed for isomerization over the defined methylpentane conversion catalyst. The methylpentane reactor **41** contains a bed of the aluminum chloride-absorbent solid catalyst described above. In this reactor methylpentane is isomerized to produce near-equilibrium quantities of dimethylbutane. Isomerization of n-butane to isobutane and unconverted n-pentane to isopentane also is effected. Suitable operating conditions include a temperature of about 75 to 120° F. a weight hourly space velocity in the range of about 0.01 to 1.0 $W_o/Hr.W_c$, and a pressure sufficient to maintain at least about 95% of the pentane-hexane feed in the liquid phase. HCl from source **42** is passed via line **43** into reactor feed line **39** in an amount which, when combined with HCl recycles from line **44**, will provide about 2 to 10 weight percent HCl in the feed stream to reactor **41**.

Dimethylbutane containing product is withdrawn from the isomerization reactor **41** via line **46** and passed into HCl stripper **47** wherein HCl-containing gas is distilled overhead and passed via lines **48** and **14** into the HCl absorber **13** for recovery and recycle of the hydrogen chloride. The stripper bottoms stream is passed via line **49** into topping tower **51** where a high vapor pressure, high octane butane-isopentane stream is distilled overhead and recovered as product via line **52**. The topping tower bottoms stream is passed via line **53** into depentanizer **54** wherein a normal pentane rich stream is distilled overhead for recycle via line **55** to pentane feed via line **12** and/or directly to the pentane converter via line **14**, depending upon whether this pentane is needed for absorbing HCl in absorber **13**. Depentanizer bottoms is withdrawn via line **56** and fed to product fractionator **57** wherein dimethylbutane is distilled overhead and recovered via line **58** as the low-boiling high octane product of the process. This stream contains over 95% neohexane (2,2-dimethylbutane) which is lower boiling than diisopropyl(2,3-dimethylbutane) and thus more easily separated.

Cycloparaffins are required in the feed to reactor **41** in order to suppress cracking reactions. The concentration of cycloparaffins is preferably controlled within the range of from about 2 to 15 weight percent based on paraffin feed. Cycloparaffin-containing bottoms, also containing 2,3-dimethylbutane and unconverted methylpentanes, is withdrawn from the product fractionator via line **59** and recycled to the rerun tower **34** via lines **61**, **62** and **33**. Any C_7^+ produced in reactor **41** is thus removed from the reactor feed stream with the bottoms from rerun tower **34**. Any cycloparaffin needed as make-up is passed from source **63** via line **64** into cycloparaffin recycle line **62**.

Therefore, it may be seen that by using the above described process, high octane dimethylbutane may be produced from normal pentane in good yields. This surprising result is obtained by combining two process steps in a new and novel manner. The first step is the disproportionation of the normal pentane to the major products of methylpentane and isobutane. This is done in the presence of an aluminum chloride-hydrocarbon complex catalyst and also in the presence of a controlled amount of isobutane which acts as a buffer to limit the net amount of isobutane formed. Although the amount of normal pentane converted to non-C_5 products may be high in a single pass, this is controlled in order to limit the occurrence of undesired side reactions. The catalyst is partially deactivated to limit the conversion while the unconverted pentanes are recycled so as to give optimum results. The methylpentanes formed by disproportionation are an ideal hexane feed to the second process stage which is a low temperature fixed bed isomerization reactor using aluminum chloride on alumina with association hydrogen chloride as the catalyst. This feed does not contain the catalyst deactivator, benzene, which is difficult to remove from the usual feeds to the process. Thus, the described combination of disproportionation with low temperature isomerization provides a significant and unexpected improvement to the latter.

What is claimed is:

1. A two-stage process for the production of dimethylbutanes from normal pentane, which process includes:

(a) contacting said pentane in a first stage at a temperature in the range from about 50° F. to about 250° F., with hydrogen chloride, sufficient hydrogen to exert a partial pressure of from about 20 p.s.i. to about 200 p.s.i., and in the presence of a liquid aluminum chloride-hydrocarbon complex, said catalyst complex comprising the reaction product of aluminum chloride, hydrogen chloride, and a substantially saturated hydrocarbon; said catalyst complex being formed at a temperature in the range of between about 50° F. and 175° F., so that at least a portion of said normal pentane disproportionates to a substantially benzene-free and substantially olefin-free effluent including isobutane and methylpentanes;

(b) contacting said effluent in a second stage at a temperature in the range from about 75° F. to about 120° F. with a cycloparaffin, hydrogen chloride, and in the presence of a supported aluminum chloride catalyst, said supported aluminum chloride catalyst comprising aluminum chloride positioned on a surface-hydroxyl-containing adsorbent solid selected from the group consisting of alumina, silica-alumina, silica gel, and mixtures thereof, so that at least a portion of said methylpentanes is isomerized to dimethylbutanes;

(c) separating said dimethylbutanes from unreacted pentane and methylpentane; and

(d) recycling at least a portion of said unreacted pentane to said first stage.

2. The process of claim 1 wherein said catalyst in said second stage comprises aluminum chloride and hydrogen chloride on alumina.

3. The process of claim 1 wherein said isobutane is separated from said effluent from said first stage prior to said contacting said effluent in said second stage.

4. The process of claim 3 wherein at least a portion of said isobutane is recycled to said first stage to control the ratio of hexane to isobutane formed in said first stage.

5. The process of claim 3 wherein said catalyst in said second stage comprises aluminum chloride positioned on

surface-hydroxyl-containing alumina, associated with a hydrogen chloride promoter.

References Cited

UNITED STATES PATENTS

2,270,669	1/1942	de Simo et al.	260—676
2,938,936	5/1960	Belden	260—683.73
3,280,213	10/1966	Mullen et al.	260—683.74
3,007,985	11/1961	Binning	260—676

FOREIGN PATENTS

498,463	1/1939	Great Britain.

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